# Vol. I

k Proceedings of a Symposium, Bombay, 15–19 December 1964



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NTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA. 1965

# INELASTIC SCATTERING OF NEUTRONS

VOL.I

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# INELASTIC SCATTERING OF NEUTRONS

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In two volumes

# VOL.I

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#### FOREWORD

The general technique of using neutron interactions - and in particular the inelastic scattering of neutrons - to study the dynamics of matter, and the interatomic forces which determine dynamics, is now well established. This area of physics research is of increasing interest to developing countries as well as to many advanced research centres of the world. Three international symposia have already been devoted to the subject of neutron inelastic scattering: the first was held in Stockholm in 1957; the second and third were convened by the IAEA in Vienna in October 1960, and in Chalk River, Canada, in September 1962. In view of continuing and expanding activity in this field, the IAEA convened the present Symposium at Bombay from 15 to 19 December 1964 on the invitation of the Government of India and the Indian Atomic Energy Commission.

A total of 66 papers representing 15 countries and 1 international organization were presented at Bombay. The meeting concentrated on experimental results and interpretation rather than on equipment and techniques; thus neutron inelastic scattering has "come of age" and is indeed now fully established as a versatile and powerful research tool.

Gratitude is expressed to authors of papers, chairmen of sessions, and discussion participants for their contributions to the success of the Bombay Symposium.

## EDITORIAL NOTE

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For the sake of speed of publication the present Proceedings have been printed by composition typing and photo-offset lithography. Within the limitations imposed by this method, every effort has been made to maintain a high editorial standard; in particular, the units and symbols employed are to the fullest practicable extent those standardized or recommended by the competent international scientific bodies.

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# THEORETICAL ASPECTS OF PHONON DISPERSION CURVES FOR METALS

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#### Abstract — Résumé — Аннотация — Resumen

THEORETICAL ASPECTS OF PHONON DISPERSION CURVES FOR METALS. Reasonably complete knowledge of the phonon dispersion curves for at least a dozen metallic elements and intermetallic compounds has now been obtained from neutron inelastic scattering experiments. The results have one feature in common: when analysed in terms of interatomic force constants they reveal the presence of comparatively long-range forces extending over several atomic spacings. The results for lead are particularly interesting; it did not prove possible to fit them by a force-constant model, but the dispersion curves for wave vectors in symmetry directions when analysed in terms of force constants between planes of atoms showed an oscillatory interatomic potential extending over distances of more than 20 Å.

This review is concerned with recent theoretical work which has a bearing on the calculation of phonon dispersion curves for metals and the explanation of the long range of the interatomic potential. The best hope at present for a general treatment of atomic interaction in metals appears to lie in the "method of neutral pseudo-atoms", (a description recently coined by Ziman). This approximate theory is outlined and its relevance to Kohn anomalies in phonon dispersion curves is discussed. Experimental data for sodium is consistent with the theory, and the interatomic potential in sodium varies periodically in a distance  $\pi/k_F$ , where fik<sub>F</sub> is the Fermi momentum, as has already been demonstrated by Koenig in a different way. More exact calculations have been made for sodium by Toya and by Sham. The relationship between the different methods and other work of a more general character such as that of Harrison are discussed.

ASPECTS THÉORIQUES DES COURBES DE DISPERSION DES PHONONS POUR LES MÉTAUX. A la suite d'expériences de dispersion inélastique des neutrons, on a maintenant une connaissance assez complète des courbes de dispersion des phonons pour une douzaine de métaux et de composés intermétalliques au moins. Les résultats présentent le caractère commun suivant; si on les analyse en fonction des constantes de forces interatomiques, ils révèlent la présence de forces de portée relativement longue (plusieurs espaces atomiques). Les résultats relatifs au plomb sont particulièrement intéressants; il n'a pas été possible de les ajuster au moyen d'un modèle de constantes de forces, mais les courbes de dispersion pour les vecteurs d'ondes dans des directions de symétrie, analysées en fonction des constantes de forces entre plans d'atomes, accusent un potentiel interatomique oscillatoire qui s'étend sur des distances de plus de 20 Å.

L'auteur fait le point des travaux théoriques récents qui ont des incidences sur le calcul des courbes de dispersion des phonons pour des métaux, et tente d'expliquer la longue portée du potentiel interatomique. Il semble qu'actuellement ce soit la «méthode des pseudo-atomes neutres» (expression forgée récemment par Ziman) qui offre les meilleures chances de permettre un traitement général de l'interaction atomique dans des métaux. L'auteur donne un aperçu de cette théorie et discute son importance du point de vue des anomalies de Kohn dans les courbes de dispersion des phonons. Les données expérimentales pour le sodium sont en accord avec cette théorie et le potentiel interatomique dans le sodium varie périodiquement sur une distance  $\pi/k_F$ . fik<sub>F</sub> étant le moment de Fermi, ainsi que Koenig l'avait déjà démontré d'une autre façon. Des calculs plus exacts ont été effectués pour le sodium par Toya et par Sham. Le mémoire examine les relations entre les différentes méthodes, ainsi que d'autres travaux d'un caractère plus général, tels que ceux d'Harrison.

ТЕОРЕТИЧЕСКИЕ АСПЕКТЫ ФОНОННЫХ ДИСПЕРСИОННЫХ КРИВЫХ ДЛЯ МЕТАЛ-ЛОВ. В настоящее время в результате экспериментов по неупругому рассеянию нейтронов довольно полно изучены фононные дисперсионные кривые по крайней мере для дюжины металлических элементов и интерметаллических соединений. Результаты имеют одну общую осооенность: анализ их с точки зрения констант межатомных сил показывает наличие довольно дальнодействующих сил, простирающихся на несколько межатомных расстояний. Особый интерес представляют результаты по свинцу: оказалось невозможным подогнать их на основе модели константы силы, однако дисперсионные кривые для волновых векторов в симметричных направлениях, если анализировать их с точки зрения констант силы между плоскостями атомов, показывают наличие колебательного межатомного потенциала, простирающегося на расстояния, превышающие 20 Å.

Настоящий обзор посвящен последним теоретическим работам, имеющим отношение к расчету фононных дисперсионных кривых для металлов и объяснению дальнего действия межатомного потенциала. В настоящее время наиболее обнадеживающим методом общей трактовки взаимодействия атомов в металлах представляется "метод нейтральных псевдоатомов", который был недавно описан Зиманом. Кратко изложена эта приближенная теория и рассмотрен вопрос о ее справедливости для аномалий Кона в фононных дисперсионных кривых. Экспериментальные данные по натрию согласуются с теорией, и межатомный потенциал в натрии периодически меняется на расстоянии  $\pi/k_F$  (где hk<sub>F</sub> - момент Ферми), как было уже доказано иным путем Кенигом. Более точные расчеты по натрию произвели Тойя и Схам. Рассматривается связь между различными методами и другими работами более общего характера, например, работой Харрисона.

ASPECTOS TEÓRICOS DE LAS CURVAS DE DISPERSIÓN FONÓNICA EN METALES. Los experimentos de dispersión inelástica de neutrones han permitido acopiar datos bastante completos sobre las curvas de dispersión fonónica correspondientes a una docena, por lo menos, de elementos metálicos y de compuestos intermetálicos. Los resultados presentan una característica común: analizados en función de las constantes de fuerzas interatómicas, manifiestan la presencia de fuerzas de alcance relativamente grande, que se extienden a varios espacios interatómicos. Los resultados relativos al plomo son particularmente interesantes; no fue posible ajustarlos a un modelo de constantes de fuerza, pero las curvas de dispersión de los vectores de onda en las direcciones de simetría, analizadas en función de las constantes de fuerza entre planos atómicos, revelan la existencia de un potencial interatómico de carácter oscilatorio que se extiende a distancias superiores a 20 Å.

La memoria trata de trabajos teóricos recientes, relacionados con el cálculo de las curvas de dispersión fonónica en metales y con la explicación del largo alcance del potencial interatómico. En la actualidad, el método más prometedor para abordar con criterio general la interacción atómica en los metales parece ser el de los «pseudoátomos neutros», denominación recientemente acuñada por Ziman. Se exponen los principios de esta teoría de aproximación y se examina su relación con las anomalías de Kohn en las curvas de dispersión fonónica. En el caso del sodio, los valores experimentales concuerdan con los datos teóricos, y el potencial interatómico varía periódicamente en la distancia  $\pi/k_F$ , donde  $\hbar k_F$  es el momento de Fermi, como ha demostrado Koenig por un procedimiento diferente. Toya y Sham han realizado cálculos más exactos para el sodio; se examina las relaciones existentes entre los diferentes métodos y otros trabajos de findole más general, tales como los de Harrison.

#### 1. INTRODUCTION

Through the use of the technique of neutron inelastic scattering, phonon dispersion curves have been established with reasonable accuracy for aluminium [1, 2, 3, 4], copper [5, 6], iron [7], magnesium [8, 9], beryllium [10], lead [11], sodium [12], zinc [13], niobium [14], tungsten [15], tantalum [16], molybdenum [17], nickel [18] and  $\beta$ -brass (copper zinc) [19]. Included in most of these papers is an analysis of the experimental results in terms of a force constant model, usually with general Born-von Kármán force constants, but in some instances imposing the condition of axial symmetry [20]. (The latter condition means that the forces are central forces between the atoms, supplemented by surface forces which do not appear in the equations for the lattice dynamics of the crystal but which must be invoked to maintain equilibrium of the system, unless the elastic constants are to satisfy the Cauchy relations. This is a point to which we shall return later). The results have one feature in common, force constants connect atoms which are relatively widely separated in the crystal. The results for lead [11] are particularly interesting; it did not prove possible to fit them by a force constant model, but the dispersion curves for wave vectors in symmetry directions when analysed in terms of force constants between planes of atoms showed an interatomic potential which varied periodically and extended over a distance of more than 20 Å.

Early theoretical work, such as that of FINE [21] and of LEIGHTON [22], who attempted to derive the frequency distribution of the normal modes and hence the specific heat of metals on the basis of interactions between nearest and next nearest atoms turns out therefore to have been misdirected. Somewhat later attempts were made, for example by BHATIA [23], to calculate the dispersion curves by including the effect of the conduction electrons as a compressible gas. This approach has been reviewed by de LAUNAY [24]. The most successful theory of this type is that of SHARMA and JOSHI [25].

Turning now to papers in which the dispersion curves are calculated from something more nearly approaching first principles, the earliest such attempt was that of FUCHS [26] who considered shearing deformations of a crystal of sodium in which the volume is unchanged. The corresponding elastic constants are  $C_{44}$  and  $\frac{1}{2}(C_{11} - C_{12})$ . Point ions were considered to be immersed in a uniform background of negative charge, and it was assumed that the energy change in the type of displacement considered comes entirely from the change in electrostatic energy of the ions, which can be evaluated by the Ewald method. The fact that the volume is unchanged is not in itself sufficient to justify excluding the electrons from consideration, but Fuchs' results are in fact confirmed by the more recent work of TOYA [27] and others and are in good agreement with experimental results for sodium [12]. This of course amounts only to a calculation of two transverse branches of the phonon dispersion curve for wave vector  $\vec{q} \rightarrow 0$ . CLARK [28] extended Fuchs' calculation to all values of  $\vec{q}$  in the directions [100], [110] and [111], still treating the problem as an electrostatic one in which point ions move in a uniform distribution of negative charge which does not respond to their motion. Fairly plausible results were obtained for transverse modes, but the longitudinal mode had the characteristics of an optic branch in that it approached a finite frequency  $\omega_L(0)$  for  $\vec{q} \rightarrow 0$ . This (circular) frequency is given by

$$(\omega_{\rm L}(0))^2 = \frac{4\pi {\rm e}^2}{{\rm M}{\rm v}}$$
, (1.1)

where v is the unit cell volume, containing an ion of mass M and charge e, and a uniform distribution of charge -e. In fact  $\omega_L(0)$  is just the plasma frequency of the ions. This non-physical result is not obtained when the electrons are allowed to adjust to the motion of the ions and screen out the Coulomb interaction of the latter, as had already been shown by BARDEEN and PINES [29] for example. Their paper was primarily concerned with the effect of screening and the role of electron-electron interactions on the electron-phonon interaction. The Bohm-Pines collective description of the electron motion was used, and it was found that electron screening produces

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the correct behaviour of the longitudinal branch,  $\omega_L(\vec{q}) \rightarrow 0$  as  $\vec{q} \rightarrow 0$ . The elastic constant  $C_{11}$  in fact came out in broad agreement with TOYA's Hartree-Fock calculation [27, 30] for sodium.

#### 2. A SIMPLE THEORY OF INTERATOMIC FORCES IN METALS

Rather than first attempt to describe the detailed calculations of TOYA [27], SHAM [31] and others, we turn our attention now to the "method of neutral pseudo-atoms" in the theory of metals, an unflattering description invented by ZIMAN in a recent review [32]. This approximate theory of metals is of course of much wider application than the calculation of phonon dispersion curves and has been used for the calculation of electronic band structure, the shape of the Fermi surface, the scattering of electrons by defects, and the resistivity of liquid metals. What it lacks in rigour is more than made up, for the purpose of this review, by the fact that it gives a simple picture of the processes involved and can be used as a guide to more sophisticated theories. When some of the parameters of the theory are left to be determined by comparison with observed results, it is probable that its predictions are as reliable as can be made by any method at the present time (ZIMAN [32]). The following is a condensed account of the theory; the influence of Ziman's article will be apparent to anyone who reads both.

We begin by considering the problem of electron screening in a gas of N free electrons confined to unit volume. On introducing a small "imposed" charge distribution  $eZ(\vec{r})$  confined to a limited space round the origin the electrons will pile up there with an extra charge distribution  $eZ_e(\vec{r})$  in such a way that the field of the external charge is completely screened at large distances, in other words

$$\int (Z(\vec{\mathbf{r}}) + Z_e(\vec{\mathbf{r}})) d^3 \mathbf{r} = 0$$
 (2.1)

when the integral is taken over a <u>limited</u> space around the origin. To find the relation between the two charge distributions it turns out to be easier to work with the Fourier transforms of charge distributions and potentials, defined by

$$Z(\vec{K}) = \int Z(\vec{r}) \exp(+i\vec{K}\cdot\vec{r}) d^{3}r$$

and conversely

$$Z(\vec{\mathbf{r}}) = \int Z(\vec{\mathbf{K}}) \exp\left(-i\vec{\mathbf{K}}\cdot\vec{\mathbf{r}}\right) d^{3}\mathbf{K}/(2\pi)^{3}, \qquad (2.2)$$

where  $\vec{K}$  is a general vector in reciprocal space. In what follows we shall simplify the situation a little by assuming that  $Z(\vec{r})$  is spherically symmetric. If V(r) is the potential of the charge distribution eZ(r), it follows from Poisson's theorem,  $\nabla^2 V(r) = -4\pi eZ(r)$ , that PHONON DISPERSION CURVES FOR METALS

$$V(K) = \frac{4\pi e Z(K)}{K^2} .$$
 (2.3)

The transform of the screened potential of the imposed charge is given by

$$V_{s}(K) = V(K) + V_{e}(K)$$
  
=  $\frac{4\pi e}{K^{2}} [Z(K) + Z_{e}(K)].$  (2.4)

To cut the story short, it was first shown by BARDEEN [33] that in the selfconsistent-field or Hartree approximation

 $V_{s}(K) = \frac{V(K)}{\epsilon(K)}, \qquad (2.5)$ 

so that

$$Z_{\epsilon}(K) = -Z(K) [1 - 1/\epsilon(K)],$$
 (2.6)

where  $\epsilon(K)$  is the dielectric function for a free electron gas, and is given by

$$\epsilon(K) = 1 + \frac{6\pi Ne^2}{K^2 E_F} \left( \frac{1}{2} + \frac{4k_F^2 - K^2}{8k_F K} \log \left| \frac{2k_F + K}{2k_F - K} \right| \right).$$
(2.7)

In this expression  $E_F$  and  $k_F$  are the energy and wave number of an electron, at the Fermi surface. The equations quoted can be derived by a simple application of perturbation theory to the wave equation for free electrons, the perturbing potential being  $V_s$  (r) and the perturbed wave function

$$\Psi(\mathbf{kr}) = \exp\left(\mathbf{i}\vec{k}\cdot\vec{r}\right) + \sum_{\vec{k}} \frac{eV_{s}\left(\mathbf{K}\right)}{\mathbf{E}\left(\vec{k}+\vec{K}\right) \cdot \mathbf{f}} \exp\left[\mathbf{i}\left(\vec{K}+\vec{k}\right)\cdot\vec{r}\right] .$$
(2.8)

However it is necessary that

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$$Z_{e}(\mathbf{r}) = \sum_{\mathbf{k}} (|\Psi(\mathbf{kr})|^{2} - 1)$$

and this, together with the result

$$\sum_{\mathbf{k} < \mathbf{k}_{F}} (E(\vec{k} + \vec{K}) - E(\vec{k}))^{-1} = \frac{3N\left(\frac{1}{2} + \frac{4k_{F}^{2} - K^{2}}{8k_{F}K} \log \left|\frac{2k_{F} + K}{2k_{F} - K}\right|\right)}{O},$$

is sufficient to give Eq. (2.5) as quoted. The same approximate result has been obtained by Gell-Mann and Brueckner using the mathematical apparatus

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Fig. 1

The function  $\epsilon$  (k) for sodium in the Hartree approximation



The distributions  $Z(\mathbf{r})$  and  $Z_{\mathbf{e}}(\mathbf{r})$  (schematic)

of many-body theory, and to some extent the dielectric function can be modified to improve on the Hartree approximation and allow for exchange and correlation effects in the electron interaction, without changing the form of Eq. (2.5). The dielectric function  $\epsilon$  (K) for an electron density which corresponds to that of the conduction electrons in sodium is shown in Fig.1, and in Fig.2 we illustrate schematically a charge distribution eZ(r) and the screening electron distribution  $eZ_e(r)$  which surrounds it. As the imposed charge eZ(r) moves around it carries a cloud of electron density with it; if several imposed charges are introduced, provided their potentials are sufficiently weak, effects superimpose linearly (in the Hartree approximation) and each imposed charge carries its cloud of screening electrons with it. The interaction energy of two charge distributions  $eZ_1(r)$  and  $eZ_2(|\vec{r} - \vec{R}|)$  is given simply by

$$\Phi(\mathbf{R}) = \int \frac{4\pi e^2 Z_1(\mathbf{K}) Z_2(\mathbf{K})}{\mathbf{K}^2 \epsilon(\mathbf{K})} \exp\left(i\vec{\mathbf{K}} \cdot \vec{\mathbf{R}}\right) \frac{d^3 \mathbf{K}}{(2\pi)^3}, \qquad (2.9)$$

using Eq. (2.5). (If the charge distributions were in vacuo instead of in a dense electron gas, the same expression would apply with  $\epsilon(K) = 1$ , and if they were point charges  $eZ_1$  and  $eZ_2$  it would of course reduce to  $Z_1Z_2e^2/R$ .) In Eq. (2.9) we can regard the energy as made up of two components, the direct Coulomb interaction between the two imposed charge distributions involving  $Z_1(K)Z_2(K)$  and an indirect action through the electrons (which is just the change in energy of the electrons) involving  $-Z_1(K)Z_2(K)$  ( $1-1/\epsilon(K)$ ). In writing Eq. (2.9) we therefore implicitly assume the adiabatic approximation, that any change in the energy of the electrons constitutes an effective potential for the interaction of the imposed charges.

We note from Fig. 2 that the field of an imposed charge is not completely screened at moderate distances, because of the periodic variation in  $eZ_e(\mathbf{r})$ . The wave number of this ripple is approximately  $2k_F$ ; we may say that it arises from the fact that the screening electron cloud has to be built up from wave functions whose wave number does not exceed  $k_F$ . More quantitatively, we note (see Fig. 1 and Eq. (2.7)) that the slope of  $\epsilon(\mathbf{K})$  is logarithmically infinite at  $K = 2k_F$ , and (from Eq. (2.6)) that  $Z_e(\mathbf{K})$  therefore also has this feature. This discontinuity in slope of  $Z_e(\mathbf{K})$  is the source of the ripples in  $Z_e(\mathbf{r})$ . That these ripples are to be expected was first noticed by FRIEDEL [34] in an investigation of the screening of an impurity atom in a metal. Friedel showed that at moderately large values of  $\mathbf{r}$ , both  $Z_e(\mathbf{r})$  and the screened potential  $V_s(\mathbf{r})$  should vary as  $\mathbf{r}^{-3} \cos 2k_F\mathbf{r}$ . LANGER and VOSKO [35] have made quantitative calculations of the effect when the imposed charge is a point charge. Here then is a possible source of the comparatively long-range interactions between atoms in a metal.

We have however anticipated somewhat by equating the imposed distribution eZ(r) with an ion in a metal. Near the core of an ion the electron is in a potential well which is much too deep for the above simple analysis to apply. It can be shown however that the electrons, still represented by simple plane waves, really experience a much weaker potential as a result of the cancellation of the 'bare' potential of the ion core by a repulsive pseudo-potential. The origin of the pseudo-potential is to be sought in the requirement of orthogonality of the wave functions of the conduction electrons to those of the core electrons (PHILLIPS and KLEINMAN [36]); it has in fact somewhat elusive properties and its matrix element between states of wave numbers  $\vec{k}$  and  $\vec{k} + \vec{k}$  is only approximately independent of  $\vec{k}$ . We shall not discuss the calculation of the pseudo-potential, and hence of the effective potential, but merely note that in principle it is determined by the wave functions and energy levels of the core electrons; for discussion and further references the reader is referred to a review article by SHAM and ZIMAN [37]. In what follows we simply assume that the unscreened ion is the source of an effective potential which well outside the core is Ze/r but inside the core varies smoothly to some finite value at r=0. For interaction with an

electron therefore we can represent the ion by a fictitious positive charge distribution eZ(r) which is localized at the core, since this will have the required properties. The ionic charge is given by

$$Ze = e \int Z(r) d^3r \qquad (2.10)$$

and the electrons are still represented by simple plane waves.

If now two identical ions are introduced as imposed charges in the electron gas, we can treat them as point ions in evaluating their direct Coulomb interaction, but the change of electron energy will involve the interaction of a positive charge distribution  $eZ(\mathbf{r})$  with a negative charge distribution  $eZ_e(|\vec{R} - \vec{r}|)$ . Expressing this part of the energy in terms of the corresponding Fourier transforms, the total energy change is

$$\Phi(\mathbf{R}) = \frac{Z^2 e^2}{\mathbf{R}} - \int \frac{4\pi e^2 Z^2(\mathbf{K})}{\mathbf{K}^2} \left[1 - 1/\epsilon(\mathbf{K})\right] \exp(i\vec{\mathbf{K}} \cdot \vec{\mathbf{R}}) \frac{d^3 \mathbf{K}}{(2\pi)^3}.$$
 (2.11)

Noting that  $Z = \int Z(\mathbf{r}) d^3\mathbf{r} = Z(K = 0)$  we find that  $\Phi(\mathbf{R})$  must go to zero for moderate values of R. The charge distribution  $eZ(\mathbf{r})$ , surrounded by the more diffuse distribution of electrons

$$eZ_e(\mathbf{r}) = -e \int Z(\mathbf{K}) \left[1 - 1/\epsilon(\mathbf{K})\right] \exp\left(-i\vec{\mathbf{K}}\cdot\vec{\mathbf{r}}\right) \frac{d^3\mathbf{K}}{(2\pi)^3}$$

is what Ziman has dubbed a neutral pseudo-atom. If two atoms come rather close together it will be necessary to supplement the two terms of Eq.(2.11) by a third which allows for the repulsive exchange interaction between core electrons. In alkali metals this is believed to be given by the Born-Mayer formula

$$\Phi^{(B)}(R) = A \exp(-R/\lambda)$$
 (2.12)

Thus we are led to the conclusion that the interatomic potential in a metal, in this approximation, is given by

$$\Phi(R) = \Phi^{(B)}(R) + \Phi^{(C)}(R) + \Phi^{(E)}(R) ,$$

where

$$\Phi^{(C)}(\mathbf{R}) = \frac{Z^2 e^2}{\mathbf{R}} = \int \frac{4\pi e^2 Z^2}{K^2} \exp(i\vec{K} \cdot \vec{R}) \frac{d^3 K}{(2\pi)^3}$$

and

$$\Phi^{(E)}(R) = -\int \frac{4\pi e^2 Z^2(K)}{K^2} [1 - 1/\epsilon(K)] \exp(i\vec{K} \cdot \vec{R}) \frac{d^3K}{(2\pi)^3}$$
$$= \frac{-2e^2}{\pi} \int_0^\infty Z^2(K) [1 - 1/\epsilon(K)] \left(\frac{\sin KR}{KR}\right) dK , \qquad (2.13)$$

using the fact that the function has spherical symmetry. Note that we have assumed throughout that the system is confined to a constant volume; the value of  $\Phi(R)$  will depend on the free electron density.

Suppose now there are n identical ions immersed in the electron gas, not necessarily in a regular array. Denote the position of each by  $\vec{R}_j$ . The total energy (for simplicity neglecting the Born-Mayer term) is

$$\mathscr{E} = \frac{1}{2} \sum_{j \neq j'} \Phi(\vec{\mathbf{R}}_j - \vec{\mathbf{R}}_{j'}). \qquad (2.14)$$

Writing

$$\Phi(\mathbf{K}) = \Phi^{(C)}(\mathbf{K}) + \Phi^{(E)}(\mathbf{K})$$
$$= \frac{4\pi e^2}{\mathbf{K}^2} \left[ Z^2 - Z^2(\mathbf{K}) \right] \left[ 1 - 1/\epsilon(\mathbf{K}) \right], \qquad (2.15)$$

we then have

$$\mathscr{E} = \frac{1}{2} \sum_{j \neq j^*} \int \Phi(K) \exp \left[ i \vec{K} \cdot (\vec{R}_j - \vec{R}_{j^*}) \right] \frac{d^3 K}{(2\pi)^3}.$$
 (2.16)

Introducing a structure factor

$$F(\vec{K}) = \sum_{j=1}^{n} \exp(i\vec{K} \cdot \vec{R}_{j}),$$
 (2.17)

we find that Eq.(2.16) becomes

$$\mathscr{E} = \frac{1}{2} \int \Phi(\mathbf{K}) \ (|\mathbf{F}(\vec{\mathbf{K}})|^2 - \mathbf{n}) \ \frac{\mathrm{d}^3 \mathbf{K}}{(2\pi)^3} \ . \tag{2.18}$$

This is a result whose significance has been emphasized by HARRISON [38]; the variation of energy at constant volume can be written so as to involve the product of two factors, only one of which varies as the atomic positions vary. Harrison in fact considers the Coulomb energy separately, but his function E(K) is essentially our  $\Phi^{(E)}(K)$  apart from a constant of proportionality. Although Harrison's theory did not involve some of the approximations made in the outline given above, the same general conclusions were reached. The above results are also essentially the same as were derived by COHEN [39] using an improved formulation of the screening problem. Cohen's work was directed at obtaining an expression for the cohesive energy by this method. The formula obtained for the total energy can be expressed as a sum of three contributions: (a) terms which depend only on the electron density, (b) terms which depend on both atomic composition and electron density and (c) the term which we have given as Eq. (2.14).

#### 3. DI

# DISPERSION CURVES AND THE INTERATOMIC POTENTIAL

We are now about ready to consider the "neutral pseudo-atoms" as forming a crystal, but there is an objection which must first be met. When the atomic density is comparable with the electron density, and if every ion carrying a charge e is surrounded by a screening cloud amounting to one electron, the assumption that the electron density is constant, or nearly so, is apparently no longer valid. Paradoxically, this is not so; the screening clouds are sufficiently diffuse that by overlapping they build up a constant density in the perfect crystal. The necessary condition for a constant density is that  $K^2\Phi^{(E)}(K)$  be zero for  $\vec{K} = \vec{H}$ , where  $\vec{H}$  is any vector of the reciprocal lattice, but have a definite value for  $K \rightarrow 0$ .

It is now quite a simple matter to find how the energy of the crystal is affected by lattice vibrations. Since we have an expression for the interatomic potential  $\Phi(\vec{R}_1 - \vec{R}_{1'})$  we can proceed by defining force constants

$$\Phi_{xy}(1 \ 1') = \left(\frac{\partial^2 \Phi(\mathbf{R})}{\partial x \ \partial y}\right)_{\mathbf{R}} = \left|\vec{\mathbf{R}}_{1} - \vec{\mathbf{R}}_{1'}\right|$$
(3.1)

and elements of the dynamical matrix

$$M_{xy}(\vec{q}) = \sum_{1'} \Phi_{xy}(1 \ 1') \exp \left[i \vec{q} \cdot (\vec{R}_1 - \vec{R}_{1'})\right]. \qquad (3.2)$$

The frequencies  $\omega(\vec{q})$  and polarization vectors  $\vec{u}(\vec{q})$  of lattice vibrations are then determined by the usual equations

$$\mathbf{M}\,\omega^{2}(\vec{\mathbf{q}})\mathbf{u}_{\mathbf{x}}(\vec{\mathbf{q}}) = \sum_{\mathbf{y}} \mathbf{M}_{\mathbf{x}\mathbf{y}}(\vec{\mathbf{q}})\mathbf{u}_{\mathbf{y}}(\vec{\mathbf{q}}) \,. \tag{3.3}$$

We are assuming for simplicity that there is only one atom of mass M per primitive unit cell, but the general result can obviously be obtained without difficulty.

It may be more convenient to use instead of Eq. (3.2) the reciprocal space representation of  $M_{xy}(\vec{q})$ , which, using the Ewald method (see also [40]), is

$$M_{xy}(\vec{q}) = \frac{1}{v} \sum_{\vec{H}} (\vec{q} + \vec{H})_x (\vec{q} + \vec{H})_y \Phi(\vec{q} + \vec{H}). \qquad (3.4)$$

In practice it is convenient to split  $M_{xy}(\vec{q})$  into three terms involving respectively  $\Phi^{(B)}$ , whose contribution is evaluated from Eq. (3. 2);  $\Phi^{(C)}$  whose contribution is evaluated partly from Eq. (3. 2) and partly from Eq. (3. 4) (see for example [41]); and finally  $\Phi^{(E)}$  whose contribution is evaluated from Eq. (3. 4). Since  $\Phi(R)$  is a two-body central interaction there can be only two independent force constants between any pair of atoms,

$$\Phi_{\text{radial}}(1\ 1') = \left(\frac{\partial^2 \Phi(\mathbf{R})}{\partial \mathbf{R}^2}\right)_{\mathbf{R}} = |\vec{\mathbf{R}}_1 - \vec{\mathbf{R}}_1| \qquad (3.5)$$

and

$$\Phi_{\text{tangential}} (1 \ 1') = \left(\frac{1}{R} \frac{\partial \phi(R)}{\partial R}\right)_{R} = \left|\vec{R}_1 - \vec{R}_{1'}\right|^2$$

Nevertheless the Cauchy relations between the elastic constants cannot be expected to apply because the crystal is <u>not</u> maintained in equilibrium by the interatomic potential  $\Phi(R)$  alone and the force constants therefore are of the axially symmetric type [20]. The elastic constants are in principle given by the method of long waves [41], thus involving  $\Phi(R)$  only, and if the theory is self-consistent the compressibility obtained in this way should agree with the result obtained by differentiating the total energy, which as we have seen involves other volume-dependent terms. This point, which is of considerable interest since it is usually assumed in the theory of lattice dynamics that the force constants ought to satisfy the equilibrium condition, has not been checked by a full calculation, except in the related work of TOYA [27] who found the two expressions for the compressibility to agree, at least in their principal terms.

#### 4. THE INTERATOMIC POTENTIAL IN SODIUM

In principle it should be possible to apply the above theory in reverse and derive the interatomic potential  $\Phi(\mathbf{R})$  from the phonon dispersion curves determined by experiment. This would be very valuable as  $\Phi(\mathbf{R})$  determines a variety of atomic properties of a metal, and if Z and  $\epsilon(K)$  could be assumed to be known, Z(K) and thus a variety of electronic properties of the metal could also be calculated. Unfortunately a unique result cannot be obtained in this way, as has already been pointed out by HARRISON [38], for the measured frequencies can depend only on  $\partial^2 \Phi / \partial R$  and  $R^{-1} \partial \Phi / \partial R$  for  $R = |\vec{R}_1 - \vec{R}_1|$ . In particular, we can vary  $\Phi(R)$  as we please at distances somewhat less than the minimum interatomic separation R<sub>0</sub>, without affecting the phonon dispersion curves. This means that we can add to  $\Phi(K)$  any function  $\Delta \Phi(K)$  which satisfies  $K^2 \Delta \Phi(K) = 0$  for K = 0 and whose Fourier transform is zero for  $r > R_0$ . Suppose however that the contributions of  $\Phi^{(B)}(K)$  and  $\Phi^{(C)}$  (K) to  $M_{xy}(\vec{q})$  of Eq. (3.4) are known and can be subtracted. It is then necessary to find only a  $\Phi^{(E)}(K)$ , if such exists, which will account for the phonon frequencies. While this function is similarly arbitrary it should satisfy other conditions. The theory of section 2 gives

$$\Phi^{(E)}(K) = -\frac{4\pi e^2 Z^2(K)}{K^2} \left[1 - 1/\epsilon(K)\right]$$
(4.1)

(see Eq. (2.12)), so that  $\Phi^{(E)}(K) \leq 0$ , and we also expect  $\Phi^{(E)}(K)$  to be relatively small for  $\vec{K} = \vec{H}$ , where  $\vec{H}$  is a non-zero vector of the reciprocal lattice. Any other result is inconsistent with the assumption of nearly free electrons

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which should be a particularly good approximation for sodium. Using the experimental measurements of the dispersion curves for sodium [12], it proved possible to construct a smoothly varying function  $\Phi^{(E)}(K)$  which, together with  $\Phi^{(B)}$  and  $\Phi^{(C)}$ , would account for the measured frequencies for  $\vec{q}$  in symmetry directions and would satisfy the other conditions. Results were given (see [40]) as values of

$$G(K) = -\frac{K^2 \Phi^{(E)}(K)}{4\pi e^2}.$$
 (4.2)

From these results it is possible to calculate  $\Phi(R)$ . This has now been done and the result is shown as Fig. 3. This curve shows some agreement with a calculation of the interatomic potential for liquid sodium made by JOHNSON and MARCH [42], whose result is also shown in Fig. 3. For first and second neighbour distances the results agree within a factor of two; thereafter Johnson and March's curve has, at positions corresponding to atomic separations in the crystal, a curvature which is much too great to be consistent with the experimental force constants [12] for the crystal.

#### 5. THE KOHN EFFECT

KOHN [43] drew attention to the fact that the "kink" in the dielectric function  $\epsilon(K)$  at  $K = 2k_F$  (Fig. 1) should produce a corresponding discontinuity in the gradient of the dispersion curve, at values of  $\vec{q}$  satisfying

$$\vec{q} + \vec{H} = 2\vec{k}_F . \qquad (5.1)$$

This can be seen immediately from the fact that  $\Phi^{(E)}(K)$  involves  $\epsilon(K)$  and contributes to each element  $M_{xy}(\vec{q})$  of the dynamical matrix a term

$$\frac{1}{v}\sum_{\vec{H}} (\vec{q} + \vec{H})_x (\vec{q} + \vec{H})_y \Phi^{(E)} (\vec{q} + \vec{H})$$

(see Eq. (3, 4)).

Two estimates of the order of magnitude of the effect were made by WOLL and KOHN [44]. Their first calculation consisted in treating the ions as point charges interacting with free electrons. In terms of the results given in sections 2 and 3 it amounts to setting Z(K) = 1. This gave numerical results in semi-quantitative agreement with discontinuities or neardiscontinuities which are present in the measured dispersion curves for lead [11]. The second estimate consisted in setting

$$Z(K) = \frac{3}{(Kr_s)^3} (\sin Kr_s - Kr_s \cos Kr_s), \qquad (5.2)$$

where  $r_s$  is the radius of the atomic sphere. The significance of this function, which derives from the work of BARDEEN [33], will be discussed in a later



Fig. 3

The solid line shows the interatomic potential  $\Phi(R)$  for sodium as derived from the phonon dispersion curves.  $(\Phi^{(B)}(R)$  has been neglected.)

For comparison, the potential derived by Johnson and March for liquid sodium is shown by the dotted line. The positions of near neighbours in the crystal are indicated by the numbers 1, 2, ..., 7.

section. The predicted magnitude of the kink in a dispersion curve was then reduced much below a level that could be detected by neutron inelastic scattering.

KOENIG [45] has drawn attention to another aspect of the Kohn effect which we have already mentioned in section 2. The discontinuity in slope of  $\epsilon(K)$  should lead to an oscillatory behaviour of the interatomic potential  $\Phi(R)$ , varying as R<sup>-3</sup> cos(2k<sub>F</sub>R) at moderately large distances. Koenig has analysed the force constants between planes of atoms in sodium and found that they vary in just the predicted manner. The interatomic potential for



The function  $\Phi^{(E)}(k)$  calculated for zinc by W.A. Harrison [HARRISON, W.A., Phys. Rev. 129 (1963) 2516]

sodium, shown in Fig. 3, has an oscillation, rapidly damped out, of precisely the predicted period. If however we accept this result it is difficult to accept that the discontinuity in slope of  $\Phi^{(E)}$  (K) is responsible for the variation since for sodium this function, as determined empirically, has fallen to a negligible value at K =  $2k_F$ . HARRISON [38] has already suggested that the oscillatory behaviour of  $\Phi(R)$  and the related kinks in phonon dispersion curves is to be sought in the general shape of  $\Phi^{(E)}(K)$  and not merely in its dependence on  $\epsilon(K)$ . Harrison's derivation of  $\Phi^{(E)}(K)$  from the pseudo-potential, which is calculated from first principles and not left essentially as a parameter as in our section 2, did not involve some of the further approximations made there. In particular it was not assumed that the matrix element of the pseudopotential between electron states of wave numbers  $ec{k}$  and  $ec{k}+ec{k}$  was independent of  $\vec{k}$ , and the dielectric function was not found to factor out in the way it does in Eq.(4.1). As a result, Harrison's  $\Phi^{(E)}(K)$  is not everywhere negative (see the calculated values for zinc given as Fig. 4) and changes sign about  $K = 2k_F$ . This behaviour is however quite different from that of the empirically determined  $\Phi^{(E)}(K)$  for sodium; the function G(K) (see Eq. (4.2)) is everywhere positive and falls rather abruptly to zero at K =  $2k_F$  [40]. Evidently this point cannot be regarded as settled, particularly since  $\Phi^{(E)}(K)$  is not absolutely unique when determined from the phonon dispersion curves (see section [4]). In particular, it seems unlikely that the rather pronounced kinks in the dispersion curves for lead can be accounted for except in terms of the behaviour of the dielectric function.

#### 6. RECENT CALCULATIONS OF PHONON DISPERSION CURVES

While the discussion given in previous sections throws some light on the relationship between screening, the effective potential for electron-core interaction and the interatomic potential, the theory even in its simplest form cannot be used for actual calculations of phonon dispersion curves for a particular metal until the effective potential is known. In this section we



The dispersion curves of sodium for  $\vec{q}$  in the [100], [110] and [111] directions. The solid lines show the results calculated by Toya. [WOODS, A.D.B., BROCKHOUSE, B.N., MARCH, R.H. and BOWERS, R., Proc. phys. Soc. <u>79</u> (1962) 440]

Longitudinal
 Transverse

review briefly those few papers in which numerical calculations have been reported, and relate them to the theory given in earlier sections.

The first attempt to calculate dispersion curves for sodium by a satisfactory method was made by TOYA [27] with considerable success in that the calculations, which preceded by some years the experimental measurements, proved to be in rather good agreement with them (see Fig. 5). At first sight Toya's method seems quite different from the one outlined in earlier sections of this paper, but in fact it can be expressed in similar language. The Coulomb and Born-Mayer interactions,  $\Phi^{(C)}$  and  $\Phi^{(B)}$ , are separated as before. To evaluate the contribution of  $\Phi^{(E)}$  to the dynamical matrix, Toya starts from a perfect crystal in which a lattice vibration of wave vector  $\vec{q}$  is excited, and considers the change in the energy of the conduction electrons. This involves the matrix element for electron-phonon interaction. (It is worth noting that this quantity usually appears in connection with processes in which energy is conserved, for instance the scattering of phonons by electrons in the theory of thermal conductivity. Here however we are concerned with a virtual process in which a phonon creates an electron-hole pair which recombine to emit a phonon with energy and wave vector unchanged, but before doing so they interact with the other electrons. The constant energy of the phonon depends on such repeated onephonon processes.) The matrix element involves the Fourier transform of the gradient of the potential around the displaced ions. This however is very simply related to the transform of the potential around an ion, which takes us back to the factor  $4\pi eZ(K)/K^2$ . In evaluating the screening effect, the exchange interaction between conduction electrons is taken into account by using Slater's approximation, that is by introducing an "exchange density"

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of electrons which has the result of diminishing the effectiveness of screening. A further somewhat empirical correction is made to allow for correlation effects in the motion of the electrons; the net result is to modify the expression for  $\epsilon(K)$  which we had earlier from

$$\epsilon(\mathbf{K}) = 1 + \frac{8\pi \mathrm{N}\mathrm{e}^2}{\mathrm{K}^2} \sum_{\vec{k}} [\mathrm{E}(\vec{k} + \vec{K}) - \mathrm{E}(\vec{k})]^{-1}$$

to

$$\epsilon(\mathbf{K}) = 1 + \left(\frac{8\pi \mathrm{Ne}^2}{\mathrm{K}^2} - \mathrm{B}\right) \frac{\mathrm{D}}{\mathrm{D}_0} \sum_{\vec{k}} [\mathrm{E}(\vec{k} + \vec{K}) - \mathrm{E}(\vec{k})]^{-1} , \qquad (6.1)$$

where B and  $D/D_0$  are constants whose numerical values were estimated. The central problem of course is the form of the matrix element for electronphonon interaction, and Toya relies on the classic solution of BARDEEN [33] of this problem for an alkali metal. In our notation, it amounts to setting

$$\frac{4\pi e^2 Z(K)}{K^2} = \left\{ \frac{4\pi e^2}{K^2} + \gamma v \left[ V(r_s) - E_0 \right] \right\} g(Kr_s), \qquad (6.2)$$

where

$$g(x) = 3x^{-3} (\sin x - x \cos x)$$
 (6.3)

and for sodium  $\gamma = 1$ .

In Eq. (6.2)  $V(r_s) - E_0$  is the difference between the Hartree-Fock potential at  $r = r_s$  and the energy of the lowest electron level. For sodium this term is small enough to be ignored, and in terms of the fictitious charge distribution Z(r) which is to give the effective potential for electron-core interaction, Eq. (6.2) then simply corresponds to

$$Z(\mathbf{r}) = \left(\frac{4\pi}{3} \mathbf{r}_{s}^{3}\right)^{-1} \text{ for } \mathbf{r} < \mathbf{r}_{s}$$

$$= 0 \qquad \text{ for } \mathbf{r} > \mathbf{r}_{s} . \qquad (6.4)$$

According to SHAM and ZIMAN [37] there is not much theoretical justification for taking Bardeen's result at its face value; it fits the facts because for sodium the effective potential happens to be rather like what would be produced by spreading a charge +e uniformly throughout a sphere of radius  $r_s$ . When Eq. (6.1) for  $\epsilon(K)$  and Eq. (6.2) for Z(K) are substituted in the formulae given in section 4, Toya's results for sodium are obtained. The calculation has been repeated for the other alkali metals [46], and has been extended to the consideration of anharmonic effects [47], but this topic lies outside the scope of our review.

TOYA [48] has made a similar calculation for copper. Whereas in the alkali metals the term  $\Phi^{(B)}$  is relatively unimportant, in copper it is dominant and since it was calculated using the Thomas-Fermi approximation, the calculation of phonon frequencies is correspondingly uncertain. Lead presents an even more difficult problem which TOYA [49] has tackled somewhat as follows. It would be wrong to assume that the density of conduction

electrons is even approximately constant in lead, as was assumed for sodium. Toya therefore writes

$$\rho(\vec{r}) = \rho_{\text{const.}} + \sum_{1} \rho_{b}(\vec{r} - \vec{R}_{1}),$$
 (6.5)

where  $\vec{R}_1$  is a vector to the origin of the l<sup>th</sup> unit cell. The term  $\rho_{const.}$  is adjusted so that  $\rho_b(\vec{r} - \vec{R}_1) = 0$  for  $r > r_s$ . The first term is associated with "free" and the second with "bound" conduction electrons. The latter are supposed to move rigidly with the core electrons and not to take part in the screening process. This step is justified by noting that the perturbed wave function in the crystal will have the form

$$\Psi(\mathbf{kr}) = \Psi_0(\mathbf{kr}) + \sum_{\vec{H}} b_{\vec{H}} \Psi_0(\vec{k} + \vec{q} + \vec{H}), \qquad (6.6)$$

where

$$b_{\vec{H}} = \int \Psi_0^* (\vec{k} + \vec{q} + \vec{H}) [\delta V_i(\vec{r}) + \delta V_\rho(\vec{r})] \Psi_0(kr) d^3r [E(\vec{k} + \vec{q} + \vec{H}) - E(\vec{k})]^{-1} . \quad (6.7)$$

Here  $\delta V_i(\vec{r})$  is the potential change resulting from the displacement of the ions in a mode of vibration of wave vector  $\vec{q}$  and  $\delta V_\rho(\vec{r})$  is that potential resulting from the change in density of the screening electrons. The change of this density is

$$\delta \rho(\vec{\mathbf{r}}) = \sum_{\mathbf{k}} \{ |\Psi(\mathbf{kr})|^2 - |\Psi_0(\mathbf{kr})|^2 \}$$

and is divided into two parts,  $\delta \rho_f$  and  $\delta \rho_b$ , on the basis that  $\rho_f$  is to involve terms for which  $\vec{k} + \vec{q} + \vec{H}$  and  $\vec{k}$  are in the same zone while  $\rho_b$  is to involve terms for which  $\vec{k} + \vec{q} + \vec{H}$  and  $\vec{k}$  are in different zones. The former thus involves virtual intra-zone transitions, the latter virtual inter-zone transitions for which the energy denominator in  $b_{\vec{H}}$  of Eqs. (6.6) and (6.7) is sufficiently large that the distortion of the density can be neglected. The two electrons in the first zone, which is completely filled, contribute only to  $\rho_b$ . The effective charge of an ion is defined as

$$eZ_{eff} = e[4 - \int \rho_b(\mathbf{r}) d^3\mathbf{r}]$$

and is estimated as 1.5e. Thereafter the calculation proceeds much as for sodium, although there are complications caused by the different screening properties of electrons in the second and third zones respectively. The matrix element for electron-phonon interaction is assumed to involve a modification of the expression appearing on the right hand side of Eq. (6.2), the quantity $\gamma_v[V(r_s) - E_0]$  being regarded essentially as an adjustable parameter for electrons in the different zones. This is perhaps the chief weakness of the calculation. The magnitude of the exchange repulsion between cores is also uncertain. The final agreement between measured and calculated frequencies was only qualitative. The calculated curves are said to exhibit Kohn anomalies; the extent and positions of these are not clear from the published diagrams and in any event the expression used for  $\epsilon(K)$  (Eq. (6.1)) was assumed to have a discontinuous change of slope at a value of K such that  $\epsilon(K) = 1$ , thereby apparently introducing another source of "kinks" which is certainly non-physical.

The method used by Sham in Reference [37] is based on the concept of a pseudo-potential, and so far has been applied only to sodium. Two calculations were made. In the first it was assumed that the pseudo-potential can be regarded as localized; each ion then carries with it a relatively weak effective potential, as discussed in earlier sections of this paper. In the second calculation this approximation was not made; the fact that the calculated dispersion curves were changed very little may be regarded as justifying the assumption of an effective potential which is independent of  $\vec{k}$ , at least in sodium. The effective potential was calculated from the true ion potential, taken to be the Prokofjew potential, which reproduces correctly the energy levels of an isolated ion. What makes Sham's formulae more general and considerably more complicated than those we have met so far is that the density of conduction electrons is not taken to be constant. We therefore have to deal with the dielectric function of a crystal and not of a free electron gas. The former is a matrix  $\epsilon(\vec{q} + \vec{H}, \vec{q} + \vec{H}')$ , when we have to deal with a potential variation which results from a lattice vibration of wave vector  $\vec{q}$  [37]. It is found that if we write the electronic contribution to  $M_{xv}(\vec{q})$ of Eq. (3.3) as  $M_{xy}^{(E)}(\vec{q})$ , then

$$M_{xy}^{(E)}(\vec{q}) = \sum_{\vec{H},\vec{H}'} X_{xy}(\vec{q} + \vec{H}, \vec{q} + \vec{H}') - X_{xy}(\vec{H}, \vec{H}'), \qquad (6.8)$$

where

$$X_{xy}(\vec{q} + \vec{H}, \vec{q} + \vec{H}') = \frac{1}{v} \left\{ \frac{4\pi e^2}{|\vec{q} + \vec{H}|^2} \left[ 1 - f(\vec{q} + \vec{H}) \right] \right\}^{-1}$$

$$\times \{ \epsilon^{-1} (\vec{q} + \vec{H}, \vec{q} + \vec{H}') - \delta_{\vec{H}, \vec{H}'} \} (\vec{q} + \vec{H})_{x} (\vec{q} + \vec{H}')_{y} \vee (-\vec{q} - \vec{H}) \vee (\vec{q} + \vec{H}').$$
 (6.9)

In this expression V(K) is the Fourier transform of the effective potential. In the numerical work it was assumed that off-diagonal terms ( $\vec{H} \neq \vec{H}$ ') were small enough to be neglected; Eq.(6.9) then reverts to that of previous sections, apart from the appearance of the factor

$$1 - f(\vec{q} + \vec{H}) = 1 - \frac{\frac{1}{2}(\vec{q} + \vec{H})^2}{(\vec{q} + \vec{H})^2 + k_F^2 + k_s^2}.$$

This factor results from the inclusion of a screened exchange interaction between the conduction electrons, which diminishes the effectiveness of screening. The second term on the right of Eq. (6.8) did not appear in our earlier equations, since if the density is constant  $X_{xy}(\vec{H}, \vec{H}^{i})=0$  for  $\vec{H} \neq 0$ . It is necessary to ensure the correct behaviour of  $\omega(\vec{q})$  as  $\vec{q} \rightarrow 0$ , and Sham shows that it can be ascribed to intrinsic two-phonon processes in which an electron interacts simultaneously with two phonons. The agreement between calculated and measured dispersion curves for sodium was about as good as was achieved by Toya; in particular the agreement for the lower transverse branch in the [110] direction remained rather poor. However the test of the pseudopotential method for sodium has been fairly encouraging for extending it to other metals.

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#### DISCUSSION

K. SINGWI: The enormous discrepancy between the effective interatomic potential as given by the calculations of Johnson and March and the value you have derived from the phonon dispersion relation could very well be due to the fact that X-ray determination of the pair correlation function  $g(\vec{r})$  is not very reliable. Small errors in the determination of  $g(\vec{r})$  might lead to violent changes in the potential  $V(\vec{r})$ , if the latter is derived from the former. Dr.A. Rahman at Argonne has recently looked into the reliability of X-ray determination of  $g(\vec{r})$ .

W. COCHRAN: The effective interatomic potential which I have shown applies, of course, to the solid and not the liquid, but one would not expect such a great discrepancy.

S.SINHA: There should be an easy way of checking the validity of the simple theory you have talked about, i.e. the picture of axially symmetric forces between atoms immersed in a free-electron gas. Applying the equilibrium condition for the lattice, it should be found that  $C_{12} - C_{44} = -2P$ , where P = the sum of the kinetic, exchange and correlation pressures of the free-electron gas. I wonder whether such a check has been made for sodium. Working out the values for copper I have found  $-2P = 3.092 \times 10^{11} \text{ dyn/cm}$  and the experimental value of  $C_{12} - C_{44} = 4.32 \times 10^{11} \text{ dyn/cm}$ .

W. COCHRAN: I believe this check is essentially the same as showing that the method of long waves and the method involving calculation of the second derivative of the cohesive energy lead to the same result for the compressibility. Professor Toya's results for sodium do show agreement of the more important terms in the expressions for the compressibility obtained by these two different routes. As far as I know, however, this point has not been checked in work other than Toya's.

J.L. WARREN: The dielectric constant  $\epsilon(K)$  that you used in your presentation depends only on wave vector. The wave vector and <u>frequency</u>dependent dielectric constant  $\epsilon(K,\omega)$  for the free electron gas is known. Can this be used to go beyond the adiabatic approximation inherent in the present formulation of the problem?

W. COCHRAN: In principle, I believe it could. Professor Toya has proposed a method for sodium going beyond the adiabatic approximation, and perhaps he could give a more authoritative answer.

T. TOYA: The non-adiabatic terms in the dielectric function correspond to the dynamic interactions of electrons with zero-point vibrations. They are not important at high temperatures, but are important at low ones. The superconductivity is due to these terms, and anomalies of electronic specific heat at very low temperatures might also be attributed to them.

R.P. SINGH: The noble metals, copper, silver and gold, have a large ionic core which would be distorted during lattice vibration. Could you indicate how best this can be taken into account in calculating the phonon dispersion curves of these metals?

W. COCHRAN: Possibly by a "shell model" approximation, as has in fact already been suggested by Dr.S. Sinha.

B. BURAS: By assuming that  $Z(\vec{r})$  is spherically symmetrical, it follows immediately that  $Z(\vec{K})$  is spherically symmetrical. How good is this approximation, especially in the case of crystals with high anisotropy?

W. COCHRAN: If one knew about an anisotropy in the static distribution  $Z(\vec{r})$ , it would be quite possible to take it into account. The kind of anisotropy which is probably important, however, is that introduced only when an ion core is displaced, i.e. polarization of the core.

G. CAGLIOTI: With reference to Fig. 3 of your paper, I would like to point out that at high values of the distance r the discrepancy between the interatomic potential as derived from dispersion curves (solid line) and that derived from diffraction by liquid sodium (dotted line) could be due to the difficulty of exploring the intensity associated with very small momentum transfers in diffraction experiments.

P. EGELSTAFF: In reply to Dr.Caglioti's point, I think Johnson and March would claim that the oscillations in the potential at large r are related to a singularity in the liquid structure factor at a value of  $Q \sim 2k_F$ .

W. COCHRAN: I should like to ask Dr. Egelstaff whether he thinks there is good evidence for a kink at  $Q \sim 2k_F$ .

P. EGELSTAFF: The direct experimental evidence for singularities in the liquid structure factor is not very strong. However, in the case of liquid tin and bismuth there is an anomaly at  $Q \sim 2k_F$ . It is not yet clear whether this is due to "molecular" effects or to a type of Kohn effect.

K.SINGWI: I might comment here that a colleague of mine, who has recently been investigating structure factors in liquids, has given a mathematical formula for testing how good these pair correlation functions are. Most of the X-ray work that he has examined turns out to be extremely poor, particularly when one is interested in the detailed shapes of the curves, for example first or second derivatives. He has also compared the neutron data and has found that the data obtained for liquid argon are very much better than the X-ray data. A paper to be published in the Physical Review describes the test one has to apply on the structure factor. It should not be assumed that the structure factor as given by X-ray is really good – it all depends on what one is looking at.
# ELECTRON-PHONON INTERACTIONS AND LATTICE DYNAMICS

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#### Abstract — Résumé — Аннотация — Resumen

ELECTRON-PHONON INTERACTIONS AND LATTICE DYNAMICS. It is usual to apply the Born-yon Kármán theory to the discussion on dynamical properties of metals. Recent experimental results by neutron spectrometry have shown that the interaction between atoms in metals is of long-range force, so that more than ten force constants are required as parameters to explain experimental dispersion relation of frequency versus wave number vector of normal vibrations. It is more rational to derive both the dispersion relation and force constants from the Hamiltonian of a metal. The interaction between atoms in a metal consists of three parts, i.e. the exchange or overlap potential between ion cores, the Coulomb potential between ions and the potential induced by electron-phonon interaction, including electron-electron interaction. The latter two potentials are essentially of long-range force, whereas the first is of short-range force. The dispersion relation, hence force constants, was previously derived by formulating the contributions of the respective potential to the adjabatic potential of normal vibrations. The exchange and correlation effects on screening by conduction electrons, the matrix element of electron-phonon interaction and the force constants are discussed by comparing the theoretical dispersion relation with the observed one of sodium. The parameters in the appropriately assumed expression of the overlap potential between ion cores of copper may be determined by analysing the observed dispersion curves with the assumption of quasi-free electron model. The parameters thus determined seem to be more accurate than those determined by other methods. Properties of monovalent metals related to lattice dynamics are also discussed.

The observed dispersion relations of multivalent metals such as lead, niobium and aluminium, have in general complicated features. On the basis of a method previously developed numerical investigations into the dispersion relation are made, assuming simple overlapping band structures. The calculated dispersion curves for a fictitious metal with triply-degenerate bands and a quasi-free electron per metal atom reveal Kohn anomalies similar to those observed in the curves of lead. The force range between atoms is strongly dependent on band structure.

INTERACTIONS ÉLECTRON/PHONON ET DYNAMIQUE DES RÉSEAUX. On applique habituellement la théorie de Born et von Kármán à l'examen des propriétés dynamiques des métaux. Les résultats d'expériences récentes à l'aide de la spectrométrie des neutrons ont montré que l'interaction entre atomes dans les métaux est de la nature d'une force à longue portée, de sorte qu'il faut, comme paramètres, plus de dix constantes de forces pour expliquer la courbe de dispersion expérimentale exprimant la fréquence en fonction du vecteur d'ordre pour les vibrations normales. Il est plus rationnel de déduire, aussi bien la courbe de dispersion que les constantes de forces, de l'hamiltonien d'un métal, L'interaction entre atomes dans un métal se compose de trois parties, savoir: le potentiel d'échange ou de chevauchement entre noyaux d'ions, le potentiel coulombien entre les ions, et le potentiel induit par les interactions électron/phonon, y compris les interactions électron/électron. Les deux derniers potentiels sont essentiellement de la nature d'une force à longue portée et le premier, d'une force à courte portée. Auparavant, d'autres chercheurs avaient obtenu la courbe de dispersion - et de là, les constantes de forces - en établissant les contributions respectives des potentiels au potentiel adiabatique des vibrations normales. L'auteur discute les effets d'échange et de corrélation sur l'écran constitué par les électrons de conduction, l'élément matrice des interactions électron/phonon et les constantes de forces, en comparant la courbe de dispersion théorique avec celle qui a été observée pour le sodium. On peut déterminer les paramètres, dans l'expression convenablement formulée du potentiel de chevauchement entre les noyaux d'ions du cuivre, en analysant les courbes de dispersion observées dans l'hypothèse d'un modèle d'électrons quasi libres. Il semble que les paramètres ainsi déterminés soient plus précis que ceux qui le sont par une autre méthode. L'auteur discute aussi les propriétés de métaux monovalents ayant un rapport avec la dynamique des réseaux.

# Τ. ΤΟΥΑ

D'une manière générale, les courbes de dispersion obtenues pour des métaux multivalents tels que plomb, niobium et aluminium, présentent des caractéristiques assez complexes. L'auteur fait des études numériques sur la courbe de dispersion en supposant des structures simples de bandes en chevauchement et en se fondant sur la méthode qui a déjà été mise au point et qui fait l'objet d'un travail encore inédit. Pour un métal fictif à bandes triplement dégénérées et un électron quasi libre par atome de métal, les courbes de dispersion calculées révèlent des anomalies de Kohn analogues à celles qui ont été observées pour les courbes du plomb. Les forces entre les atomes dépendent dans une grande mesure de la structure de bandes.

ЭЛЕКТРОННО-ФОНОННЫЕ ВЗАИМОДЕЙСТВИЯ И ДИНАМИКА РЕШЕТКИ. Для рассмотрения динамических свойств металлов обычно применяется теория Борн фон Кармана. Результаты последних экспериментов, выполненных с помощью нейтронной спектрометрии, показали, что взаимодействие между атомами металлов имеет жарактер дальнодействующей силы, так что больше 10 констант силы необходимы в качестве параметров для объяснения экспериментального дисперсионного соотношения частоты и числового волнового вектора нормальных колебаний. Как дисперсионное соотношение, так и константы силы более рационально получать по гамильтониане металла. Взаимодействие между атомами металла состоит из трех элементов: ооменного или перекрывающего потенциала между сердцевинами ионов, кулоновского потенциала между ионами и потенциала, индуцированного электронно-фононным взаимодействием, включая электронно-электронное взаимодействие. Последние два потенциала являются, по существу, дальнодействующими силами, тогда как первый является близкодействующей силой. Дисперсионное соотношение, а следовательно, и константы силы, получались раньше путем составления формул, выражающих роль соответствующего потенциала в адиабатическом потенциале нормальных колебаний. Влияние обмена и корреляции на экранирование электронов проводимости, матричный элемент электронно-фононного взаимодействия и константы силы рассматриваются на основе сравнения теоретических дисперсионных соотношений с наблюдаемым соотношением для натрия. Параметры принимаемого выражения для перекрывающего потенциала между сердцевинами ионов меди могут быть определены путем анализа наблюдаемых дисперсионных кривых, если предположить при этом квазисвободную электронную модель. Представляется, что полученные таким образом параметры являются более точными, чем полученные другим методом. Рассматриваются также свойства одновалентных металлов, связанные с динамикой решетки.

Наблюдаемые дисперсионные соотношения многовалентных металлов, например, свинца, ниобия и алюминия, имеют, как правило, сложный характер. Цифровые расчеты дисперсионного соотношения выполнены на основе ранее разработанного метода, исходя из предположения о простых перекрывающихся полосных структурах. Рассчитанные дисперсионные кривые для фиктивного металла с трижды вырожденными полосами и квазисвободным электроном на каждый атом металла показали существование аномалий Кона, аналогичных аномалиям, наблюдаемым в кривых для свинца. Радиус взаимодействия между атомами сильно зависит от полосной структуры.

INTERACCIONES ELECTRÓN-FONÓN Y DINÁMICA RETICULAR. La teoría de Born-von Kármán suele aplicarse al análisis de las propiedades dinámicas de los metales. Los resultados experimentales recientemente obtenidos por espectrometría neutrónica muestran que en los metales de interacción atómica adopta la forma de fuerza de gran alcance, de modo que es preciso recurrir a más de diez constantes de fuerza, como parámetros, para poder explicar la relación de dispersión experimental de la frecuencia en función del vector de número de onda de las vibraciones normales. Es más lógico deducir la relación de dispersión y las constantes de fuerza del hamiltoniano de un metal. La interacción de los átomos de un metal consta de tres partes, a saber, el potencial de intercambio o de superposición entre los núcleos iónicos, el potencial coulombiano entre los iones y el potencial inducido por la interacción electrón-fonón, incluida la interacción electrónelectrón. Estos dos últimos potenciales revisten esencialmente la forma de fuerzas de gran alcance, mientras que la fuerza correspondiente al primero es de corto alcance. La relación de dispersión, y de aquí las constantes de fuerza, se dedujeron formulando las contribuciones del potencial respectivo al potencial adiabático de las vibraciones normales. Se analizan, comparando la relación de dispersión teórica con la observada en el sodio, los efectos de intercambio y de correlación en el blindaje producido por los electrones de conducción, el elemento matriz de la interacción electrón-fonón y las constantes de fuerza. Los parámetros de la expresión hipotética correcta del potencial de superposición entre núcleos iónicos de cobre pueden determinarse por análisis de las curvas de dispersión observadas admitiendo un modelo de electrones cuasi libres. Los parámetros determinados de esta manera parecen ser más exactos que los establecidos por otros métodos. Se estudian, asimismo, las propiedades de los metales monovalentes en relación con la dinámica reticular.

Las relaciones de dispersión observadas en el caso de metales polivalentes tales como el plomo, niobio y alumínio presentan, en general, características complejas. Se procede al análisis numérico de la relación de dispersión suponiendo estructuras sencillas de bandas superpuestas, conforme al método previamente establecido. Las curvas de dispersión calculadas para un metal ficticio con bandas triplemente degeneradas y un electrón cuasi libre por átomo de metal revelan anomalías de Kohn semejantes a las observadas en las curvas correspondientes al plomo. El alcance de las fuerzas entre los átomos depende estrechamente de la estructura de las bandas.

# 1. INTRODUCTION

Recently the dispersion relation of frequency versus wave vector for metals has been extensively investigated by inelastic scattering of neutrons. Force constants between atoms are derived from the observed dispersion relation in accordance with the Born-von Kármán theory, with the remarkable conclusion that they are of long-range force. The interaction between atoms in a metal is divided into three parts, i.e. the exchange or overlap potential between ion cores, the Coulomb potential between ions, and the potential induced by electron-phonon interactions inclusive of electronelectron interactions [1-3]. The last two are essentially of long-range force. The present author has worked out the respective parts as follows [1]. The contribution to the adiabatic potential of normal vibration from the exchange potential was readily calculated, since it was of short-range force. That from the Coulomb potential was given by Ewald's method [4]. The potential induced by valence electrons was formulated by extending the Hartree-Fock method to work it out numerically. In the present paper, the potential induced by valence electrons is formulated alternatively by the variation method, which is suitable for discussing qualitatively the exchange and correlation effects without ambiguity, and the theoretical conclusions thus obtained are verified by the experimental results for sodium [5]. In the case of copper, the exchange potential is determined conversely from the observed dispersion relation of copper, the potential being not yet worked out accurately. Electric conductivity, specific heat and thermal expansion of monovalent metals are discussed on the same base, with special reference to the electron-electron interactions.

The dispersion relation for multivalent metals is in general complicated, being associated with anomalies. Experimental results are not accounted for in terms of a simple model, where the band structure is ignored. Thus, it is necessary to take into account the band structure. The effect of band structure on the dispersion relation is investigated by calculating it for a fictitious metal with triply-degenerate bands and a quasi-free electron per atom, the exchange repulsion between atoms as well as the lattice constant being assumed to be the same with those of copper. The overall dispersion curves are remarkably different from those of copper and reveal anomalies.

# 2. GENERAL FORMULATION

# 2.1. Hamiltonian for a metal

The Hamiltonian for a monovalent metal, containing N electrons and N ions in unit volume, is given by

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \tag{1}$$

$$\mathscr{H}_{1} = (1/2 \text{ m}) \sum_{i} \vec{p}_{i}^{2} + (1/2) \sum_{i,j} e^{2} / |\vec{r}_{i} - \vec{r}_{j}| + \sum_{i,\ell} v_{i} (\vec{r}_{i} - \vec{R}_{\ell}), \qquad (2)$$

$$\mathscr{H}_{2} = (1/2) \sum_{\ell,\ell'} e^{2/2} \left| \vec{\mathbf{R}}_{\ell} - \vec{\mathbf{R}}_{\ell'} \right| + (1/2) \sum_{\ell,\ell'} v_{\mathbf{R}} (\vec{\mathbf{R}}_{\ell} - \vec{\mathbf{R}}_{\ell'}) + \sum_{\ell} (M/2) \vec{\mathbf{R}}_{\ell}^{2}, \qquad (3)$$

where the first term in Eq.(2) is the kinetic energy of valence electrons, the second term the Coulomb potential between electrons, the third term the potential of electrons in the field of metal ions, the first or the second term in Eq.(3) is the Coulomb or the exchange potential between ion cores, respectively, and the last one the kinetic energy of ions;  $\vec{p}_i$  or  $\vec{r}_i$  is the momentum or the co-ordinate vector of the i-th electron, i = 1...N; m or M the mass of an electron or an ion, and  $\vec{R}_{\ell}$  or  $\vec{R}_{\ell}$  the co-ordinate or velocity vector of the  $\ell$ -th ion,  $\ell = 1...N$ .

Equation (1) is reduced to the Hamiltonian  $\mathcal{H}_0$  of a perfect crystal, where each ion is at rest on the equilibrium lattice point  $\vec{R}_{\ell}^0$ . The lattice vibration of wave vector  $\vec{q}$  and polarization  $\vec{e}_q$  causes the displacement  $\vec{u}_{\ell} = \vec{R}_{\ell} - \vec{R}_{\ell}^{*}$  of the  $\ell$ -th ion from its equilibrium position  $\vec{R}_{\ell}^0$ , which is described in terms of normal co-ordinates  $a_q$  and  $a_{\bar{q}}^*$  as

$$\vec{u}_{\ell} = N^{-\frac{1}{2}} \vec{e}_{q} [a_{q} \exp\left(i\vec{q}\vec{R}_{\ell}^{0}\right) + a_{q}^{*} \exp\left(-i\vec{q}\vec{R}_{\ell}^{0}\right)].$$
(4)

The direction of  $\vec{e}_{-q}$  is taken in the same sense as  $\vec{e}_q$  so that  $a_{-q} = a_q^*$ . The  $\mathscr{H}_0$  is the zeroth order term in the expansion of  $\mathscr{H}$  with respect to  $a_q$  and  $a_q^*$ . The third term in Eq.(2) yields the first order term in the expansion, i.e.

$$\delta \mathbf{v}_{i} = -\mathbf{N}^{\frac{1}{2}} \sum_{\ell} \left[ \mathbf{a}_{\mathbf{q}} \exp\left(i\vec{\mathbf{q}} \cdot \vec{\mathbf{R}}_{\ell}^{0}\right) \vec{\mathbf{e}}_{\mathbf{q}} \text{ grad } \mathbf{v}_{i} \left(\vec{\mathbf{r}} - \vec{\mathbf{R}}_{\ell}^{0}\right) + \text{comp. conj.} \right].$$
(5)

The second order terms,  $E^{II}$ ,  $E^{C}$  and  $E^{R}$ , comprising  $a_{q} a_{q}^{*}$  arise from the third term in Eq.(2), the first term in Eq.(3) and the second term in Eq.(3) respectively, the coefficients of which are readily derived [1]. The variation method is applied as follows to work out the contribution from valence electrons perturbed by Eq.(5) to the adiabatic potential of the normal vibration, which will be designated hereafter as  $E^{I}$ , the ion-electron-ion potential.

# 2.2. The variation method

We assume the wave function of valence electrons and the lattice vibration as

$$\Phi(\vec{k}_1,\ldots,\vec{k}_N;n_q) = \Psi(\vec{k}_1,\ldots,\vec{k}_N;a_q)Q_{n_q}(a_q), \qquad (6)$$

where  $k_i$  is the wave vector of an electron,  $Q_{n_q}(a_q)$  the wave function of harmonic oscillator with quantum number  $n_q,\,$  and

$$\Psi(\vec{k}_1,\ldots,\vec{k}_N;a_q) = (N!)^{\frac{1}{2}} \det \left| \psi(\vec{k}_i,\vec{r}_j;a_q) \right|, \tag{7}$$

with

$$\psi(\vec{k}_{i}, \vec{r}_{j}; a_{q}) = [1 - (1/2)\sum_{h} (|b_{h+}(\vec{k}_{i})|^{2} + |b_{h-}(\vec{k}_{i})|^{2})]\psi_{0}(\vec{k}_{i}, \vec{r}_{j})$$
  
+  $\sum_{h} [b_{h+}(\vec{k}_{i}) \psi_{0}(\vec{k}_{i} + \vec{q} + \vec{h}, \vec{r}_{j}) + b_{h-}(\vec{k}_{i}) \psi_{0}(\vec{k}_{i} - \vec{q} - \vec{h}, \vec{r}_{j})].$  (8)

The  $\psi_0(\vec{k}, \vec{r})$  in Eq.(8) is the wave function of the Hartree equation for a perfect crystal, i.e.<sup>1</sup>

$$[-(\hbar^2/2 m)\Delta + V(\vec{r})]\psi_0(\vec{k},\vec{r}) = E_0(\vec{k})\psi_0(\vec{k},\vec{r}), \qquad (9)$$

where

$$\mathbf{V}(\vec{\mathbf{r}}) = \sum_{\ell} \mathbf{v}_{i}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_{\ell}^{0}) + \mathbf{e}^{2} \int \rho_{0}(\vec{\mathbf{r}}') / \left| \vec{\mathbf{r}} - \vec{\mathbf{r}}' \right| d\vec{\mathbf{r}}',$$

 $\rho(\vec{r'}) = \sum_{k'} \psi_0^*(\vec{k'}, \vec{r'}) \psi_0(\vec{k'}, \vec{r'})$  and  $E_0(\vec{k})$  is the Hartree energy. It is normalized in unit volume. The  $\vec{h}$  in Eq.(8) is  $2\pi$  times the reciprocal lattice vector  $\tau$ , and  $b_{h+}(\vec{k})$  or  $b_{h-}(\vec{k})$  is the variation parameter proportional to  $a_q$  or  $a_q^{\pi}$  respectively. Orthogonality requirements between  $\psi(\vec{k}, \vec{r}; a_q)$ 's are

$$b_{h+}(\vec{k}) + b_{h-}^{*}(\vec{k} + \vec{q} + \vec{h}) = 0$$
, and  $b_{h-}(\vec{k}) + b_{h+}^{*}(\vec{k} - \vec{q} - \vec{h}) = 0$ . (10)

The integral

$$\int \Psi^* \mathscr{H}_{\cdot} \Psi \, \mathrm{d}\vec{r}_1 \dots \mathrm{d}\vec{r}_N \tag{11}$$

is now readily expressed in terms of  $b_{h+}(\vec{k})$  and  $b_{h-}(\vec{k})$  to the second order with respect to the displacement  $\vec{u}_{\ell}$  of Eq.(4), as

{Hartree-Fock energy for a perfect crystal}

$$+ \sum_{\substack{k,h \\ k,h}} \{ | b_{h+}(\vec{k})|^{2} [E_{0}(\vec{k} + \vec{q} + \vec{h}) + v_{ex}(\vec{k} + \vec{q} + \vec{h}) - E_{0}(\vec{k}) - v_{ex}(\vec{k})] \\ + | b_{h-}(\vec{k})|^{2} [E_{0}(\vec{k} - \vec{q} - \vec{h}) + v_{ex}(\vec{k} - \vec{q} - \vec{h}) - E_{0}(\vec{k}) - v_{ex}(\vec{k})] \\ + (b_{h+}(\vec{k}) + b_{h-}^{*}(\vec{k})) [\delta v_{ih}^{*} + \frac{1}{2} \delta v_{\rho h}^{*} + \frac{1}{2} \delta v_{exh}^{*}] \\ + (b_{h-}(\vec{k}) + b_{h+}^{*}(\vec{k})) [\delta v_{ih} + \frac{1}{2} \delta v_{\rho h} + \frac{1}{2} \delta v_{exh}] \},$$
(12)

where

The subscript to k or r is omitted in what follows, except in case of particular necessity.

$$\begin{aligned} v_{ex} (\vec{k}) &= \int \psi_0^* (\vec{k}, \vec{r}) (e^2 \rho(\vec{r}, \vec{r'}) / |\vec{r} - \vec{r'}|) \psi_0(\vec{k}, \vec{r'}) d\vec{r} d\vec{r'} \\ v_{ex} (\vec{k} + \vec{q} + \vec{h}) &= \int \psi_0^* (\vec{k} + \vec{q} + \vec{h}, \vec{r}) (e^2 \rho(\vec{r}, \vec{r'}) / |\vec{r} - \vec{r'}|) \psi_0(\vec{k} + \vec{q} + \vec{h}, \vec{r'}) d\vec{r} d\vec{r'} \\ \rho(\vec{r}, \vec{r'}) &= \sum_{k'} \psi_0^* (\vec{k} \cdot, \vec{r}) \psi_0(\vec{k} \cdot, \vec{r'}) \\ \delta v_{ih} &= \int \psi_0^* (\vec{k} + \vec{q} + \vec{h}, \vec{r}) \delta v_i \psi_0(\vec{k}, \vec{r}) d\vec{r}, \end{aligned}$$
(13)  
$$\delta v_{\rho h} &= \int \psi_0^* (\vec{k} + \vec{q} + \vec{h}, \vec{r}) \delta v_{\rho} \psi_0(\vec{k}, \vec{r}) d\vec{r}, \\ \delta v_{exh} &= \int \psi_0^* (\vec{k} + \vec{q} + \vec{h}, \vec{r}) \delta v_{ex} \psi_0(\vec{k}, \vec{r}) d\vec{r}, \\ \delta v_{\rho} (\vec{r}) &= e^2 \int \delta \rho(\vec{r'}) / |\vec{r} - \vec{r'}| d\vec{r'}, \end{aligned}$$

and

$$\delta \rho(\vec{r}') = \sum_{k,h} \{ [b_{h+}(\vec{k})\psi_0^*(\vec{k},\vec{r}')\psi(\vec{k}+\vec{q}+\vec{h},\vec{r}')+b_{h-}^*(\vec{k})\psi_0^*(\vec{k}-\vec{q}-\vec{h},\vec{r}')\psi_0(\vec{k},\vec{r}') ] + \text{complex conjugate} \}.$$
(14)

The expression of  $\delta v_{\text{ex}},$  which includes the exchange operator, is not reproduced for the sake of brevity.

Now the minimum of Eq.(11), developed in Eq.(12), is determined by varying Eq.(12) with respect to the independent variables  $b_{h+}^{*}(\vec{k})$ ,  $b_{h-}^{*}(\vec{k})$ , and  $b_{h-}(\vec{k})$ . Noting that  $\delta v_{\rho h}$  or  $\delta v_{exh}$  is a linear function of  $b_{h-}(\vec{k})$ , and  $b_{h+}^{*}(\vec{k})$ , that  $\delta v_{\rho h}^{*}$  or  $\delta v_{exh}^{*}$  is a linear function of  $b_{h+}(\vec{k})$ , and  $b_{h-}^{*}(\vec{k})$ , and that

$$\sum_{k} \left[ b_{h+}(\vec{k}) + b_{h-}^{*}(\vec{k}) \right] d(\delta v_{\rho h}^{*} + \delta v_{exh}^{*}) / d[b_{h+}^{*}(\vec{k})] = \delta v_{\rho h} + \delta v_{exh} ,$$

we have

$$b_{h+}(\vec{k}) = \delta v_{ph} / [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{h})],$$
 (15)

$$b_{h-}(\vec{k}) = \delta v_{ph}^{*} / [E(\vec{k}) - E(\vec{k} - \vec{q} - \vec{h})], \qquad (16)$$

and their complex conjugate equations, where

$$E(\vec{k}) = E_0(\vec{k}) + v_{ex}(\vec{k}),$$
 (17)

$$E(\vec{k} + \vec{q} + \vec{h}) = E_0(\vec{k} + \vec{q} + \vec{h}) + v_{ex}(\vec{k} + \vec{q} + \vec{h}),$$

and where

$$\delta v_{ph} = \delta v_{ih} + \delta v_{ph} + \delta v_{exh}$$
(18)

is the matrix element of effective electron-phonon interaction including the effects of other electrons on the interaction of an electron with the lattice

vibration. The  $b_{h+}(\vec{k})$  and  $b_{h-}(\vec{k})$  of Eqs.(15) and (16) satisfy the conditions of Eq.(10). Hence, the ion-electron-ion potential is given by Eqs.(12), (15) and (16)

$$E^{I} = \Sigma \left[ \frac{\delta v_{ih}^{*} \delta v_{ph}}{E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{h})} + \frac{\delta v_{ih} \delta v_{ph}^{*}}{E(\vec{k}) - E(\vec{k} - \vec{q} - \vec{h})} \right].$$
(19)

# 2.3. The exchange effect on $\delta v_{ph}$

The energy  $E(\vec{k})$  or  $E(\vec{k}+\vec{q}+\vec{h})$  of Eq.(17) now includes the exchange potential  $v_{ex}(\vec{k})$  or  $v_{ex}(\vec{k}+\vec{q}+\vec{h})$ , either of which is singular at the Fermi surface  $[\vec{k}] = k_F$ ,  $(dE(\vec{k})/d[\vec{k}])_{|\vec{k}|=k_F}$  being infinite; hence the level density of electrons is zero [1, 6]. However, this singularity disappears by taking the correlation effect into account as well; the exchange and correlation affect the level density of electrons only slightly [6]. Another effect of exchange energy on the effective electron-phonon interaction  $\delta v_{ph}$  and on the ion-electron-ion potential of Eq.(19) is due to  $\delta v_{ex}$  in Eq.(18). The evaluation of the magnitude of this effect is conducted by means of Slater's simplified expression for the exchange potential,

$$-3e^{2}[(3/8\pi)(\rho_{0}+\delta\rho)]^{\frac{1}{9}} = -3e^{2}(3/8\pi)^{\frac{1}{9}}\rho_{0}^{\frac{1}{9}}\left[1+\frac{1}{3}\frac{\delta\rho}{\rho_{0}}-\frac{1}{9}\left(\frac{\delta\rho}{\rho_{0}}\right)^{2}-\ldots\right].$$
 (20)

The  $\delta v_{exh}$  is expressed by Eqs.(14) and (20), with the approximation

$$\psi_0(\vec{\mathbf{k}},\vec{\mathbf{r}}) = U_0(\vec{\mathbf{r}}) \exp(i\vec{\mathbf{kr}}), |U_0(\vec{\mathbf{r}})|^2 \approx 1$$
 (21)

as

$$\delta v_{\text{exh}} = -(5e^2/6N)(3N/8\pi)^{\frac{1}{5}}\sum_{\mathbf{k}'} [b_{\mathbf{h}+}(\vec{\mathbf{k}'}) + b_{\mathbf{h}-}^*(\vec{\mathbf{k}'})].$$
(22)

With the approximation of Eq.(21), we have simply

$$\delta v_{\rho h} = 4\pi e^2 / |\vec{q} + \vec{h}|^2 \sum_{k'} [b_{h+}(\vec{k'}) + b^*_{h-}(\vec{k'})].$$
(23)

Hence, according to Eqs. (15), (16), (18), (22) and (23)

$$\delta v_{\rho h} + \delta v_{exh} = -[S'/(1+S')] \delta v_{ih}$$
(24)

and from Eqs.(18) and (24)

$$\delta v_{\rm ph} = (1 + S')^{-1} \delta v_{\rm ih} \tag{25}$$

with

$$S' = [8\pi e^2 / |\vec{q} + \vec{h}|^2 - (5e^2 / 3N)(3N / 8\pi)^{\frac{1}{2}}] \sum_{k} [E(\vec{k} + \vec{q} + \vec{h}) - E(\vec{k})]^{-1}$$
$$= [8\pi e^2 / |\vec{q} + \vec{h}|^2] [1 - 1.25(|\vec{q} + \vec{h}| / 2k_F)^2] \sum_{k} [E(\vec{k} + \vec{q} + \vec{h}) - E(\vec{k})]^{-1}.$$
(26)

The factor  $(1+S')^{-1}$  represents the screening effect by conduction electrons, which decreases the matrix element  $\delta v_{ih}$  of the perturbation due to the displacements of ions.<sup>2</sup> The exchange effect is numerically represented by the second term in the first square brackets of Eq. (26); the value of the term is too large by about 25%, as discussed previously [1].

# 2.4. The correlation effect on $\delta v_{ph}$

The assumption of Eqs.(6), (7) and (8) for the wave function of a metal is not complete, inasmuch as the state  $(\vec{k}_1, \ldots, \vec{k}_i, \ldots, \vec{k}_j, \ldots, \vec{k}_N)$  is coupled with the states, e.g.  $(\vec{k}_1, \ldots, \vec{k}_i + \vec{g}, \ldots, \vec{k}_j - \vec{g}, \ldots, \vec{k}_N)$  or  $(\vec{k}_1, \ldots, \vec{k}_i + \vec{g}, \ldots, \vec{k}_j + \vec{q} + \vec{n} - \vec{g}, \ldots, \vec{k}_N)$  through the term  $e^2/|\vec{r}_i - \vec{r}_j|$  in the Hamiltonian of Eq.(2); in other words,  $\vec{k}_i$ -electron collides against  $\vec{k}_j$ -electron, the participants being virtually excited to the respective levels  $\vec{k}_i + \vec{g}$  and  $\vec{k}_j - \vec{g}$  or  $\vec{k}_j + \vec{q} + \vec{h} - \vec{g}$ , when coupled with the lattice vibration. The collisions between electrons result in the correlation between electrons, similar to the exchange between parallel spin electrons. However, perturbation energy diverges, as discussed by HEISENBERG [8]. MACKE [9] has allowed for the reaction of polarization, i.e. the polarization of the neighbourhood of an electron due to collisions between electrons to give the effective potential between a pair of electrons as  $\exp(-\kappa |\vec{r}_j - \vec{r}_j|)/|\vec{r}_j - \vec{r}_j|$ . A more detailed calculation has been conducted for free electron gas by GELL-MANN and BRUECKNER [10] and SAWADA et al. [11, 12].

Now, the excited states due to collisions are taken into account in discussing the correlation effect on the electron-phonon interaction and on the ion-electron-ion potential, by starting from the wave function

$$\Sigma c \Psi(\vec{k}_1, \ldots, \vec{k}_N; a_q)$$
(27)

in place of Eq. (7). The coefficients c are determined by Macke's method.<sup>3</sup> The integral

$$\int (\Sigma \mathbf{c} * \Psi *) \mathcal{H}_1(\Sigma \mathbf{c} \Psi) d\vec{\mathbf{r}}_1 \dots d\vec{\mathbf{r}}_N$$
(28)

replaces the integral in Eq.(11), the former comprising the variation parameters  $b_{h+}(\vec{k})$  and  $b_{h-}(\vec{k})$ . It is found, after rather lengthy calculations, that the expression,

{correlation energy for a perfect crystal}

$$+ \sum_{\mathbf{k},\mathbf{h}} \{ |\mathbf{b}_{\mathbf{h}^{+}}(\vec{\mathbf{k}})|^{2} [\mathbf{v}_{c}(\vec{\mathbf{k}}+\vec{\mathbf{q}}+\vec{\mathbf{h}}) - \mathbf{v}_{c}(\vec{\mathbf{k}})]$$

$$+ \left| |\mathbf{b}_{\mathbf{h}^{-}}(\vec{\mathbf{k}})|^{2} [\mathbf{v}_{c}(\vec{\mathbf{k}}-\vec{\mathbf{q}}-\vec{\mathbf{h}}) - \mathbf{v}_{c}(\vec{\mathbf{k}})]$$

$$+ \left| |\mathbf{b}_{\mathbf{h}^{+}}(\vec{\mathbf{k}}) + \mathbf{b}_{\mathbf{h}^{-}}^{*}(\vec{\mathbf{k}})\right] \left[ \frac{1}{2} \delta \mathbf{v}_{ch}^{*} \right]$$

$$+ \left[ \mathbf{b}_{\mathbf{h}^{-}}(\vec{\mathbf{k}}) + \mathbf{b}_{\mathbf{h}^{+}}^{*}(\vec{\mathbf{k}})\right] \left[ \frac{1}{2} \delta \mathbf{v}_{ch} \right] \}$$

$$(29)$$

<sup>2</sup> The factor (1+S') was originally derived by BARDEEN [7] in Hartree approximation and is often referred to as the dielectric constant.

<sup>3</sup> It will be more general to leave  $\kappa$  as a variation parameter.

should be added to expression (12). The  $v_c(\vec{k})$  or  $v_c(\vec{k}+\vec{q}+\vec{h})$  is the correlation potential of the  $\vec{k}$ - or  $(\vec{k}+\vec{q}+\vec{h})$ -electron, and  $\delta v_{ch}$  or  $\delta v_{ch}$  is the matrix element of electron-phonon interaction due to the perturbation  $\delta v_c$ of the correlation potential; the explicit expressions of the above-mentioned quantities are not reproduced.

The  $E(\vec{k})$  or  $E(\vec{k}+\vec{q}+\vec{h})$  and  $\delta v_{ph}$  are now given as

$$E(\vec{k}) = E_0(\vec{k}) + v_{e_x}(\vec{k}) + v_c(\vec{k}),$$

$$E(\vec{k} + \vec{q} + \vec{h}) = E_0(\vec{k} + \vec{q} + \vec{h}) + v_{e_x}(\vec{k} + \vec{q} + \vec{h}) + v_c(\vec{k} + \vec{q} + \vec{h})$$
(30)

and

$$\delta v_{ph} = \delta v_{ih} + \delta v_{exh} + \delta v_{ch} = (1+S)^{-1} \delta v_{ih}$$
(31)

which replace Eqs.(17) and (18), respectively. The S allows both for the exchange and the correlation effects. The correlation effect is estimated at about one fourth of the exchange effect [1], hence

$$S = \frac{8\pi e^2}{|\vec{q} + \vec{h}|^2} \left[ 1 - B(|\vec{q} + \vec{h}|/2k_F)^2 \right] \sum_{k} \left[ E(\vec{k} + \vec{q} + \vec{h}) - E(\vec{k}) \right]^{-1}, \quad (32)$$

where B is taken to be ~1.25 on account of the 25% overestimation of Slater's expression for the exchange potential (cf. section 2.3). Equation (32) states that S is negative for B( $|\vec{q} + \vec{h}|/2k_F^{\circ} > 1$ , which is physically impossible; we should in consequence assume

S=0 for B(
$$|\vec{q}+\vec{h}|/2k_F)^2 > 1.$$
 (33)

The density of levels at the Fermi surface as derived from Eq.(30) deviates slightly from that as derived from  $E_0(\vec{k})$ , as mentioned previously. This deviation shifts the value of S through the summation in Eq.(32) from that obtained by ignoring the exchange and correlation effects. Taking the effects into account we have approximately

$$\sum_{i} \left[ \mathbf{E} (\vec{k} + \vec{q} + \vec{h}) - \mathbf{E} (\vec{k}) \right]^{-1} = (D/D_0) \sum_{i} \left[ \mathbf{E}_0 (\vec{k} + \vec{q} + \vec{h}) - \mathbf{E}_0 (\vec{k}) \right]^{-1}$$
(34)

where D or D<sub>0</sub> is the density of levels with or without exchange and correlation effects. With the approximation  $E_0(\vec{k}) = E_0 + (\hbar^2/2m)k^2$ , we have

$$\sum_{k} \left[ E_{0}(\vec{k} + \vec{q} + \vec{h}) - E_{0}(\vec{k}) \right]^{-1} = (3N/4E_{F})f(\left|\vec{q} + \vec{h}\right|/2k_{F}),$$
(35)

hence

з

$$\sum_{k} \left[ E(\vec{k} + \vec{q} + \vec{h}) - E(\vec{k}) \right]^{-1} = (D/D_0)(3N/4E_F)f(\left|\vec{q} + \vec{h}\right|/2k_F), \quad (36)$$

where  $E_F = (\hbar^2/2m)k^2$  and  $f(t) = \frac{1}{2} + \frac{1-t^2}{4t} \log \left| \frac{1+t}{1-t} \right|$ .

Recently, BAILYN [13] has discussed the exchange and correlation effects on the (1+S) on the basis of Bardeen-Pines formulation by a collective description method, giving results similar to the present one [14]. 2.5.Results

We have, according to BARDEEN [7],

$$\delta v_{ih} = i N^{\frac{1}{2}} a_q \cos(\vec{e}_q, \vec{q} + \vec{h}) (4\pi e^2 / |\vec{q} + \vec{h}|) G(t), \qquad (37)$$

where

$$G(t) = [1 + (V(r_s) - E_0)(3\pi/e^2k_F)t^2]g(2k_Fr_s t), \qquad (38)$$

 $g(x) = 3(\sin x - x \cos x)/x^3$ ,  $r_s$  is the radius of the sphere of atomic volume,  $V(r_s)$  the Hartree potential at  $r_s(V(r_s) \approx 0)$ , and  $t = |\vec{q} + \vec{h}|/2k_F$ . We have now from Eqs.(31), (32), (33) and (37),

$$\delta v_{ph} = i N^{\frac{1}{2}} a_q (\vec{e}_q, \vec{q} + \vec{h}) M(\vec{q} + \vec{h})$$
(39)

$$M(\vec{q} + \vec{h}) = \frac{2D_0}{3D} E_F G(t)F(t)^{-1}, \qquad (40)$$

where

$$\begin{split} \mathbf{F}(t) &= \left[ \frac{D_0}{D} \frac{\left| \vec{q} + \vec{h} \right|^2 \mathbf{E}_F}{6\pi \mathrm{Ne}^2} + (1 - \mathrm{B}t^2) \mathbf{f}(t) \right]; \, \mathrm{B}t^2 < 1, \\ \mathbf{F}(t) &= \frac{D_0}{D} \frac{\left| \vec{q} + \vec{h} \right|^2 \mathbf{E}_F}{6\pi \mathrm{Ne}^2}; \quad \mathrm{B}t^2 > 1. \end{split}$$
(41)

The ion-electron-ion potential  $E^{I}$  for the normal vibration of wave vector  $\vec{q}$  and  $\vec{e}_{q}$  is hence given by Eqs.(19), (36), (37) and (39) as

$$E^{I} = -4\pi Ne^{2} \left| a_{q} \right|^{2} \sum_{h} \cos^{2} \left( \vec{e}_{q}, \vec{q} + \vec{h} \right) \Lambda \left( \vec{q} + \vec{h} \right)$$
(42)

$$\Lambda(\vec{q} + \vec{h}) = G(t)^2 F(t)^{-1} f(t).$$
(43)

In the case of the Hartree approximation, we have, by neglecting the exchange and correlation effect instead, i.e. by putting B=0 and  $D/D_0=1$ ,

$$M(\vec{q} + \vec{h}) = \frac{2}{3}E_F G(t)F'(t),$$
 (44)

$$\Lambda(\vec{q} + \vec{h}) = G(t)^2 F'(t)^{1} f(t), \qquad (45)$$

in place of Eqs.(40) and (43), and

$$\mathbf{F}'(t) = \left[\frac{|\vec{\mathbf{q}} + \vec{\mathbf{h}}|^2 \mathbf{E}_{\mathbf{F}}}{6\pi \mathrm{Ne}^2} + \mathbf{f}(t)\right].$$
(46)

Now, the potential  $4\pi^2 M \nu^2 |a_q|^2$  of the wave equation of  $Q_{n_q}(a_q)$  is given by

$$4\pi^{2}M\nu \, a_{q} |^{2} = E^{I} + E^{II} + E^{C} + E^{R} , \qquad (47)$$

from which the frequency  $\nu$  is given as a function of  $\vec{q}$  and  $\vec{e}_q$ .

It is necessary to quantize  $a_q$  and  $a_q^*$  in the non-adiabatic formulation. The dispersion relation is similarly derived by the variation method, expressing the non-adiabatic terms in terms of quantized  $a_q$  and  $a_q^*$ .

The dispersion relation for multivalent metals has been derived previously [14].

# 3. NORMAL VIBRATION OF MONOVALENT METALS

# 3.1. Normal vibration of sodium of body-centred cubic (bcc) lattice

Recently, WOODS et al. [5] observed the dispersion relation for sodium. In Fig.1 the solid circles show the observed frequencies of the longitudinal modes and the open circles those of the transversal modes. The theoretical frequencies of the normal modes of vibration are calculated at fifty equally spaced points in each direction by Eqs. (38), (41), (42) and (43) on the base of  $r_s$  = 3.96 atomic units,  $E_F$  = 3.17 eV, B = 1.21, D/D<sub>0</sub> = 0.90 and V( $r_s$ )- $E_0$  = 0.08 eV. The exchange potential between ion cores is given according to Born-Mayer as  $v_R(R) = 1.25 \exp[(1.75 - R)/0.345]$  erg, where  $R = |\vec{R}_{\ell} - \vec{R}_{\ell'}|$  in Å. The exchange potential, due to the first and the second nearest neighbours, is taken into account, contributions from farther neighbours practically vanishing. The summation in Eq.(42) is taken for such h's satisfying  $|\vec{h}| \leq \sqrt{14}(2\pi/a)(a; lattice constant)^4$ . Each solid line in Fig.1 has been drawn smoothly through these fifty points. In the previous calculation the summation in Eq. (42) was taken for such h's satisfying  $|\vec{h} + \vec{q}| \leq \sqrt{3}(2\pi/a)$ , and the exchange repulsions from the second nearest neighbours were neglected. The present and the previous calculations agree within 2% and are in good agreement with the experimental values except for the  $T_1$  branch of the [110] direction; by taking into account the repulsions from the second nearest





<sup>&</sup>lt;sup>4</sup>  $\Lambda(\vec{t})$  is subtracted from  $\Lambda(\vec{q} + \vec{h})$  in order to correct the errors due to  $g(r_s|\vec{h}|) \neq 0$ . This correction is negligible except at  $\vec{q} \approx 0$ .

neighbours, as observed by DAYAL and SRIVASTAVA [15], the present theoretical values are actually closer to the experimental values than the previous ones. The cause of the slight discrepancy between theory and experiment might be attributed to the approximation in deriving the exchange and correlation effects as well as to that in deriving f(t) in Eq. (36) and g(x)in Eq.(38). The f(t) has been derived by ignoring the discontinuity of energy at the zone boundary, which might even give rise to slight anomalies in the dispersion relation, if the discontinuity were appreciable. In the case of sodium, however, the approximation might be close enough. The g(x),  $x = 2k_F r_s t = r_s |\vec{q} + \vec{h}|$ , was obtained by replacing the integral over the atomic polyhedron with that over the Wigner-Seitz atomic sphere. It is inferred that the approximation is close at small values of  $|\vec{q} + \vec{h}|$ , but it is not so at large values of  $|\vec{q} + \vec{h}|$ ; actually, g(x) does not vanish at  $\vec{q} = 0$  and  $h \neq 0$ , where g(x) = 0 in the exact evaluation. The dashed line (---) in Fig.1 is obtained covering the poor approximation at these points by replacing  $g(\mathbf{r}_{s} | \mathbf{\vec{q}} + \mathbf{\vec{h}} |)$  in Eq.(38) with

$$g(r_{s}|\vec{q}+\vec{h}|) + 0.019[(q_{x}+h_{x})^{4} + (q_{y}+h_{y})^{4} + (q_{z}+h_{z})^{4}] - 0.014|\vec{q}+\vec{h}|^{4},$$

which vanish at such points  $|\vec{q} + \vec{h}| = \sqrt{2}(2\pi/a)$  and  $2(2\pi/a)$ . The summation in Eq.(42) was taken only over  $|\vec{h}|(a/2\pi) = 0$ ,  $\sqrt{2}$ , 2 and  $\sqrt{6}$ . The dashed lines deviate only slightly from the solid lines, overlapping almost in whole regions.

DAYAL and SRIVASTAVA [15] have, on the other hand, modified g(x) by multiplying the argument x by a constant 1.04. The calculated dispersion relation is shown by chain lines (----) in Fig.1. The appreciable discrepancy for the T<sub>1</sub> branch of the [110] direction has been reduced. However, there is a slight increase in discrepancy for L branches in the [110] and [111] directions. The Debye temperature  $\Theta$  as calculated by Dayal and Srivastava is shown by a solid line in Fig.2. The open circles show values observed by MARTIN[16] and the solid circles, values observed by PARKINSON and QUARRINGTON[17]. Good agreement is obtained above 40%. The discrepancy below 40% was attributed to the phase transformation of sodium [18].

A more reasonable comparison of theoretical value with the experimental one would be that of  $\Lambda(\vec{q}+\vec{h})$  in Eq.(42). COCHRAN [3] has determined  $\Lambda(\vec{q}+\vec{h})$  from the experimental data, which is shown by a solid line in Fig.3. The deviation of the individual experimental values from the smooth curve is within 0.005. The crosses are the theoretical values calculated by Eq.(43) taking the exchange and correlation effects into account, and the dots are the values calculated by Eq.(45) ignoring the exchange and correlation effects. The good agreement at  $|\vec{q}+\vec{h}| < 0.9(2\pi/a)$  between the experimental values and the theoretical values allowing for exchange and correlation seems to indicate the validity of the discussions in sections 2.3 and 2.4 of this paper, since g(x) and f(t) are rigorous enough for such  $|\vec{q}+\vec{h}|$ . The slight deviation of the theoretical values with or without the exchange and correlation effects at  $|\vec{q}+\vec{h}| > 0.9(2\pi/a)$  may be attributed to the approximation implied in the derivation of g(x) on the one hand, and to the inaccuracy in the Born-Mayer repulsion on the other, which affects the ex-



PARKINSON and QUARRINGTON [17]

perimental values of  $\Lambda(\vec{q} + \vec{h})$ . The slight discrepancy between the experimental and the theoretical values of  $\Lambda(\vec{q} + \vec{h})$  at  $|\vec{q} + \vec{h}| > 0.9(2\pi/a)$  results in the appreciable discrepancy between the theory and the experiment of dispersion relation as seen in Fig.1. The modification of Dayal and Srivastava is justified at  $|\vec{q} + \vec{h}| > 0.9(2\pi/a)$ , but not at  $|\vec{q} + \vec{h}| < 0.9(2\pi/a)$ .

Cochran has further determined the values of G(t) by the experimental values of  $\Lambda(\vec{q}+\vec{h})$ . In Fig. 4 the crosses or dots are the values in terms of Eq.(41) with the exchange and correlation effects or of those in terms of Eq.(46) without them, respectively, and the solid line is the theoretical G(t) as given by Eq.(38). The agreement between the crosses and the theoretical curve of G(t) is good again for  $|\vec{q}+\vec{h}| < 0.9(2\pi/a)$ . The discrepancy for  $|\vec{q}+\vec{h}| > 0.9(2\pi/a)$  appears to originate from the same approximations as mentioned above. The values of G(t) were quite uncertain beyond  $|\vec{q}+\vec{h}| > 1.2(2\pi/a)$ , but Cochran thought that the function changed sign, as shown by the dashed line in Fig.4, which would be consistent with the magnitude of the band gap in the [110] direction, being related to G(t) for  $|\vec{q}+\vec{h}| = \sqrt{2}(2\pi/a)$ . The G(t) is the form factor of the effective potential in the orthogonalized plane wave method. The effective potential as derived from the values of crosses allowing for exchange and correlation was given approximately as

$$-e^2/r$$
 for  $r > r_s$  and  $-[(3e^2/2r_s) - (e^2r^2/2r_s^2) + V(r_s) - E_0]$  for  $r < r_s$ .

from which we had  $\delta v_{ih}$  of Eq.(37). Force constants as well as elastic constants were derived by Cochran on the base of the experimentally determined  $\Lambda(\vec{q}+\vec{h})$ . The values of  $M(\vec{q}+\vec{h})$  as determined similarly for two cases, according to Eqs.(40) and (44), are shown in Fig.5. These values of  $M(\vec{q}+\vec{h})$  lead to the values 3.5 and 2.6 eV of the interaction constants C, which decide the electrical conductivity; the former value of C, allowing for



exchange and correlation is in good agreement with the experimental value  $3.2 \sim 3.6$  eV.

# 3.2. Normal vibration of sodium of face-centred cubic (fcc) lattice

The stable form of sodium is bcc at higher temperatures, T = 40 K, but at temperatures below 40 K, the close-packed form of hcp (hexagonal close packed) or fcc is more stable than bcc and the martensitic phase transformation takes place at about 35 K. From the above phase transformation



Normal vibration of Na (fcc)

we are led to the conclusion that (i) the sum of the electronic energy and the zero-point vibrational energy of fcc or hcp is lower than that of bcc, and that (ii) the Debye temperatures of these close-packed lattices are higher than that of bcc. The dispersion relation of sodium of fcc is calculated as shown in Fig.6 with the same parameters as given for bcc sodium in section 3.1, except the lattice constant, which is  $2\frac{1}{2}$  times that of the bcc lattice constant. The  $\Theta$  at lower temperatures is estimated at ~ 160°K, which is higher than that of bcc sodium (cf. Fig.2) in conformity with conclusion (ii).

The interplanar force constants  $\Phi_n$  in the [100] direction, as defined by FOREMAN and LOMER [19], are derived from the dispersion relation of fcc sodium, as shown in Table I, and are compared with those of bcc sodium, as well as with the experimental values of bcc sodium. It is interesting to note that force is of short range for fcc as compared with the case of bcc.

# TABLE I

|   | $\Phi_{\rm h}~(10^{12}{\rm dyn/cm})$ |       |                 |       |                 |      |  |  |
|---|--------------------------------------|-------|-----------------|-------|-----------------|------|--|--|
| п | fcc<br>(theor.)                      |       | bcc<br>(theor.) |       | bcc<br>(exptl.) |      |  |  |
|   | L                                    | Т     | L               | Т     | L ,             | T    |  |  |
| 1 | 108.05                               | 48.29 | 85.85           | 86.72 | 93.6            | 98.2 |  |  |
| 2 | -2.22                                | 0,86  | 11,61           | 0.18  | 8.7             | 2.1  |  |  |
| 3 | -0.07                                | 0,13  | 1.42            | 0.47  | 3.4             | -1.1 |  |  |
| 4 | -0.15                                | 0.09  | 0.43            | 0.14  |                 |      |  |  |
| 5 | -0.04                                | 0.04  | -0.16           | -0.04 |                 |      |  |  |

# $\Phi_{\rm p}$ OF SODIUM

# 3.3. Normal vibration of copper

ZENER [20] and HUNTINGTON [21] have derived the exchange potential between ion cores of copper, assuming that the Coulomb interaction is all or half compensated by the contribution from the ion-electron-ion interaction. However, the derivation is not accurate enough to calculate the dispersion relation from it. The author [22] has derived the exchange repulsion conversely from the dispersion relation observed by JACOBSEN [23]. It is inferred from a number of investigations on the electronic structure of copper that the quasi-free electron model with Hartree energy  $E_0 = -2.7 \sim -4.2$  eV is adequate. The calculations are carried out for three cases, i.e. (a)  $E_0 = -3.33$  eV, (b)  $E_0 = -3.70$  eV and (c)  $E_0 = -4.07$  eV. The appropriate exchange repulsions of Born-Mayer type are thus determined as

- (a)  $v_R(R) = 0.123 \exp [10.94(R_e R)/R_e] eV$ ,
- (b)  $v_R(R) = 0.156 \exp [10.12(R_e R)/R_e] eV$ ,
- (c)  $v_R(R) = 0.192 \exp \left[ 9.46(R_e R)/R_e \right] eV$ ,

where  $R_e = a/\sqrt{2}$  and a is the lattice constant of copper. The dispersion relations derived from the three sets of values (a), (b) and (c) coincide with each other within a few per cent [22]. In Fig. 7 the dispersion relation of case (b) is shown in comparison with the experiment of Jacobsen, where open and closed circles represent longitudinal and transversal vibrations, respectively.



Normal vibration of Cu

The elastic constants  $c_{11}$ ,  $c_{44}$  and  $c_{11} - c_{12}$  are estimated from the long wavelength limit of the dispersion relation of case (b) to be 14.0, 8.2 and 4.6 in units of  $10^{11}$  dyn/cm<sup>2</sup>, respectively. The ion-electron-ion potential compensates ~80 or 20% of the contribution to  $c_{44}$  or  $c_{11} - c_{12}$  from the Coulomb potential, respectively. The value of  $c_{11}$  is somewhat small as compared with the experimental value of  $17.0 \times 10^{11}$  dyn/cm<sup>2</sup>. The discrepancy might be attributed to the free electron approximation as well as to the central force model implied in the Born-Mayer exchange potential. CRIBIER <u>et al</u> [24 a] and SINHA and SQUIRES [24] recently observed the dispersion relation by inelastic scattering of neutrons and Sinha has made extensive theoretical investigations, although the author is not acquainted with details [24].

If the two parameters in the Born-Mayer expression of exchange repulsion are adjusted to the longitudinal and the transversal frequencies of the maximum wave number propagating in the [111] direction, observed by Sinha and Squires, we have

$$v_{R}(R) = 0.209 \exp [9.033(R_{e}-R)/R_{e}] eV$$
,

on the base of  $V(r_s) - E_0 = 3.7 \text{ eV}$ . The dispersion relation calculated by making use of this exchange repulsion is found to be in good agreement with that observed by Cribier et al. and Sinha and Squires.

## 3.4. Thermal expansion of monovalent metals

The dispersion relation is rigorously formulated in section 2 with the lattice constant as a parameter; hence  $\gamma_q = -d \log \nu/d \log V$  is derived exactly from the formula obtained. The thermal expansion coefficient  $\alpha$  is now given by the Grüneisen relation

$$\alpha = \gamma \chi C_V / V, \tag{48}$$

where  $C_V$  is the heat capacity at constant volume, V the volume,  $\chi$  the com-

pressibility and the Grüneisen constant  $\gamma$  is given by the mean of  $\gamma_q~$  with weights

 $(h\nu/kT)^2 \exp(h\nu/kT) [\exp(h\nu/kT) - 1]^{-2}$ .

The  $\gamma$ 's of alkali metals are evaluated at T > $\Theta$ , as

Na K Rb Cs. (theory) 1.24 1.46 1.76 1.93

which are compared with  $\gamma$ 's determined by the observed  $\alpha$ ,  $\chi$  and C<sub>V</sub> according to Eq.(48), as described in Reference [25].

(experiment) 1.37 1.41 1.86 1.60

The  $\gamma$  of copper is similarly calculated as a function of temperature and compared with the values experimentally determined by RUBIN, ALTMAN and JOHNSTON [26] and by SIMMONS and BALLUFFI [27] according to Eq. (48), as shown in Fig. 8.



Fig. 8

Grüneisen constant versus temperature for Cu

RUBIN, ALTMAN and JOHNSTON [26]
 SIMMONS and BALLUFFI [27]

### 4. NORMAL VIBRATION OF MULTIVALENT METALS

The dispersion relation of lead (fcc) by inelastic scattering of neutrons was observed by BROCKHOUSE <u>et al.</u> [28]. The interatomic forces are of long range, and anomalies are observed at  $(2\pi/a)(0.42, 0.42, 0.42)$ ,  $(2\pi/a)(0.88, 0.88, 0)$ ,  $(2\pi/a)(0.32, 0.32, 0)$  and  $(2\pi/a)(0.90, 0, 0)$ , which are attributed to KOHN anomalies [29] except for the last one.

The dispersion relation of niobium (bcc), as observed by NAKAGAWA et al. [30], shows certain unusual features, as compared with that of monovalent bcc metals; these are: (1) [100] L and T branches intersect at  $(2\pi/a)$ (0.7, 0, 0); (2) the two non-degenerate [110] T<sub>1</sub> and T<sub>2</sub> branches intersect at  $(2\pi/a)(0.3, 0.3, 0)$ ; (3) [100] T and [110] T<sub>2</sub> have positive second derivatives for low values of  $\vec{q}$ , and (4) [100] L has an anomaly at  $(2\pi/a)(0.6,$ 0, 0). In the case of aluminium (fcc) [31-35], the overall dispersion relations are rather similar to those of monovalent fcc metals, except that [110]  $T_1$  and  $T_2$  branches nearly overlap at shorter wavelength, or, in other words  $c_{44} \approx \frac{1}{2}(c_{11}-c_{12})$ .

The above experimental results are not accounted for without reference to the overlapping band structures [14]. The dispersion relation was calculated for a fictitious metal with triply-degenerate bands and a quasi-free electron per atom, the exchange repulsive potential between ion cores as well as the lattice constant,  $D/D_0$  and B being assumed to be the same as those of copper. Two cases, (a) for  $V(r_s) - E_0 = 2.0$  eV and (b) for  $V(r_s) - E_0 \approx 3.7 \text{ eV}$ , were calculated. The overall dispersion relations were remarkably different from that of copper, revealing anomalies as shown in Figs. 9(a) and (b), notwithstanding the smaller electron-phonon interactions in the case of (a) than those in the case of copper. The anomalies are attributed to the smaller value of  $k_F$  of the fictitious metal, i.e.  $3^{-\frac{1}{3}}$ times that of copper. The anomaly occurs at  $|\vec{q} + \vec{h}|/2k_F = 1$  according to Eq.(43), and its magnitude is approximately proportional to  $g(r_s |\vec{q} + \vec{h}|)$ . Hence, the anomaly occurs at smaller  $|\vec{q} + \vec{h}|$  for smaller  $k_F$ , and in consequence the magnitude of anomaly increases, because  $g(r_s|\vec{q}+\vec{h}|)$  decreases monotonically with increase of  $|\vec{q}+\vec{h}|$  for  $|\vec{q}+\vec{h}| < 1.4(2\pi/a)$ . The breadth of anomaly is also proportional to  $k_{\rm F}$ , so that the anomaly will be more visible for smaller  $k_F$ .

The interplanar force constants  $\Phi_n$  in the [110] direction of the fictitious metal are shown in Table II and compared with those (theoretical) of copper. The  $\Phi_n$  of the fictitious metal for  $n \approx 11 \sim 15$  are ten times larger than those of copper.

#### TABLE II

# $\Phi_n$ OF COPPER AND COPPER-LIKE FICTITIOUS METALS

|   | Φn (10 <sup>12</sup> dyn/cm) |        |          |        |              |        |  |  |
|---|------------------------------|--------|----------|--------|--------------|--------|--|--|
| n | Case (a)                     |        | Case (b) |        | Copper       |        |  |  |
|   | Ĺ                            | Т      | L        | Т      | L            | Т      |  |  |
| 1 | 1284.47                      | 684.12 | 704.23   | 595.35 | 1046.91      | 531.29 |  |  |
| 2 | 11.74                        | 2.36   | 89,93    | 6.45   | 24.80        | 7.66   |  |  |
| 3 | -24.51                       | -0.05  | -55.19   | -0.03  | -0.18        | 2.20   |  |  |
| 4 | 19.80                        | 0,04   | 36.17    | -0.03  | -3.06        | 1.19   |  |  |
| 5 | -14.48                       | 0.11   | -24.90   | 0.15   | <b>0.</b> 11 | 0.54   |  |  |
| 6 | 10.82                        | 0.04   | 18.00    | 0.01   | 0.67         | -0.20  |  |  |



Normal vibration of a fictitious metal (a)  $\nabla(\mathbf{r}_s) = 2.0 \text{ eV}$ 



Normal vibration of a fictitious metal (b)  $\nabla(\mathbf{r}_s) = 3.7 \text{ eV}$ 

Figure 10 shows the dispersion relation of a bcc fictitious metal with a quasi-free electron per atom, which is distributed among the triplydegenerate bands. The lattice constant a, atomic radius  $r_s$ ,  $V(r_s) - E_0$ ,  $D/D_0$ and B are assumed to be the same as those of sodium. The exchange repulsive potential between ion cores is assumed tentatively to be three times as large as that of sodium. The anomalies are seen at  $(2\pi/a)(0.89, 0, 0)L$ ,  $(2\pi/a)(0.39, 0.39, 0)L$  and  $(2\pi/a)(0.50, 0.50, 0.50)L$  and T. No anomalies are seen at  $(2\pi/a)(0.62, 0.62, 0.62)$  and  $(2\pi/a)(0.72, 0.72, 0.72)$ , where  $2k_F = |\vec{q} + \vec{h}|$  for  $h = (2\pi/a)(-1, -1, 0)$ . The curve L of the longitudinal mode is lower than curve T of the transversal mode of the wave propagating in the [100] direction. Force constants  $\Phi_n$  are shown in Table III.

Some kinds of anomalies, which might possibly be due to the approximation of the quasi-free electron, cannot be accounted for at the moment.

Other calculations of the dispersion relation of metals with overlapping bands are now in progress on the basis of the theory previously developed



Fig. 10 Normal vibration of a fictitious metal

### TABLE III

# $\Phi_n$ OF SODIUM-LIKE FICTITIOUS METAL

| п | Φ <sub>n</sub> (10 <sup>12</sup> dyn/cm) |        |   | Φn (10 <sup>12</sup> dyn/cm) |       |  |
|---|--|--------|---|------------------------------|-------|--|
|   | L .                                      | Т      |   | L                            | Т     |  |
| 1 | 97.54                                    | 113.13 | 4 | , <b>-5.</b> 71              | 0.03  |  |
| 2 | -18.76                                   | 0.56   | 5 | 4.09                         | -0.08 |  |
| 3 | 13.81                                    | -0.61  | 6 | -0.93                        | -0.05 |  |

[14], in order to gain an insight into the details of the dispersion relation of multivalent metals.

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# DISCUSSION

T. TOYA: I should like to add that in certain studies (not reported in the paper) which have been conducted on the relations between  $\Lambda(\vec{q}+\vec{h})$ ,  $\Phi(n)$ and Kohn anomalies, the conclusion is reached that the periodicity of  $\Phi(n)$ with respect to n for longitudinal vibrations of monovalent metals is not the reflection of discontinuity of  $\Lambda(\vec{q}+\vec{h})$ , but only the Fourier transform of  $G^2(t)$ , and that  $\Phi(n)$  decreases as  $n^{-2}$ . In the case of multivalent metals accompanied by Kohn anomalies, the periodicity is the reflection of the discontinuity of  $\Lambda(\vec{q}+\vec{h})$ , and  $\Phi(n)$  decreases as  $n^{-1}$ . W. COCHRAN: The approximate result for the dielectric function could be less than one, and to avoid this you introduce a discontinuity of slope. Is it possible that this procedure is responsible for non-physical anomalies in calculated dispersion curves?

T. TOYA: The discontinuity of slope introduced in the expression for the dielectric function is so small that non-physical anomalies are not perceptible.

W. COCHRAN: Are you satisfied that it is physically meaningful to use Bardeen's result, involving  $G(t) = \{1 + \alpha [V(r_s) - E_0]\}g(2k_Fr_st)$ , in discussing electron-phonon interaction in polyvalent metals?

T. TOYA: It is physically meaningful at least for long waves, on the basis of the effective mass method of Slater and Bardeen, since  $E_s (\equiv \alpha E_0/d \log V) = (V(r_s) - E_0) - 0.2 e^2/r_s$ , where V is the volume of the atomic sphere.

S. SINHA: In principle, the expression  $G(t) \equiv \{1 + \alpha[V(r_s) - E_0]\}g(2k_Fr_st)$ should, at the points  $t = |\vec{H}/2k_F|$  ( $\vec{H} \equiv$  reciprocal lattice vector), determine the band gaps in the perfect crystal, according to the pseudo-potential formalism. However, one finds that these generally prove to be smaller than observed, due to the high damping of the factor  $g(2k_Fr_st)$ . How can one reconcile the requirements of band structure and of lattice dynamics?

T. TOYA: I do not know how we can reconcile them. In the case of copper, the pseudo-potential formalism is not accurate enough. Accurate evaluation of G(t) is desirable, although it would be extremely complicated.

P. EGELSTAFF: In presenting his survey paper<sup>\*</sup>, Professor Cochran said, in substance, that in the case of metals other than alkali and noble metals, we have no real understanding of the dispersion curves. Professor Toya, however, indicates that the treatment which he is presenting explains some anomalies and provides a plausible analysis of multivalent metals. Could he state what new point he has introduced that was not known to Professor Cochran?

T. TOYA: What I have introduced is a possible method for separating the various contributions to the adiabatic potential by analysing  $\Phi(n)$  as determined from the observed dispersion relation.

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# A COMPARISON BETWEEN THE ELECTRON-PHONON INTERACTIONS OF TOYA AND BAILYN

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# Abstract — Résumé — Аннотация — Resumen

A COMPARISON BETWEEN THE ELECTRON-PHONON INTERACTIONS OF TOYA AND BAILYN. To study the thermal properties of the monovalent metals, Toya considered the screening of the ionic perturbation. His approach is an extension of Bardeen's work and includes the effects of exchange in the screening on the lines of the Hartree-Fock theory. It is a step forward in the theory of screening but it inherits some of the weaknesses of the Hartree-Fock theory. To consider the effects of the Hartree-Fock approximation with regard to (1) the drastic reduction of the density of states near the Fermi surface and (2) the lack of proper correlation. Toya made two modifications in his expression for screening which he obtained by this approximation. Firstly he multiplied the energy denominator appearing in the matrix element by D/D<sub>0</sub>, where D and D<sub>0</sub> are the densities of states near the Fermi surface with and without exchange and correlation respectively. Secondly he replaced the exchange term in the expression for screening by  $2B\pi e^2/k_{\rm T}^2$ , where B is a parameter assumed independent of the phonon wave vector and includes the effect of correlation of the anti-parallel spins also,  $k_{\rm F}$  being the Fermi radius. His calculated vibration frequencies in the symmetry directions show slight disagreement for sodium and marked disagreement for copper with the neutron diffraction results.

Bailyn has also extended Bardeen's work and relied upon the Hartree-Fock theory. He considers the correlated exchange in the light of Bohm and Pines'work. Using his expression for the total matrix element and approximating the energy expression with the true energy the author has recalculated the vibration frequencies in the two cases. The calculated vibration spectra for the symmetry directions show better agreement with the neutron diffraction results. The calculated  $\theta$ -T curves are also in better agreement with the experimental curves. Further it has a distinct advantage over Toya's work because it is able to dispense with the uncertain corrections appearing in his theory.

COMPARAISON DES INTERACTIONS ÉLECTRONS-PHONONS ÉTABLIES PARTOYA ET BAILYN. Pour étudier les propriétés thermiques des métaux monovalents. Toya a envisagé d'éliminer la perturbation ionique par un effet d'écran (screening). Sa méthode constitue une extension des travaux de Bardeen et tient compte de l'échange dans l'effet d'écran sur la base de la théorie de Hartree-Fock. Elle marque un progrès dans la théorie de l'effet d'écran mais elle possède encore certains des points faibles de la théorie de Hartree-Fock. Pour tenir compte des effets de l'approximation de Hartree-Fock, en ce qui concerne 1. la diminution brusque de la densité des états au voisinage de la surface de Fermi et 2. l'absence d'une corrélation appropriée. Toya a apporté deux modifications à l'expression de l'effet d'écran qu'il avait établie au moyen de cette approximation. Tout d'abord il a multiplié le dénominateur de l'expression de l'énergie qui apparaît dans l'élément matriciel par D/D<sub>0</sub>, où D et D<sub>0</sub> sont les densîtés des états au voisinage de la surface de Fermi, respectivement avec et sans échange et corrélation. Puis il a remplacé le terme relatif à l'échange dans l'expression du screening par  $2B\pi e^2/k_F^2$ , où B est un paramètre supposé indépendant du vecteur d'onde des phonons qui englobe l'effet de corrélation des spins anti-parallèles, et k<sub>F</sub> le rayon de Fermi. Les valeurs qu'il a calculées pour les fréquences de vibration dans les directions de symétrie accusent, par rapport aux résultats obtenus par la diffusion des neutrons, un léger écart pour le sodium et un écart très net pour le cuivre.

Bailyn a lui aussi développé les travaux de Bardeen en s'appuyant sur la théorie de Hartree-Fock. Il a étudié l'échange corrélé sur la base des travaux de Bohm et Pines. En utilisant son expression pour l'élément matriciel total et en déterminant l'expression de l'énergie par approximation au moyen de l'énergie réelle, l'auteur a refait le calcul des fréquences de vibration dans les deux cas. Les spectres de vibration calculés pour les directions de symétrie concordent mieux avec les résultats obtenus par diffusion des neutrons. Les courbes théoriques 0-T sont également plus conformes aux courbes expérimentales. En outre, cette méthode présente un avantage indéniable sur les travaux de Toya, en ce sens qu'elle permet de se passer des corrections très incertaines qui apparaissent dans sa théorie.

# P. L. SRIVASTAVA

СРАВНЕНИЕ ЭЛЕКТРОН-ФОНОННЫХ ВЗАИМОДЕЙСТВИЙ ТОЙЯ И БАЙЛИНА. Чтобы изучить тепловые свойства одновалентных металлов, Тойя занялся рассмотрением экранирования ионной пертуроации. Его метод является развитием работ Бардеена и включает эффекты обмена при экранирования. Осинако он не лишен некоторых слабых сторон теории Хартри-Фока. Чтобы рассмотреть приближения эффектов Хартри-Фока в отношении 1) резкого уменьшения плотности состояний вблизи поверхности Ферми и 2) отсутствия точной корреляции. Вопервых, он умножил знаменатель энергии в матричном элементе на D/D<sub>0</sub>, где D и D<sub>0</sub> означают плотности состояний вблизи поверхности Ферми с обменом и без обмена и корреляции. Вопервых, он умножил знаменатель энергии в матричном элементе на D/D<sub>0</sub>, где D и D<sub>0</sub> означают плотности состояний вблизи поверхности Ферми с обменом и без обмена и корреляции соответственно. Во-вторых, он замения член обмена в выражении для экранирования на  $2B\pi^2/k_{\rm F}$ , где В означает параметр, считающийся независимым от волнового вектора фонона, и включает также эффект корреляции антипараллельных спинов, а k<sub>F</sub> – радиус Ферми. Вычисленные им частоты колебаний в симметричных направлениях показывают некоторое расхождение с результатами дифракций нейтронов для натрия и заметное расхождение для меди.

Байлин также продолжал работу Бардеена и исходил из теории Хартри-Фока. Он рассматривает коррегированный обмен в свете работы Бома и Пина. Используя свое выражение для общего матричного элемента и аппроксимируя выражение для энергии с действительной энергией, автор вновь вычислил частоты колебаний для двух случаев. Вычисленные спектры колебаний для симметричных направлений показывают лучшее согласие с результатами дифракции нейтронов. Рассчитанные кривые  $\Theta$ - Т также лучше согласуются с экспериментальными кривыми. Кроме того, существенным преимуществом над работой Тойи является то, что можно обойтись без неопределенных поправок, содержащихся в его работе.

COMPARACIÓN DE LAS INTERACCIONES ELECTRÓN-FONÓN DE TOYA Y BAILYN. Con el fin de investigar las propiedades térmicas de los metales monovalentes. Toya estudió el efecto de pantalla de la perturbación iónica. Abordó la cuestión sirviéndose de una ampliación de los trabajos de Bardeen, y considera la influencia del intercambio en el efecto de pantalla, conforme a la teoría de Hartree-Fock. Su enfoque representa un progreso en la teoría del efecto de pantalla, pero recoge algunos de los puntos débiles de la teoría de Hartree-Fock. Para contrarrestar los efectos de la aproximación de Hartree-Fock en lo que respecta 1) a la disminución radical de la densidad de estados en las inmediaciones de la superficie de Fermi, y 2) a la falta de correlación apropiada. Toya introdujo dos modificaciones en su expresión del efecto de pantalla obtenida según dicha aproximación. En primer lugar, multiplicó por  $D/D_0$  el denominador de la expresión de la energía que aparece en el elemento matriz, siendo D y Do las densidades de estados en las inmediaciones de la superficie de Fermi con y sin intercambio y correlación, respectivamente. En segundo lugar, sustituyó el término de intercambio en la expresión del efecto de pantalla por  $2B\pi e^2/k_{\rm e}^2$ , donde B es un parámetro que se supone independiente del vector de onda fonónico y comprende el efecto de correlación de los spines antiparalelos, siendo ke el radio de Fermi. Las frecuencias de vibración por él calculadas en las direcciones de simetría discrepan ligeramente de los resultados obtenidos por difracción neutrónica en el caso del sodio. y considerablemente en el caso del cobre.

Por su parte, Bailyn también ha ampliado los trabajos de Bardeen y recurrido a la teoría de Hartree-Fock Considera el intercambio correlacionado a la luz de los trabajos de Bohms y Pines. Utilizando su expresión del elemento matriz total y formulando una expresión de la energía más próxima a la energía verdadera, el autor ha vuelto a calcular las frecuencias de vibración en ambos casos. Los espectros de vibración calculados para las direcciones de simetría concuerdan más satisfactoriamente con los resultados obtenidos por difracción neutrónica. Las curvas  $\theta$ -T calculadas se ajustan también mejor a las curvas experimentales. Además, este trabajo posee sobre el de Toya la neta ventaja de que permite prescindir de las correcciones inciertas que aparecen en la teoría de este último autor.

A metal consists of ions and valence electrons. The interaction between ions is well known but the conduction electrons create complications in the rigorous study of the interaction. When a phonon of wave vector  $\vec{q}$ , say, disturbs the lattice, the electrons undergo a change in potential. They redistribute themselves under the influence of the varying potential of the vibrating ions and produce a screening effect on them. This effect was con-

4.

sidered by BARDEEN [1] in the study of the conductivity of monovalent metals. Basing his work on the Hartree theory he obtained the matrix element  $V_{ph+}$  for the total perturbation in terms of the matrix element for the bare lattice  $V_{ih+}$ . The relation between the two, according to him, is given as

$$V_{ph+} = SV_{ih+}$$
 ,

where

$$S = \frac{1}{1 - (8 \pi e^2 / |\vec{q} + \vec{K}_h|^2) \sum_{\vec{k}} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_h)]^{-1}}, \quad (1)$$

 $\vec{K_h}$  being the reciprocal lattice vector and  $\vec{E(k)}$  the energy of the electron in the k-state. The calculated values of the conductivity of alkali metals are about twice the experimental values. The phonon spectrum of sodium calculated on the basis of this theory does not show agreement with the neutron diffraction results of WOODS et al.[2]. The disagreements were considered to be the result of treating the theory in terms of the Hartree approximation, which suffers from the defect that it does not take correlation into account. It was with this in mind that TOYA [3] and BAILYN [4] at about the same time attempted to improve Bardeen's theory of screening by including the effect of exchange and correlations on the screening of the ionic perturbation in the framework of this theory.

Proceeding along the lines of Bardeen, TOYA [3] considered the screening of the ionic perturbation in the Hartree-Fock approximation and obtained S with the use of Slater's simplification for the exchange potential as

$$S = \frac{1}{1 - [(8\pi e^2/|\vec{q} + \vec{K}_h|^2) - (5/6) (2e^2/N) (3N/8\pi)^{1/3}] \sum_{\vec{k}} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_h)]^{-1}}$$
(2)

This expression differs from that obtained by BARDEEN [1] with respect to the second term in the first square bracket of the denominator of Eq. (2). This term arises on account of the inclusion of exchange effect in the theory. In the above theoretical structure the correlation of the anti-parallel spins has not been considered. This has some repercussion on the physical properties of metals. Because of the consequences of relying upon the Hartree-Fock approximation, with its drastic reduction of the density of states near the Fermi surface and neglect of proper correlation, Toya made two modifications in his expression for S. Firstly he multiplied the energy denominator  $\Sigma [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_h)]^{-1}$  appearing in the matrix elements by  $D/D_0$ , where D and  $D_0$  are the densities of states near the Fermi surface with and without exchange and correlation, respectively. Secondly he replaced the exchange term in the expression for S by  $2B\pi e^2/k_{\rm E}^2$ , where B is a parameter which is assumed independent of the phonon wave vector and includes the effect of the correlation of the anti-parallel spins also. The numerical value of B is determined by comparing the expression for compressibility with that obtained from the theory of Wigner and Seitz.  $D/D_0$ 

is obtained from the work of BLATT [5]. Under the above modifications the expression for S becomes

$$S = \frac{1}{1 - [(8\pi e^2 / |\vec{q} + \vec{K}_h|^2) - 2B\pi e^2 / k_F^2] D / D_0 \sum_{\vec{k}} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_h)]^{-1}}.$$
 (3)

The expression used for  $E(\vec{k})$  by Toya is the same as that used by Bardeen in the Hartree approximation, i.e.

$$E(\vec{k}) = E_0 + \frac{\hbar^2 k^2}{2m}$$
 (4)

Toya further developed the expression for the adiabatic potential energy of the valence electrons from which he found the electronic contribution to the coupling coefficients of the secular determinant. He calculated the vibration frequencies of the alkali metals [6,7] and copper [8,9] for the three symmetry directions. The disagreement with the neutron diffraction is slight in the case of sodium [6] but large in the case of copper.

BAILYN [4] has also extended Bardeen's work and relied upon the Hartree-Fock theory. His work differs from that of Toya in the evaluation of the exchange potential. He considers the correlated exchange in the light of BOHM and PINE's work [10]. The advantage in this case is that a better correlation is taken into account in considering the screening of the ionic perturbation and difficulties as regards reduction of density of states near the Fermi surface do not appear. Naturally, therefore, he need not make any empirical correction of his expression for S like Toya. The expression for the energy in the above framework is given as

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} + W(\vec{k}), \qquad (5)$$

where

$$W(\vec{k}) = -\frac{2e^2k_F}{\pi}h(x)$$

and

$$h(x) \begin{cases} = f(x) - \beta & 0 < x < 1 - \beta \\ = \frac{1}{4} - \frac{\beta}{2} + \frac{1 - x^2}{4x} \ln \frac{1 + x}{\beta} + \frac{3x^2 - 1 + \beta^2}{8x} & 1 - \beta < x < 1 + \beta \\ = f(x) & 1 + \beta < x < 3 \\ x = \frac{k}{k_F} \\ f(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|; \end{cases}$$

$$\beta = 0.353 (r_s/a_0)^{1/2}$$

 $r_s$  is the radius of the Seitz sphere and  $a_{\,0}$  is the Bohr radius.

For the convenience of integration  $E(\vec{k})$  in Eq. (5) is approximated by

$$E(\vec{k}) = \frac{\hbar^2 k_F^2}{2m} (px^2 - pqx^4),$$
 (6)

where p and q are the parameters obtained for a good fit.

Bailyn obtained an integral equation for the total matrix element V<sub>pht</sub> as

$$V_{ph+}(\vec{k}) = V_{ih+}(\vec{q}) - \lambda \sum_{\vec{k}'} a_s(\vec{k}, \vec{k}') V_{ph+}(\vec{k}'), \qquad (7)$$

where k and k' are the states of the electrons,  $a_s(\vec{k}, \vec{k'})$  is a function of  $\vec{k}, \vec{k'}$ and  $\lambda = 4\pi e^2/\Delta |\vec{q} + \vec{k}_h|^2$ ,  $\Delta$  being the crystal volume.

Equation (7) was solved by him in the zeroth approximation.  $V_{\text{ph+}}\xspace$  is then given as

where

$$V_{ph+} = SV_{ih+}, \qquad (8)$$

S = 
$$\frac{1}{1 + [(9\pi/4)^{1/3}\pi]^{-1} (r_s/a_0) [F(u) - G(u,h)]/u^2}$$
, (8a)

$$G(u,h) \approx \frac{3u}{2p} \int_{x_0}^{1+2u} dx x h(x) [(1+2qx^2) Q(x,u) + qR(x,u)], \qquad (9)$$

$$F(u) = \frac{1}{p} f(u) + \frac{q}{p} \left[ \frac{1 - u^4}{4u} \ln \left| \frac{1 + u}{1 - u} \right| + \frac{u^2}{2} + \frac{3}{2} \right],$$
(10)

$$f(u) = 0.5 + \frac{1-u^2}{4u} \ln \left| \frac{1+u}{1-u} \right|,$$

where  $x_0 = 1 - 2u$  for u < 0.5 or  $x_0 = 0$  for u > 0.5; Q(x, u) and R(x, u) are only functions of x and u, and  $u = |\vec{q} + \vec{K}_h|/2k_F$ .

Since his treatment of the screening seems more satisfactory than that given by Toya, the vibration frequencies for sodium and copper were recalculated by the author using Bailyn's total matrix element  $V_{ph+}$ . For this purpose Bailyn's matrix element  $V_{ph+}$  is substituted in the following expression for the coupling coefficient  $[XY]^E$  derived by Toya:

$$[XY]^{E} = + \frac{2}{|\mathbf{a}_{q}|^{2}} \sum_{h} \sum_{\vec{k}} V_{ph*}^{*} V_{ih*} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_{h})]^{-1} + \frac{4\pi}{3} Ne^{2} \delta_{xy*} (11)$$

 $V_{ih+}$  is the same as that derived by Bardeen, namely

$$V_{ih+} = iN^{-1/2} a_q(\hat{e}_q, \vec{q} + \vec{K}_h) \left[ \frac{4\pi N e^2}{|\vec{q} + \vec{K}_h|^2} + V(r_s) - E_0 \right] g(x), \quad (12)$$

where  $a_q$  is the normal co-ordinate,  $\hat{e}_q$  the polarization vector, N the number of ions in a unit volume, V( $r_s$ ) the potential at the surface of the Seitz sphere and  $E_0$  the energy of the electron in the lowest state.

$$g(x) = \frac{3(\sin x - x \cos x)}{x^3},$$
 (13)

where  $\mathbf{x} \approx |\vec{\mathbf{q}} + \vec{\mathbf{K}}_{\mathbf{h}}| \mathbf{r}_{\mathbf{s}}$  and

$$\sum_{\vec{k}} \left[ E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_{h}) \right]^{-1} = \int \frac{d\vec{k}}{E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_{h})}$$

Using Eq. (6) for  $E(\vec{k})$  we have

$$\sum_{\vec{k}} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_{h})]^{-1} = -\frac{3NF(u)}{4W_{F}}, \qquad (14)$$

where  $W_{F}$  is the Fermi energy.

Substituting the value of  $V_{ph+}$  from Eq. (8),  $V_{ih+}$  from Eq. (12) and  $\sum_{\vec{k}} [E(\vec{k}) - E(\vec{k} + \vec{q} + \vec{K}_h)]^{-1}$  from Eq. (14) in Eq. (11), we get

$$[XY]^{E} = Ne^{2} \left[ \frac{4\pi}{3} \delta_{xy} - 4\pi \sum_{h} \frac{(q_{x} + K_{hx}) (q_{y} + K_{hy})}{|\vec{q} + \vec{K}_{h}|^{2}} \frac{6F(u)}{4W_{F}} \frac{4\pi Ne^{2}}{|\vec{q} + \vec{K}_{h}|^{2}} S G^{2}(u) \right], (15)$$

where G(u) =  $\left[1 + (V(r_s) - E_0) \frac{u^2 k_F^2}{\pi N e^2}\right] g(x)$  and S is given by Eq.(8a).

The numerical values of the parameters p and q for sodium, as taken from Bailyn's work, are p = 1.325 and q = 0.018; the values for copper, as calculated by the author, are p = 1.246 and q = 0.022.

The other parameters which appear in the expression for  $[XY]^E$  are the same as those used by Toya, namely for sodium  $V(r_s) - E_0 = 0.08 \text{ eV}$ ,  $r_s = 3.96 a_0$ ,  $W_F = 3.17 \text{ eV}$  and for copper  $V(r_s) - E_0 = 3.7 \text{ eV}$ ,  $r_s = 2.68 a_0$ ,  $W_F = 6.95 \text{ eV}$ .

The vibration frequencies for the two metals were calculated using Bailyn's  $V_{ph+}$  in the electronic coupling coefficients. The dispersion curves of the three symmetry directions for sodium have been plotted in Figs. 1, 2 and 3 and for copper in Figs. 4, 5 and 6. They have been compared with the neutron diffraction results of WOODS <u>et al.</u>[2] for sodium and CRIBIER <u>et al.</u> [11] and SINHA and SQUIRES [12] for copper. The curves show that the agreement is better than that obtained by Toya in the case of sodium and there is remarkable improvement in the agreement for the case of copper.

To give a further test to the expression for the matrix element, the Brillouin zone was divided into  $10 \times 10 \times 10 \times 10$  cells and the vibration frequencies were calculated for the representative points lying in the irreducible 1/48-th



Fig. 1

Dispersion curve for sodium for [100] direction

author's theoretical
 Toya's theoretical
 experimental points for longitudinal branch
 x experimental points for transverse branch





Dispersion curve for sodium for [110] direction

----- author's theoretical

# --- Toya's theoretical

O experimental points for longitudinal branch

× experimental points for transverse branches



Fig. 3

Dispersion curve for sodium for [111] direction

author's theoretical
 Toya's theoretical
 experimental points for longitudinal branch
 x experimental points for transverse branch





Dispersion curve for copper for [100] direction

- author's theoretical
- Toya's longitudinal
- x Toya's transverse
- O experimental (CRIBIER et al. [11])
- experimental (SINHA and SQUIRES [12])





Dispersion curve for copper for [110] direction

- author's theoretical
- Toya's longitudinal
- X Toya's transverse
- O experimental (CRIBIER et al. [11])
- experimental (SINHA and SQUIRES [12])





Dispersion curve for copper for [111] direction

author's theoretical

- × Toya's longitudinal and transverse
- O experimental (CRIBIER et al. [11])



part of the zone. The specific heats have been calculated by numerical computation. Figure 7 shows that the agreement in the case of sodium is almost exact with the experimental  $\theta$ -T curve of MARTIN [13] above 35°K which is the transition point. Below this temperature sodium changes its structure to hexagonal close-packed and does not retain the body-centred cubic structure for which the calculations have been made. Naturally, therefore, one may not expect good agreement with the experimental results of FILBY and MARTIN [14] below 35°K. The maximum disagreement is 8%. The agreement in the case of copper (shown in Fig. 8) with the experimental results of MARTIN [15] above 30°K and FRANK et al. [16] below this temperature is fairly good. The disagreement is nowhere greater than 3%.

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# INTERPRETATION OF SLOW NEUTRON SCATTERING DATA IN METALS

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### Abstract — Résumé — Аннотация — Resumen

INTERPRETATION OF SLOW NEUTRON SCATTERING DATA IN METALS. The slow neutron scattering technique has now been developed to yield very detailed information on phonon dispersion curves in single crystals. This calls for a proper interpretation of the experimental data. The theoretical calculations are normally based on Born-von Kármán's theory for lattice vibrations and it has been shown that also in metals the interatomic interaction extends over a fairly large distance in contrast to what was assumed earlier. Recent computations, particularly those of Cochran and collaborators, have demonstrated that the deformation of the electron density within the ions plays an essential role for the lattice vibrations. Similarly the polarization of the conduction electrons gives rise to the famous Kohn effect.

It is shown in this paper that a slight modification of the Born-von Karman scheme makes it possible to include properly the response of the electrons, where we have restricted ourselves to purely harmonic motions in normal metals. The force constants are expressed in terms of the electronic properties of the crystal and in this way a direct physical significance is given to the force constants. In this formulation the Cochran model as well as the Kohn effect is easily visualized. It is stressed which physical effects are important for the calculations of phonon spectra.

The procedure followed in the derivations is similar to that used earlier by Bardeen and Pines and others when calculating the effective electron-phonon interaction. We have, however, included the periodicity of the lattice and in fact made no approximations concerning the electronic motions. We obtain in this way rigorous definitions of the force constants. The results are analogous to those obtained recently by Baym but our derivation is more direct and in accordance with the conventional formulations of the theory of lattice vibrations.

INTERPRETATION DES DONNÉES OBTENUES AU MOYEN DE LA DIFFUSION DES NEUTRONS LENTS PAR LES MÉTAUX. La méthode de la diffusion des neutrons lents a été perfectionnée de manière à fournir des renseignements très détaillés sur les courbes de dispersion des phonons dans les monocristaux. Pour cela, il faut interpréter les données expérimentales de façon appropriée. Les calculs théoriques sont normalement fondés sur la théorie de Born et von Kármán pour les vibrations de réseau et on a montré que dans les métaux également les interactions atomiques s'étendent à une distance assez grande, contrairement à ce qui était admis antérieurement. Des calculs récents, notamment ceux de Cochran et de son équipe, ont prouvé que la modification de la densité électronique à l'intérieur des ions exerce une influence déterminante sur les vibrations de réseau. De même, la polarisation des électrons de conduction donne lieu au fameux effet de Kohn.

Une légère modification de la théorie de Born et von Kármán permet d'inclure la réponse des électrons de façon satisfaisante dans les cas où l'on se limite aux mouvements purement harmoniques dans les métaux normaux. Les constantes de force sont exprimées en fonction des propriétés électroniques du cristal et acquièrent ainsi une signification physique directe. Grâce à cette formulation, le modèle de Cochran de même que l'effet de Kohn peuvent être facilement concrétisés. Les auteurs indiquent les effets physiques qui revêtent une importance pour les calculs des spectres de phonons.

Ils ont suivi une méthode semblable à celle que Bardeen et Pines ainsi que d'autres chercheurs avaient employée antérieurement pour calculer l'interaction efficace électron-phonon. Mais ils ont en outre tenu compte de la périodicité du réseau et n'ont procédé, en fait, à aucune approximation concernant les mouvements électroniques. Ils ont défini ainsi rigoureusement les constantes de force. Les résultats sont analogues à ceux récemment obtenus par Baym, mais la méthode utilisée par les auteurs est plus directe et elle est conforme aux formulations classiques de la théorie des vibrations de réseau.

ИНТЕРПРЕТАЦИИ ДАННЫХ ПО РАССЕЯНИЮ МЕДЛЕННЫХ НЕЙТРОНОВ В МЕ-ТАЛЛАХ. В настоящее время разработан метод рассеяния медленных нейтронов для получения весьма подробной информации о кривых фононной дисперсии в отдельных кристаллах. Это требует необходимой интерпретации экспериментальных данных. Теоретические расчеты обычно основываются на теории Борна фон Кармана для колебаний решетки, и показано, что также в металлах внутриатомное взаимодействие распространяется на довольно большое расстояние по сравнению с первоначальными предположениями. Расчеты, которые недавно произвели, в частности Кохран и сотрудники, показали, что деформация плотности электронов в ионах играет основную роль для колебаний решетки. Подобным образом поляризация электронов проводимости вызывает известный эффект Кона.

В данном докладе показано, что небольшая модификация схемы Борна фон Кармана позволяет должным образом включать воздействие электронов, где мы ограничивались чисто гармоническими движениями в обычных металлах. Константы силы выражаются в виде электронных свойств кристалла и таким образом прямое физическое значение придается константам силы. В этой формулировке отчетливо проявляется модель Кохрана, а также эффект Кона. Указываются физические эффекты, которые играют важную роль для расчетов фононных спектров.

Метод применяемый для вывода формул, аналогичен методу, который использовали ранее Бардеен и Пинес и другие при расчете эффективного электронно-фононного взаимодействия. Однако мы включили периодичность решетки и фактически не делали никаких аппроксимаций относительно движений электронов. Мы получили таким образом точные определения константов силы. Эти результаты аналогичны результатам, полученным недавно Баймом, но наш вывод является более полным и соответствует условным формулировкам теории колебаний решетки.

INTERPRETACIÓN DE LOS DATOS DE DISPERSIÓN DE NEUTRONES LENTOS EN METALES. En el estado actual de su desarrollo, la técnica de dispersión de neutrones lentos permite obtener información muy detallada sobre las curvas de dispersión fonónica en monocristales siempre que se interpreten adecuadamente los datos experimentales. Por regla general, los cálculos se basan en la teoría de Born y von Kármán acerca de las vibraciones reticulares, y se ha demostrado que, contrariamente a lo que se suponía antes, las interacciones atómicas se extienden también a los metales hasta distancias bastante grandes. Cálculos recientes, especialmente de Cochran y colaboradores, han revelado que la deformación de la densidad electrónica en el interior de los iones desempeña un papel fundamental para las vibraciones del reticulado. Análogamente, la polarización de los electrones de conducción da origen al famoso efecto de Kohn.

En la memoria se demuestra que basta modificar ligeramente la teoría de Born y von Kármán para que abarque debidamente la respuesta de los electrones en el caso de los movimientos armónicos puros en los metales normales, a los que se han limitado los autores. Las constantes de fuerza adquieren un significado físico directo al ser expresadas en función de las propiedades electrónicas del cristal. Esta formulación permite visualizar fácilmente el modelo de Cochran y el efecto de Kohn. La memoria destaca qué efectos físicos tienen importancia para calcular los espectros fonónicos.

El procedimiento seguido en las deducciones es similar al que emplearon anteriormente Bardeen y Pines y otros autores para calcular la interacción electrón-fonón efectiva, pero los autores de la presente memoria han incluido la periodicidad del reticulado y no han hecho ninguna aproximación respecto de los movimientos electrónicos. De esta manera obtienen definiciones rigurosas de las constantes de fuerza. Los resultados son análogos a los conseguidos recientemente por Baym, pero el procedimiento de deducción seguido por los autores es más directo y concuerda con las formulaciones convencionales de la teoría de las vibraciones reticulares.

### 1. INTRODUCTION

The slow neutron scattering technique has now been developed to yield very detailed information on phonon dispersion curves in single crystals. This calls for a proper interpretation of the experimental data. The theoretical calculations are normally based on Born-von Kármán's theory for lattice vibrations and it has been shown that also in metals the interatomic interaction extends over a fairly large distance in contrast to what was assumed earlier. Recent computations particularly by COCHRAN [1] and collaborators have demonstrated that the deformation of the electron density within the ions can play an essential role for the lattice vibrations. Similarly the polarization of the conduction electrons gives rise to the famous Kohn effect [2].

It is shown in this paper that a slight modification of the Born-von Kármán scheme makes it possible to properly include the response of the electrons, where we have restricted ourselves to purely harmonic motions in normal metals. The force constants are expressed in terms of the electron properties of the crystal and in this way a direct physical significance is given to the force constants. A comparison is made with the model used recently by Toya in calculating phonon dispersion curves for monovalent metals.

The procedure followed in the derivations is similar to that used earlier by BARDEEN and PINES [3] and others when calculating the effective electron-phonon interaction. We have, however, included the periodicity of the lattice and in fact made no approximations concerning the electron motions. We get in this way rigorous definitions of the force constants. The results are analogous to those obtained recently by BAYM [4] but our derivation is more direct and in accordance with the conventional formulations of the theory of lattice vibrations.

# 2. THE BORN-VON KÁRMÁN EQUATIONS

Assuming a certain interatomic interaction potential and considering a Bravais lattice the equation of motion for the displacement vectors  $\vec{u}(\vec{R}, t)$ , where  $\vec{R}$  denotes a lattice position, has the following form:

$$M \frac{d^2}{dt^2} \vec{u}(\vec{R}, t) = \sum_{\vec{R}'} ID(\vec{R} - \vec{R}') \cdot \vec{u}(\vec{R}', t), \qquad (1)$$

where  $\mathbb{D}(\vec{R}) = (\partial^2/\partial \vec{R} \partial \vec{R}) V(\vec{R})$  for  $R \neq 0$ ,  $V(\vec{R})$  being the interaction potential, and  $\mathbb{D}(0) = -\sum_{\vec{R}} \mathbb{D}(\vec{R})$ . For the calculations of neutron scattering cross-

sections we need the correlation functions  $\langle \vec{u}(\vec{R},t)\vec{u}(\vec{R}_1,t_1)\rangle$ , where  $\langle \ldots \rangle$  denotes the statistical average at a certain temperature. Evidently these quantities satisfy the same equations as the displacement vectors. We can multiply Eq. (1) from the right with  $\vec{u}(\vec{R}_1,t_1)$  and then take the statistical average of the whole equation. This leads to

$$\mathbb{M} \frac{d^2}{dt^2} \langle \vec{u}(\vec{R},t)\vec{u}(\vec{R}_1,t_1) \rangle = \sum_{\vec{R}^{\dagger}} \mathbb{D}(\vec{R} - \vec{R}^{\dagger}) \cdot \langle \vec{u}(\vec{R}^{\dagger},t)\vec{u}(\vec{R}_1,t_1) \rangle.$$
(2)

### 3. THE "EXACT" EQUATION OF MOTION

The Hamiltonian of our system can be separated into three terms: the nuclear part, which contains the kinetic energy of the nuclei and the Coulomb repulsion between them; the corresponding part for the electrons (all the electrons will be treated on the same footing) and finally the Coulomb interaction between the nuclei and the electrons. The nuclear displacements  $\vec{u}(\vec{R},t)$  are considered small and we make the conventional expansion in powers of the displacement vectors and keep only the linear terms in the equation of motion. We then get the following equation:

$$M \frac{d^2}{dt^2} \vec{u}(\vec{R}, t) = (Ze)^2 \sum_{\vec{R}'} \mathbf{I}(\vec{R} - \vec{R}') \cdot \vec{u}(\vec{R}', t) + Ze^2 \int n(\vec{x}, t) \mathbf{I}(\vec{x} - \vec{R}) \cdot \vec{u}(\vec{R}, t) d\vec{x} + Ze^2 \int \vec{T}(\vec{R} - \vec{x})n(\vec{x}, t) d\vec{x}.$$
(3)

The vector  $\vec{T}(\vec{x})$  and the tensor  $T(\vec{x})$  stand for

$$\vec{T}(\vec{x}) = \frac{\partial}{\partial \vec{x}} \left( \frac{1}{|\vec{x}|} \right)$$
 and  $\mathbf{T}(\vec{x}) = \frac{\partial^2}{\partial \vec{x} \partial \vec{x}} \left( \frac{1}{|\vec{x}|} \right)$ , (4)

respectively, and the term T(0) appearing in the sum in Eq. (3) stands for

$$\mathbf{T}(\mathbf{0}) = -\sum_{\mathbf{R}\neq\mathbf{0}} \mathbf{T}(\mathbf{\vec{R}}).$$
 (5)

The sum on the right hand side of Eq. (3) gives the harmonic force from the bare nuclei. The second term represents the force from essentially the static electron distribution,  $n(\vec{x}, t)$  being the operator for the electron density. When considering only harmonic forces we should here replace the density operator by its average value  $\langle n(\vec{x}) \rangle$ , which is independent of time and has the same symmetry as the lattice. The last term in Eq. (3) takes into account the fact that the electron density varies in time due to the nuclear motion. If we insert the average density here this term vanishes and we have to determine the response of the electrons up to linear terms in the nuclear displacements. e denotes the electron charge and Z is the atomic number.

To find the response of the electrons we consider the motion of the electrons in the time-dependent potential

$$V_{ne}(\vec{x}, t) = Ze^{2} \sum_{\vec{R}'} \vec{T}(\vec{x} - \vec{R}') \cdot \vec{u}(\vec{R}', t), \qquad (6)$$

which arises from the nuclear displacements.  $\vec{u}(\vec{R}, t)$  is here considered as a Heisenberg observable. We shall assume that the motion of the electrons in a rigid lattice is known, i.e. we know all the eigen states and eigen energies in that case. Using ordinary time-dependent perturbation technique to lowest order we get the response of the electron density to correct order. This gives us the following expression:

$$n(\vec{x},t) - n^{0}(\vec{x},t) = \frac{Ze^{2}}{i\hbar} \sum_{\vec{R'}}^{t} \int_{-\infty}^{t} dt' \int d\vec{x}' [n^{0}(\vec{x},t); n^{0}(\vec{x}',t')] \vec{T}(\vec{x}' - \vec{R}') \cdot \vec{u}(\vec{R}',t'). \quad (7)$$

 $n^{0}(\vec{x}, t)$  denotes the electron density operator in a rigid lattice and [..;.] means an ordinary commutator. We have assumed for the derivation that the interaction in Eq. (6) was turned on infinitely slowly at the infinite past. Before the electron-phonon interaction was turned on the motion of the electrons was, of course, uncorrelated to the motion of the nuclei. After turning on the interaction it was not so; the correlation between the electron density and the nuclear displacements is given by Eq. (7). We are actually interested only in the correlation function  $\langle n(\vec{x}, t)\vec{u}(\vec{R}_{1}, t_{1}) \rangle$ , where statistical averaging is performed over both the electronic and vibrational states.  $\langle \vec{u}(\vec{R}, t) \rangle$  vanishes if  $\vec{u}(\vec{R}, t)$  stands for the displacement from the actual mean position at the temperature considered. Thermal expansion of the lattice is then automatically taken into account.

Making use of the fact that the quantities  $n^{\upsilon}(\vec{x},t)$  and  $\vec{u}(\vec{R},t)$  are uncorrelated we find that

$$\langle \mathbf{n}(\vec{\mathbf{x}}, \mathbf{t})\vec{\mathbf{u}}(\vec{\mathbf{R}}_1, \mathbf{t}_1) \rangle = Ze^{\sum_{\vec{\mathbf{x}}'} \int_{-\infty}^{\infty} d\mathbf{t}' \int d\vec{\mathbf{x}}' \mathbf{h}(\vec{\mathbf{x}}\mathbf{t}; \vec{\mathbf{x}}'\mathbf{t}') \vec{\mathbf{T}}(\vec{\mathbf{x}}' - \vec{\mathbf{R}}') \langle \vec{\mathbf{u}}(\vec{\mathbf{R}}', \mathbf{t}') \vec{\mathbf{u}}(\vec{\mathbf{R}}_1, \mathbf{t}_1) \rangle,$$
(8)

where

$$h(\vec{x}t; \vec{x}^{\dagger}t^{\dagger}) \begin{cases} = \frac{1}{i\hbar} \langle [n^{0}(\vec{x}, t); n^{0}(\vec{x}^{\dagger}, t^{\dagger})] \rangle & \text{for } t > t^{\dagger} \\ = 0 & \text{for } t < t^{\dagger}. \end{cases}$$
(9)

The commutator, averaged over the electron states, should be calculated for a rigid lattice and we shall assume this "propagator" function to be known. In the procedure followed above we have made the implicit assumption that the motion of the electrons goes continuously over to their motion in a rigid lattice when the electron-phonon interaction is turned off. We know that this is not true for a superconductor and, therefore, Eq. (8) holds only for an ordinary metal.

It should be noted that the quantity  $h(\vec{x}t; \vec{x}'t')$  enters whenever we ask for the average change of the electron density in a rigid lattice under the influence of a weak external potential  $\delta V_{ext}(\vec{x}, t)$ . We get generally

$$\langle \delta n(\vec{x},t) \rangle = \int h(\vec{x}t; \vec{x}'t') \delta V_{ext}(\vec{x}',t') d\vec{x}' dt'.$$
(10)

 $h(\vec{x}t; \vec{x}'t')$  has the same translational symmetry as the lattice, i.e.

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$$h(\vec{x} + \vec{R} t; \vec{x}' + \vec{R} t') = h(\vec{x}t; \vec{x}'t'),$$
 (11)

and it depends only on the time difference (t - t').

If all the nuclei are displaced equally, let us say with a vector  $\vec{u},$  and infinitely slowly the electrons will make the same displacement and we should have

$$\langle \mathbf{n}(\mathbf{\vec{x}}) \rangle = \langle \mathbf{n}^{0}(\mathbf{\vec{x}} - \mathbf{\vec{u}}) \rangle = \langle \mathbf{n}^{0}(\mathbf{\vec{x}}) \rangle - \frac{\partial}{\partial \mathbf{\vec{x}}} \langle \mathbf{n}^{0}(\mathbf{\vec{x}}) \rangle \cdot \mathbf{\vec{u}}.$$
 (12)

For this result to be consistent with Eq. (7) (or Eq. (8)) the following relation must hold:

$$-\frac{\partial}{\partial \vec{\mathbf{x}}} \langle \mathbf{n}^{0}(\vec{\mathbf{x}}) \rangle = Z \mathbf{e}^{2} \sum_{\vec{\mathbf{x}}^{\dagger}} \int d\mathbf{t}^{\dagger} d\vec{\mathbf{x}}^{\dagger} \mathbf{h}(\vec{\mathbf{x}}\mathbf{t}; \vec{\mathbf{x}}^{\dagger}\mathbf{t}^{\dagger}) \vec{\mathbf{T}}(\vec{\mathbf{x}}^{\dagger} - \vec{\mathbf{R}}^{\dagger}).$$
(13)

We now multiply Eq. (3) from the right with  $\vec{u}(\vec{R}_1, t_1)$ , take the statistical average of the whole equation and make use of Eq. (8). Finally we rewrite the second term on the right side of Eq. (3) using Eq. (13). We then get the following equation of motion for the displacement vectors:

$$\mathbb{M}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle \vec{\mathrm{u}}(\vec{\mathrm{R}},\mathsf{t})\vec{\mathrm{u}}(\vec{\mathrm{R}}_1,\mathsf{t}_1)\rangle = (\mathbb{Z}\,\mathrm{e})^2 \sum_{\vec{\mathrm{R}'}} \mathbb{T}(\vec{\mathrm{R}}-\vec{\mathrm{R'}}) \cdot \langle \vec{\mathrm{u}}(\vec{\mathrm{R'}},\mathsf{t'})\vec{\mathrm{u}}(\vec{\mathrm{R}}_1,\mathsf{t}_1)\rangle$$

+ 
$$(\mathbb{Z}e)^{2}\sum_{\vec{R'}}\int dt' \mathbf{\Gamma}(\vec{R}t; \vec{R't'}) \cdot \langle \vec{u}(\vec{R'}, t')\vec{u}(\vec{R_{1}}, t_{1}) \rangle.$$
 (14)

 $\Gamma(\vec{R}t; \vec{R}'t')$  depends only on the difference  $(\vec{R} - \vec{R}')$  and (t - t') and is expressed in terms of the electron correlation function as follows:

$$\mathbf{\Gamma}(\vec{R}t; \vec{R}'t') = e^2 \int \vec{T}(\vec{R} - \vec{x}) d\vec{x} h(\vec{x}t; \vec{x}'t') d\vec{x}' \vec{T}(\vec{x}' - \vec{R}') \\
-\delta_{\vec{R}\vec{R}} \delta(t - t') e^2 \sum_{\vec{p}'} \int dt'' \int \vec{T}(\vec{R} - \vec{x}) d\vec{x} h(\vec{x}t; \vec{x}'t'') d\vec{x}' \vec{T}(\vec{x}' - \vec{R}''). \tag{15}$$

We have by definition

$$\sum_{\vec{R}'} \int dt' \mathbf{\Gamma}(\vec{R}t; \vec{R}'t') = 0, \qquad (16)$$

and this guarantees translational invariance of the system. One can, by

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(15)

looking at the general translational properties of the system, also conclude that

$$\sum_{\vec{R'}} \int dt' \mathbf{\Gamma}(\vec{R}t; \vec{R't'})t' = 0$$

$$\sum_{\vec{R'}} \int dt' \mathbf{\Gamma}(\vec{R}t; \vec{R't'})t'^2 = -(2m/Ze^2)\mathbf{I},$$
(17)

where I is the unit tensor and m is the electron mass.

Equation (14) differs from Eq. (2) only with respect to the integration over the earlier time history. This is due to the fact that the electrons do not respond instantaneously to the nuclear motion. For the calculations of the phonon frequencies this time delay may not be important and we can then write the last term in Eq. (14) in the form

$$(\operatorname{Ze})^{2} \sum_{\vec{R}^{\dagger}} \left[ \int dt \, \boldsymbol{\Gamma}(\vec{R}t; \vec{R}' 0) \right] \langle \vec{u}(\vec{R}'t') \vec{u}(\vec{R}_{1}, t_{1}) \rangle, \qquad (18)$$

which makes Eq. (14) the same as the Born-von Karmán equations. The time delay is, however, responsible for damping of the phonons and this is completely neglected when using the approximation in Eq. (18).

We can solve Eq. (14) in the same way as we normally solve Born-von Kármán's equations, that is we assume

$$\langle \vec{u}(\vec{R},t)\vec{u}(0,0)\rangle = \mathbb{U} e^{i(\vec{q}\cdot\vec{R}-\omega t)},$$
 (19)

where  $\vec{q}$  is the wave vector of the phonon,  $\omega$  is its frequency and U is an amplitude tensor. We get the following secular equation to solve:

$$[\mathbf{M}\omega^{2}\mathbf{I} + \mathbf{D}(\vec{\mathbf{q}}, \omega)] \cdot \mathbf{U} = 0.$$
<sup>(20)</sup>

 $\mathbb{D}(\vec{q}, \omega)$  is given by

$$\mathbb{D}(\vec{q}, \omega) = (\mathbb{Z}e)^2 \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} [\mathbb{T}(\vec{R}) + \int e^{i\omega t} \mathbb{T}(\vec{R}t; 00) dt], \qquad (21)$$

and it differs from that obtained in the Born-von Kármán case due to the frequency dependence of the force constants. The assumption in Eq.(18) implies using the value of  $\mathbb{D}(\vec{q}, \omega)$  at  $\omega = 0$  for all frequencies.

Using  $\mathbb{D}(\vec{q}, 0)$  for all frequencies in Eq. (20) it follows generally that there are three different solutions corresponding to each wave vector  $\vec{q}$  and that the frequencies are real, assuming the lattice to be stable. For the exact solution with the proper  $\mathbb{D}(\vec{q}, \omega)$  the situation becomes more complicated. The frequencies are in general complex and more than one frequency can correspond to each wave vector and polarization direction. This would mean that the phonons are not simply exponentially damped plane waves.

It is well known that pure Coulomb interaction does not lead to sound waves  $(\omega/|\vec{q}| \rightarrow \infty \text{ for } |\vec{q}| \rightarrow 0)$  and we get plasma waves instead. To obtain meaningful results in this case the electron part in Eq. (21) must partly cancel the nuclear term. We should have

$$\mathbb{D}(\vec{q},\omega) \to 0 \quad \text{for} \quad \vec{q},\omega \to 0.$$
 (22)

The electrons will respond in such a way that they partly shield the nuclei from each other. In a non-ionic and non-metallic crystal the electrons are bound to the nuclei and the atoms or the molecules form neutral units. The electrons follow more or less rigidly and instantaneously the nuclei in their motion and only a slight deformation of the units occurs. In work, particularly by Cochran and collaborators, this deformation was described by an induced electric dipole moment attached to each nucleus and creating long-range dipolar interaction. In metals the bound electrons get a similar deformation but besides this the conduction electrons will shield the ions in a more complicated way. By an inspection of Eq. (8) we see that the problem we face is to calculate the change of the electron density when we move the nuclei from their equilibrium positions. The effect from the different nuclei is additive and we can, therefore, move only one nucleus at a time and determine the change in the average electron density around that nucleus. Such a calculation is very difficult to carry out to a high degree of accuracy and we shall not make any attempts to do that here. It is important to take properly into account the shielding of the long-range tail of the Coulomb interaction between the ions in metals. This is discussed in the next section.

### 4. THE EFFECTIVE NUCLEUS-NUCLEUS INTERACTION

We shall consider the Fourier transform of  $h(\vec{x}t; \vec{x}'t')$ ,

$$h(\vec{q}\omega; \vec{q}^{\dagger}\omega^{\dagger}) = (2\pi)^{-4} \int e^{-i(\vec{q}\cdot\vec{x}-\omega t)} d\vec{x} dt h(\vec{x}t; \vec{x}^{\dagger}t^{\dagger}) d\vec{x}^{\dagger} dt^{\dagger} e^{i(\vec{q}\cdot\vec{x}^{\dagger}-\omega^{\dagger}t^{\prime})}.$$
 (23)

Due to the fact that  $h(\vec{x}t; \vec{x}'t')$  depends only on the difference (t - t') and has the symmetry properties stated in Eq. (11),  $h(\vec{q}\omega; \vec{q}'\omega')$  is different from zero only for  $\omega = \omega'$  and  $\vec{q} - \vec{q}'$  equal to a reciprocal lattice vector. We shall write the Fourier transform in the following form:

$$h(\vec{q} + \vec{K} \omega; \vec{q'} + \vec{K'} \omega') = \delta(\omega - \omega') \delta(\vec{q} - \vec{q'}) \langle \vec{K} | h(\vec{q}, \omega) | \vec{K'} \rangle, \qquad (24)$$

where  $\vec{q}$  and  $\vec{q'}$  are restricted to the first Brillouin zone and  $\vec{K}$ ,  $\vec{K'}$  are arbitrary reciprocal lattice vectors. It is convenient to consider  $h(\vec{q}, \omega)$  in Eq. (24) as a matrix in the  $\vec{K}$ -space; the matrix elements  $\langle \vec{K} | h(\vec{q}, \omega) | \vec{K'} \rangle$  are defined by Eq. (24).

The nuclear motions create plane wave disturbances in the electron system, characterized by a wave vector  $\vec{q}$  and frequency  $\omega$ . Due to the periodicity of the lattice such a wave in the electron system will always be connected to other waves with wave vectors differing from the original one by a reciprocal lattice vector. For that reason we must consider  $h(\vec{q}, \omega)$  as a matrix in the reciprocal space, contrary to the case for a free electron gas.

To obtain a consistent matrix notation we write the instantaneous Coulomb potential in the form

$$v(xt; x't') = \frac{e^2}{|x-x'|} \delta(t-t').$$
 (25)

The corresponding Fourier components are

$$\mathbf{v}(\vec{\mathbf{q}} + \vec{K}\,\omega; \vec{\mathbf{q}}' + \vec{K}'\,\omega'\,) = \delta(\omega - \omega'\,)\,\delta(\vec{\mathbf{q}} - \vec{\mathbf{q}}'\,)\delta_{\vec{K}\vec{K}}\langle\vec{K}|\mathbf{v}(\vec{\mathbf{q}})|\vec{K}'\rangle\,, \tag{26}$$

where

$$\langle \vec{K} | \mathbf{v}(\vec{q}) | \vec{K} \rangle = 4\pi e^2 / | \vec{K} + \vec{q} |^2.$$
 (27)

 $v(\vec{q})$  is thus a diagonal matrix in the reciprocal space. It is also convenient to introduce a separate notation for the matrix

$$\langle \vec{K} | \vec{Q}(\vec{q}) | \vec{K}' \rangle = (\vec{K} + \vec{q}) \delta_{\vec{K}\vec{K}'}$$
(28)

So, for instance, we can write

$$v(\vec{q}) = 4\pi e^2 / |\vec{Q}(\vec{q})|^2$$
 (29)

Using these notations we can express  $\mathbb{D}(\vec{q}, \omega)$ , defined in Eq. (21), in a form which is very convenient for our further discussion. We have

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \mathbf{T}(\vec{R}) = -\frac{4\pi}{v_a} \sum_{\vec{K}\not\in\vec{V}} \langle \vec{K} | [\vec{Q}(\vec{q})(1/|\vec{Q}(\vec{q})|^2)\vec{Q}(\vec{q}) - \vec{Q}(0)(1/|\vec{Q}(0)|^2)\vec{Q}(0)] | \vec{K}' \rangle$$
(30)

and

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \int e^{i\omega t} \mathbf{\Gamma}(\vec{R}t; 00) dt = -\frac{(4\pi e^2)^2}{v_a} \sum_{\vec{K}\vec{K}'} \langle \vec{K} | \left[ \vec{Q}(\vec{q}) \frac{1}{|\vec{Q}(\vec{q})|^2} h(\vec{q}, \omega) \frac{1}{|\vec{Q}(\vec{q})|^2} \vec{Q}(\vec{q}) - \vec{Q}(0) \frac{1}{|\vec{Q}(0)|^2} h(0, 0) \frac{1}{|\vec{Q}(0)|^2} \vec{Q}(0) \right] | \vec{K}' \rangle.$$
(31)

 $v_a$  is the volume of the unit cell.

We notice that the matrices in Eq. (30) are diagonal and the right hand side of the equation can be written more explicitly as

$$-\frac{4\pi}{v_a}\sum_{\vec{k}}\left[\left(\vec{k}+\vec{q}\right)\frac{1}{|\vec{k}+\vec{q}|^2}\left(\vec{k}+\vec{q}\right)-\vec{k}\frac{1}{|\vec{k}|^2}\vec{k}\right].$$
(32)

Taking the above expression literally we should have certain terms where the inverse of zero appears. However, such terms should be excluded on the following basis. They originate from the fact that the total charge of the electrons is infinite, considering an infinite lattice, and similarly for the total charge of the nuclei. The combined charge is zero. One, therefore, often considers the electron system with a static positive uniform background and in the same way the nuclear system together with an equal static negative background. Nothing physically is changed but the irrelevant mathematical singularities disappear and this corresponds to excluding the terms with zero numerator. These singular terms will cancel out when we add the two expressions in Eqs. (30) and (31) and we do not really have to pay any special attention to them.

We know that  $\mathbb{D}(\vec{q}, \omega)$  should tend to zero for  $\vec{q}$  and  $\omega$  approaching zero. This is, however, not the case for the separated terms in Eqs. (30) and (31). To obtain the correct limit for the sum we must have

$$\frac{4\pi e^2}{|\vec{q}|^2} \langle 0 | h(\vec{q}, \omega) | 0 \rangle \rightarrow -1 \quad \text{for} \quad \vec{q}, \omega \rightarrow 0.$$
(33)

This cancellation effect will be made clear by referring to the physical interpretation of  $h(\vec{x}t; \vec{x}'t')$ .

Let us assume a weak external potential  $\delta V_{ext}(\vec{x}, t)$  applied on the electron system, considering a static lattice. The corresponding average linear response of the electron density is given by the expression

$$\langle \delta n(\vec{x},t) \rangle = \int h(\vec{x}t;\vec{x}'t') d\vec{x}' dt' \delta V_{ext}(\vec{x}',t').$$
 (34)

We can define an effective potential as follows:

$$\delta V_{eff}(\vec{x},t) = \delta V_{ext}(\vec{x},t) + e^2 \int \frac{1}{|\vec{x}-\vec{x}'|} \langle \delta n(\vec{x}',t) \rangle d\vec{x}', \qquad (35)$$

and we can introduce a new response function  $H(\vec{xt}; \vec{x't'})$ , which gives the response of the electron density to the effective potential and is defined by the relation

$$\langle \delta n(\vec{x}, t) \rangle = \int H(\vec{x}t; \vec{x}'t') d\vec{x}' dt' \delta V_{eff}(\vec{x}', t').$$
(36)

 $H(\vec{xt}; \vec{x't'})$  gives what we may call the local polarizability of the medium and

is the irreducible part of the electron polarization, when referring to the diagrammatic language.

We shall consider the particular case of a static point charge, giving a pure Coulomb potential, and write the relations above for the corresponding Fourier transforms, using the notation in Eq. (29). We have

$$\delta V_{\text{ext}}(\mathbf{\vec{q}}) = 4\pi \, \mathrm{e}^2 / \left| \vec{\mathbf{Q}}(\mathbf{\vec{q}}) \right|^2, \tag{37}$$

and from Eq. (35) we get

$$\delta V_{\text{eff}}(\vec{\mathbf{q}},0) = \left[ \mathbb{I} + \frac{4\pi e^2}{|\vec{\mathbf{Q}}(\vec{\mathbf{q}})|^2} h(\vec{\mathbf{q}},0) \right] \frac{4\pi e^2}{|\vec{\mathbf{Q}}(\vec{\mathbf{q}})|^2} . \tag{38}$$

The singular behaviour of  $\langle \vec{K} | V_{eff}(\vec{q}) | \vec{K}^{\dagger} \rangle$ , for  $\vec{K} = \vec{K}^{\dagger} = 0$  and  $\vec{q} = 0$ , is directly related to the long-range (1/x)-dependence of the Coulomb potential. In a metal we certainly expect the conduction electrons to shield the static Coulomb potential strongly enough to make the effective potential decrease more rapidly than (1/x) for  $x \rightarrow \infty$ . In a non-conducting medium this is not the case, thus still giving for the effective potential a (1/x)-dependence but reducing the strength by the static dielectric constant. If the external potential should vary with time the shielding effect should normally be reduced and essentially disappear for variations which are rapid compared with the relaxation time of the conduction electrons. Because of the essentially slow motion of the nuclei we do not expect this effect to be large but it is important to determine the magnitude of the effect for it is directly connected to the deviation from the so-called adiabatic appoximation for the lattice vibrations.

From the discussion above we can conclude that for a metal the  $(1/q^2)$ singularity in  $\delta V_{ext}(\vec{q})$  should not appear in  $\delta V_{eff}(\vec{q},\omega)$  and this implies the statement in Eq. (33).

It is often convenient to express our results in terms of H rather than h and this is easily done using the relation below, which is obtained by comparing Eqs. (34) and (36):

$$h(\vec{q}, \omega) = \left[ I - H(\vec{q}, \omega) \frac{4\pi e^2}{|\vec{Q}(\vec{q})|^2} \right]^{-1} H(\vec{q}, \omega).$$
(39)

 $\overline{H}(\vec{q}, \omega)$  is related to  $H(\vec{x}t; \vec{x}'t')$  in the same way as  $h(\vec{q}, \omega)$  is to  $h(\vec{x}t; \vec{x}'t')$ . All the matrix elements  $\langle \vec{K} | H(\vec{q}, \omega) | \vec{K'} \rangle$  are finite for  $\vec{q}$  and  $\omega$  tending to zero.

We can now define a proper effective total nuclear interaction potential  $V_{nn}^{eff}(\vec{x}t;\vec{x}'t')$ , in general non-local in space and time, by adding Eqs. (30) and (31) and using Eq. (39). We get for its Fourier transform the following expression:

$$V_{nn}^{eff}(\vec{q},\omega) = 4\pi (Ze)^{2} \frac{1}{\left|\vec{Q}(\vec{q})\right|} \left[ \mathbf{I} + 4\pi e^{2} \frac{1}{\left|\vec{Q}(\vec{q})\right|} h(\vec{q},\omega) \frac{1}{\left|\vec{Q}(\vec{q})\right|} \right] \frac{1}{\vec{Q}(\vec{q})}$$
$$= 4\pi (Ze)^{2} \left[ \left|\vec{Q}(\vec{q})\right|^{2} - 4\pi e^{2} H(\vec{q},\omega) \right]^{-1}.$$
(40)

Inserting this into the expression for the dynamical tensor we get

$$\mathbb{D}(\vec{q},\omega) = -\frac{1}{v_a} \sum_{\vec{k} \not\in \vec{k}} \left\langle \vec{k} \right| \left[ \vec{Q}(\vec{q}) V_{nn}^{eff}(\vec{q},\omega) \vec{Q}(\vec{q}) - \vec{Q}(0) V_{nn}^{eff}(0,0) \vec{Q}(\vec{0}) \right] \left| \vec{k} \cdot \right\rangle.$$
(41)

In the Born-von Kármán theory the corresponding expression for the dynamical tensor is

$$\mathbb{D}(\vec{q}) = -\frac{1}{v_a} \sum_{\vec{k}} \langle \vec{K} | \vec{Q}(\vec{q}) \nabla(\vec{q}) \vec{Q}(\vec{q}) - \vec{Q}(0) \nabla(0) \vec{Q}(0) | \vec{K} \rangle, \qquad (42)$$

where  $V(\vec{q})$  is the Fourier transform of the interatomic potential.

We shall in the following demonstrate the utility of the above formulation by considering some special physical situations and give the appropriate form for  $H(\vec{q}, \omega)$  in these cases.

### 5. RIGID DISPLACEMENT OF THE CORE ELECTRONS

In practical applications one normally considers a nucleus and an electron core as a rigid unit and modifies the nuclear-nuclear interaction accordingly. Let us state that  $Z^{1}(Z^{1}\leq Z)$  electrons are closely and rigidly bound to each nucleus. The ionic charge is then  $(Z - Z^{1})$  e and the interaction between the ions is assumed the same as for the nuclei except for a change  $Z \rightarrow (Z - Z^{1})$ . If we assume the valence electrons to interact with the ions only through a pure Coulomb interaction all our arguments above hold with the change that  $h(\vec{q}, \omega)$  should now represent the contribution from the valence electrons only.

The modified result is obtained by writing the original response function  $h(\vec{q}, \omega)$  in Eq. (40) as follows:

$$\mathbf{h}(\mathbf{\vec{q}},\omega) = (4\pi e^2)^{-1} \left\{ \left[ \left(1 - \frac{Z'}{Z}\right)^2 - 1 \right] \left| \mathbf{\vec{Q}}(\mathbf{\vec{q}}) \right|^2 + 4\pi e^2 \left(1 - \frac{Z'}{Z}\right)^2 \mathbf{h}_{val}(\mathbf{\vec{q}},\omega) \right\}.$$
(43)

The first term represents the response of the core electrons and the second term contains the renormalized response function of the valence electrons.

Correspondingly we get for the irreducible response function the following expression:

$$H(\vec{q}, \omega) = -(4\pi e^{2})^{-1} \left\{ \left[ \left( 1 - \frac{Z'}{Z} \right)^{-2} - 1 \right] |\vec{Q}(\vec{q})|^{2} - 4\pi e^{2} \left( 1 - \frac{Z'}{Z} \right)^{-2} H_{val}(\vec{q}, \omega) \right\}.$$
(44)

### 6. RESPONSE FROM THE CONDUCTION ELECTRONS

The conduction electrons are often considered to be uniformly distributed and for the irreducible response function  $H(\vec{q}, \omega)$  a value is taken corresponding to that for a non-interacting electron gas (random phase approximation). We have then

$$H(\vec{x}t; \vec{x}'t') \begin{cases} = \frac{1}{i\hbar} \langle [n^{0}(\vec{x}, t); n^{0}(\vec{x}', t')] \rangle & \text{for } t > t' \\ = 0 & \text{for } t < t', \end{cases}$$
(45)

where the right hand side is calculated for a system of non-interacting electrons. The corresponding Fourier transform is explicitly given in the literature and we state only the results here, restricting ourselves to zero frequency\*;

$$H(\vec{q}, 0) = -\frac{3n}{2E_{F}} \left[ \frac{1}{2} + \frac{1-x^{2}}{4x} \ln \left| \frac{1+x}{1-x} \right| \right], \qquad (46)$$

where  $x = |\vec{Q}(\vec{q})|/2k_F$ .  $E_F$  is the Fermi energy,  $k_F$  is the Fermi momentum and n is the constant average density of the conduction electrons.

The effective nuclear interaction is diagonal in the reciprocal space and we get for the dynamical tensor

$$\mathbb{D}(\vec{q}, 0) = -\frac{4\pi [(Z - Z')e]^2}{v_a} \sum_{\vec{k}} \left[ \frac{(\vec{k} + \vec{q})(\vec{k} + \vec{q})}{(\vec{k} + \vec{q})^2 - 4\pi e^2 H(\vec{k} + \vec{q}, 0)} - \frac{\vec{k}\vec{k}}{\vec{k}^2 - 4\pi e^2 H(\vec{k}, 0)} \right]$$
(47)

By writing  $(Z - Z^{\dagger})$  for Z we automatically take into account the rigid displacement of the ionic core.  $H(\vec{q}, 0)$  should then represent the response of the conduction electrons only. We see that  $H(\vec{q}, 0)$  is a continuous function of the wave vector but its first derivative becomes infinite for  $|\vec{K} + \vec{q}| = 2k_F$  and this gives rise to a sudden change in the slope of the phonon dispersion curves, the so-called Kohn effect [2].

### 7. COMPARISON WITH THE MODEL USED BY TOYA

Explicit numerical calculations of phonon dispersion curves for metals were recently carried out successfully by TOYA [5] along lines which are similar to those described here. He considers in his earlier papers monovalent metals and he separates the interaction into three parts:

(1) Interaction between the bare ions including both a long-range pure

<sup>\*</sup> See for instance: HUBBARD, J., Proc. phys. Soc. <u>A243</u> (1958) 336, 342 or KITTEL, C., Quantum Theory of Solids, John Wiley and Sons Inc., N.Y. (1963)  $1\overline{27}$ .

Coulomb interaction and a short-range exchange interaction. We shall denote the corresponding potential by  $v(\vec{x})$ .

- (2) Interaction between the bare ions and the conduction electrons which also contains a pure Coulomb part and a short-range essentially repulsive part. We use for this potential the notation  $v_1(\vec{x})$ .
- (3) Pure Coulomb interaction between the conduction electrons.

The modifications we shall make in Eq. (3) are to replace (a) in the first term on the right side of the equation

$$\mathbb{T}(\vec{R} - \vec{R}') \text{ by } \frac{\partial^2 v(\vec{R} - \vec{R}')}{\partial \vec{R} \partial \vec{R}},$$

(b) in the second and third terms on the right side

$$\mathbb{T}(\vec{R} - \vec{x}) \text{ by } \frac{\partial^2 v_1(\vec{R} - \vec{x})}{\partial \vec{R} \partial \vec{R}} \text{ and } \vec{T}(\vec{R} - \vec{x}) \text{ by } \frac{\partial v_1(\vec{R} - \vec{x})}{\partial \vec{R}}$$

We can now apply our results in Eqs. (14) and (15) if we make the change in Eq. (14) stated in (a) above and the change in Eq. (15) stated in (b). Corresponding modifications have to be made in Eqs. (21), (30) and (31).

Toya treats the conduction electrons in principle in the Hartree-Fock approximation and takes for the exchange potential a simplified expression suggested by Slater;

$$V_{\text{exch}}(\vec{x},t) = -3e^2 C[n(\vec{x},t)]^{1/3},$$
 (48)

where C =  $(3/8\pi)^{1/3}$ . Toya leaves in fact this constant open and in this way allows for some correlation effects between the conduction electrons to be included.

The effective potential on a conduction electron induced by an external potential contains both the Hartree potential and the Slater potential as follows (cf. Eq. (35)):

$$\delta V_{\text{eff}}(\vec{x},t) = \delta V_{\text{ext}}(\vec{x},t) + e^2 \int \frac{1}{\left|\vec{x} - \vec{x}^{\dagger}\right|} \langle \delta n(\vec{x}^{\dagger},t) \rangle dx^{\dagger} - e^2 \operatorname{Cn}^{-2/3} \langle \delta n(\vec{x},t) \rangle, \quad (49)$$

where n, as above, is the constant average density of the conduction electrons.

We shall define the irreducible response function as earlier, i.e.

$$\langle \delta n(\vec{x}, t) \rangle = \int H(\vec{x}t; \vec{x}'t') \delta V_{eff}(\vec{x}', t') d\vec{x}' dt'.$$
 (50)

The only change we get in Eq. (39) is that the Coulomb term is replaced as follows:

$$4\pi e^2 / |\vec{Q}(\vec{q})|^2 \rightarrow [4\pi e^2 / |\vec{Q}(\vec{q})|^2 - e^2 Cn^{-2/3}] .$$
(51)

The irreducible response function taken is that for a non-interacting electron gas, which was explicitly given in Eq. (46). The effective potential between the ions becomes diagonal in the reciprocal space and we can write

$$\mathbf{ID}(\vec{\mathbf{q}}) = -\frac{1}{v_{a}} \sum_{\vec{\mathbf{k}}} \left[ (\vec{\mathbf{k}} + \vec{\mathbf{q}}) V_{nn}^{\text{eff}} (|\vec{\mathbf{k}} + \vec{\mathbf{q}}|) (\vec{\mathbf{k}} + \vec{\mathbf{q}}) - \vec{\mathbf{k}} V_{nn}^{\text{eff}} (|\vec{\mathbf{k}}|) \vec{\mathbf{k}} \right],$$
(52)

where

$$V_{nn}^{eff}(\vec{q}) = v(\vec{q}) + v_1(\vec{q})^2 H(\vec{q}) / \left[ 1 - H(\vec{q}) \left( \frac{4\pi e^2}{q^2} - e^2 Cn^{-2/3} \right) \right].$$
(53)

 $v(\vec{q})$  and  $v_1(\vec{q})$  are the Fourier transforms of  $v(\vec{x})$  and  $v_1(\vec{x})$ , respectively. It is very easy to see that  $V_{nn}^{\text{eff}}(\vec{q})$  is finite for  $\vec{q} \rightarrow 0$ .

The explicit expressions for  $v(\vec{x})$  and  $v_1(\vec{x})$  which were used by Toya in his computations are found in Ref. [5]. Toya also makes a slight change in the definition of  $H(\vec{q})$  by multiplying it with an adjustable parameter. He argues that he can in this way take into account the actual density of states on the Fermi surface. Later comparison with experimental data of phonon dispersion curves for sodium has indeed given very good agreement [6].

### 8. CONCLUDING REMARKS

In conclusion we would like to suggest that the interpretation of the experimental data should be based on Eq. (40) with the modifications done in the direction given by Toya. On one hand we face the problem of calculating  $H(\vec{q}, 0)$  or  $h(\vec{q}, 0)$  from basic principles; on the other we can try reasonable forms for H(q, 0) with a certain number of adjustable parameters which should be fixed by the experimental values of the elastic constants, conductivity due to lattice vibrations, etc. In this respect the philosophy is the conventional one, with the modification that normally the attention is concentrated on the force constants and not on the electron response function.

This paper is unfortunately incomplete in the sense that we do not suggest at present any explicit form for  $H(\vec{q}, 0)$ . It seems reasonable to start with effective potentials which are diagonal in the reciprocal space. This will lead to considerable simplifications both in the computations and in the interpretation of the experimental data.

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### DISCUSSION

H. HAHN (Chairman): Isn't what you and the many-body theoreticians call the random-phase or time-dependent Hartree-Fock approximation really the same thing, in the present case, as the self-consistent calculation performed by Bardeen in 1936?

A. SJÖLANDER: Yes, it is.

# PHONON DISPERSION RELATIONS IN ALKALI METALS

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### Abstract — Résumé — Аннотация — Resumen

PHONON DISPERSION RELATIONS IN ALKALI METALS. It has been shown in this paper that the phonon dispersion curves of sodium in the [100], [110] and [111] symmetry directions can be explained well on the basis of a simple model, where one has to consider only central force constants between nearest and next nearest neighbours. The tangential force constant between the nearest neighbours is very much smaller as compared to the radial force constant, while for the next nearest neighbours the radial and tangential force constants are comparable.

The calculation is carried out on the basis of the model suggested by de Launay, where it is shown that the conduction electrons exert a volume force for longitudinal modes. The stiffness constant of the electron gas is its bulk modulus which in de Launay's model is equal to the Cauchy discrepancy ( $C_{12}$ - $C_{14}$ ) for the cubic crystals. The three force constants  $\alpha_i$ ,  $\alpha_i$  and  $\alpha'_i$  can be determined from the measured elastic constants and the secular equation can be solved to give the dispersion curves.

The dispersion curves have also been obtained using the calculated values of the bulk modulus of the electron gas after considering not only the exchange and correlation energies but also the Fermi kinetic energy. These also agree fairly well with experiment.

The measured elastic constants as well as calculated bulk modulus of the electron gas indicate that the Cauchy relation  $C_{12} = C_{44}$  holds good approximately in alkali metals. This result is rather surprising as it requires that the interaction between the atoms be central in nature in spite of the metallic binding.

A justification for this has been given by Cochran. A model with four force constants is being worked out. They can be determined from the three elastic constants and calculated bulk modulus of the electron gas.

RELATIONS DE DISPERSION POUR LES PHONONS DES MÉTAUX ALCALINS. Les auteurs montrent que, si l'on veut expliquer les courbes de dispersion pour les phonons du sodium dans les directions de symétrie [100], [110] et [111], on peut fort bien faire appel à un modèle simple permettant de ne prendre en considération que les constantes de force centrale agissant entre un atome et les premiers et deuxièmes voisins les plus proches. Pour les premiers voisins les plus proches la constante de force tangentielle est sensiblement plus petite que la constante de force radiale, mais pour les deuxièmes voisins les plus proches ces deux constantes sont comparables.

Le calcul est fait sur la base du modèle proposé par de Launay, d'après lequel les électrons de conduction exercent une force sur le volume pour les modes longitudinaux. La constante de rigidité du gaz d'électrons constitue son module d'élasticité lequel, dans le modèle de Launay, correspond à l'écart de Cauchy ( $C_{12}$ - $C_{44}$ ) pour les cristaux cubiques. On peut déterminer les trois constantes de force  $\alpha_1$ ,  $\alpha_2$  et  $\alpha_1'$  à partir des constantes d'élasticité et résoudre l'équation séculaire pour obtenir les courbes de dispersion.

Les auteurs ont également obtenu ces courbes en utilisant les valeurs calculées pour le module d'élasticité du gaz d'électrons, après avoir tenu compte non seulement de l'énergie cinétique de Fermi mais aussi des énergies d'échange et de corrélation. Ces courbes concordent assez bien aussi avec les données expérimentales.

Les constantes d'élasticité mesurées du gaz d'électrons et son module d'élasticité calculé indiquent que la relation de Cauchy  $C_{12} = C_{44}$  est vérifiée approximativement dans les métaux alcalins. Ce résultat est plutôt surprenant, en effet, pour qu'il en soit ainsi, il faut que l'interaction entre atomes ait le caractère d'une force centrale malgré la liaison métallique.

Cochran a justifié ce résultat. Un modèle à quatre constantes de force est en voie d'élaboration. Ces constantes peuvent être déterminées à partir des trois constantes d'élacticité du gaz d'électrons et de son module d'élasticité calculé.

ФОНОННЫЕ ДИСПЕРСИОННЫЕ СООТНОШЕНИЯ В ШЕЛОЧНЫХ МЕТАЛЛАХ. В данном докладе показано, что фононные дисперсионные кривые натрия в направлениях симметрии [100], [110] и [111] могут быть хорошо объяснены на основе простой модели, в которой следует лишь учесть постоянные центральных сил между ближайшими и следующими за ближайшими соседними атомами. Постоянная тангенциальной силы между ближайшими соседними атомами является значительно меньшей по сравнению с постоянной радиальной силы, хотя для следующих за ближайшими соседними атомами постоянные радиальной и тангенциальной сил сравнимы.

Расчет осуществляется на основе модели, предложенной де Лонэ, которая показывает, что электроны проводимости усиливают объемную силу для продольных колебаний. Постоянная жесткости электронного газа является его модулем всестороннего сжатия, который по модели Лонэ равен расхождению Коши ( $C_{12} - C_{44}$ ) для кубических кристаллов. Постоянные трех сил  $\alpha_1$ ,  $\alpha_2$  и  $\alpha_1$  могут быть определены по измеренным постоянным упругости, а для получения кривых дисперсии можно решить вековое уравнение.

Кривые дисперсии получены также путем правильного использования расчетных величин модулей всестороннего сжатия электронного газа после учета не только энергии обмена и корреляции, но и кинетической энергии Ферми. Эти кривые также достаточно хорошо согласуются с экспериментом.

Измеренные постоянные упругости, а также рассчитанные модули всестороннего сжатия электронного газа показывают, что соотношение Коши С<sub>12</sub> = С<sub>44</sub> более или менее справедливо для щелочных металлов. Этот результат является довольно неожиданным, так как он требует, чтобы взаимодействие между атомами было центральным по характеру, несмотря на металлическую связь.

Объяснение этому было дано Кохраном. Разрабатывается модель с постоянными четырех сил. Они могут быть определены по трем постоянным упругости и расчетным модулям всестороннего сжатия электронного газа.

RELACIONES DE DISPERSIÓN FONÓNICA EN LOS METALES ALCALINOS. En la memoria se demuestra que las curvas de dispersión fonónica del sodio, en las direcciones de simetría [100], [110] y [111], pueden explicarse satisfactoriamente basándose en un modelo simple en el que solo se han de tener en cuenta las constantes de fuerzas centrales que afectan a los átomos más próximos y a los siguientes en proximidad. La constante de fuerza tangencial entre los vecinos inmediatos es muy pequeña en comparación con la constante de fuerza radial, mientras que para los átomos siguientes en proximidad, las constantes de fuerza radial y tangencial son comparables.

El cálculo se ha efectuado partiendo del modelo propuesto por de Launay, con arregio al cual los electrones de conducción ejercen una fuerza volumétrica sobre los modos longitudinales. La constante de rigidez del gas electrónico coincide con su módulo de elasticidad, que en el modelo propuesto por de Launay es igual a la discrepancia de Cauchy, esto es,  $C_{12}$ - $C_{44}$ , en el caso de los cristales cúbicos. Las tres constantes de fuerza  $\alpha_1$ ,  $\alpha_2$  y  $\alpha_1$  pueden determinarse a partir de las constantes de elasticidad medidas, mientras que las curvas de dispersión pueden obtenerse resolviendo la ecuación secular.

Las curvas de dispersión se han obtenido también utilizando los valores calculados del módulo de elasticidad del gas electrónico, cuenta habida de las energías de intercambio y de correlación, así como de la energía cinética de Fermi. También estas curvas concuerdan en grado aceptable con los resultados experimentales.

Las constantes de elasticidad medidas, así como el módulo de elasticidad calculado del gas electrónico, indican que la relación de Cauchy  $C_{12} = C_{44}$  se cumple con bastante aproximación en los metales alcalinos. Este resultado es un tanto sorprendente, pues presupone que la interacción de los átomos es de carácter central a pesar del enlace metálico.

Cochran ha propuesto una explicación de este fenómeno. Se está elaborando un modelo con cuatro constantes de fuerza, que pueden determinarse a partir de las tres constantes y del módulo de elasticidad correspondiente al gas electrónico.

### 1. INTRODUCTION

The phonon spectrum of sodium has been studied extensively. WOODS <u>et al.</u> [1] recently made a very detailed study on the dispersion relations of sodium. They measured the dispersion curves experimentally by in-

elastic scattering of neutrons. A fit of the experimental dispersion curves by using the tensor force model has shown that non-central forces extending up to fifth nearest neighbours are needed to explain the experimental curves. It has also been pointed out that if the force constants for fifth nearest neighbours are significantly different from zero,' then the analysis may have to be extended up to eighth neighbours. The information regarding such a large number of force constants can be obtained only by a fit of experimental data on the dispersion curve. In calculating phonon dispersion curves one has to obtain the interatomic force constants, either by first-principle calculations such as TOYA [2] made or by using some other experimental data such as elastic constants. The number of force constants which can be obtained by the latter method thus becomes seriously limited. In the first-principle method considerable difficulty is encountered in correctly calculating the energy of the metal as a function of the position of ions and so the force constants obtained are not very reliable.

In the case of sodium the force constants have been obtained with reasonable accuracy in terms of the three measured elastic constants which are available. But the three elastic constants enable one to find only three force constants. These can be radial force constants between an atom and its first, second and third neighbours, or radial and tangential between the first neighbours and only radial between the next nearest neighbour if one works with an axially symmetrical model. In the tensor force model one needs four force constants [3] if one takes interactions up to second nearest neighbours. Of these only three can be found from the elastic constants. The number increases as one takes interaction with distant neighbours into account.

In metals the question also arises as to what role the conduction electrons play on account of their Fermi energy. It has been pointed out by several workers [4-7] that the electrons will affect the longitudinal modes but not the transverse ones, as the electron gas has a bulk modulus but no shear. In the model suggested by de LAUNAY [7] the effect of the conduction electrons is taken into account by using separate force constants for longitudinal and transverse parts of ionic displacements. He took only the central forces acting between nearest and next nearest neighbours. In this situation one has two force constants  $\alpha_1$  and  $\alpha_2$  which enter into the transverse part and the modified ones  $\alpha_1^{\dagger}$  and  $\alpha_2^{\dagger}$  which enter into the longitudinal part. Thus with central forces between nearest and next nearest neighbours only, one has four constants to evaluate. Fortunately there is one relation connecting all the force constants. For a body-centred cubic lattice, it is:  $\alpha_2^{!} = \alpha_2 + (2/3)(\alpha_1^{!} - \alpha_1)$ . Thus there are only three independent force constants to be determined and they can be expressed in terms of elastic constants by going to the acoustic limit. In this treatment de LAUNAY [7] also showed that the bulk modulus of the electron gas  $K_e$  is given in terms of the force constants  $\alpha_1'$  and  $\alpha_1$  by the relation  $K_e = (2/a)(\alpha_1' - \alpha_1)$ , where a is the lattice parameter. With the value of the force constants  $\alpha_1^+$  and  $\alpha_2$  known in terms of the elastic constants it was found that  $K_e$ =  $c_{12}$ -  $c_{44}$ , where  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  are the three elastic constants of a cubic metal.

If the bulk modulus of the electron gas is calculated from the Fermi energy it comes out to be larger by an order of magnitude than the difference between measured values of  $c_{12}$  and  $c_{44}$ . For sodium  $K_e = 8.33 \times 10^{10} \text{ dyn/cm}^2$ and  $c_{12} - c_{44} = 0.78 \times 10^{10} \text{ dyn/cm}^2$ . The actual experimental value of  $c_{12} - c_{44}$ which is quite small indicates that the interaction between atoms in sodium is predominantly central. The calculated value of the electron gas bulk modulus can be shown to be smaller if properly calculated, taking into account the exchange and correlation energies. SINGH [8] has shown that the calculated value of the bulk modulus with exchange and correlation included is  $0.61 \times 10^{10} \text{ dyn/cm}^2$ , which is in fair agreement with the experimental value. Thus both theoretical and experimental results indicate that the interaction between atoms is very closely a central one. The study of lattice dynamics of sodium by COCHRAN [3], using a method similar to that of Toya, has shown that all the elements in the dynamical matrix have the form of elements arising from central interactions. Thus it seems fairly reasonable to assume that interatomic interactions in sodium and other alkali metals are predominantly central.

The de LAUNAY model [7] with central forces between nearest and next nearest neighbours only and with electron gas modification gives a reasonable agreement for phonon dispersion curves. This is also in conformity with the observation by WOODS et al. [1], namely that the central forces between nearest and next nearest neighbours give a close fit with experimental data and that only finer features of the dispersion curves need the extension of forces to neighbours beyond the second.

In this paper we have calculated the phonon dispersion curve using de Launay's model with electron gas modification, but considering radial and tangential forces between nearest neighbours and radial forces between next nearest neighbours. We thus have force constants  $\alpha_1$ ,  $\beta_1$ ,  $\alpha_2$  for the transverse displacement of atoms and  $\alpha_1^{\prime}$ ,  $\beta_1^{\prime}$ ,  $\alpha_2^{\prime}$  for the longitudinal displacements. We have assumed that the tangential force constants  $\beta_1$  and  $\beta_1^{\prime}$  are equal, thus reducing the force constants to five. Again  $\alpha_2^{\prime}$  can be expressed in terms of  $\alpha_2$ ,  $\alpha_1^{\prime}$  and  $\alpha_1$  by the relation  $\alpha_2^{\prime} = \alpha_2 + (2/3)(\alpha_1^{\prime} - \alpha_1)$ ; thus these force constants are not independent. We have four force constants  $\alpha_1$ ,  $\beta_1$ ,  $\alpha_2$  and  $\alpha_1^{\prime}$  to be determined from the three elastic constants and the calculated value of the electron gas bulk modulus K<sub>e</sub>.

#### 2. THE SECULAR EQUATION AND DISPERSION CURVES

The secular equation for sodium with radial and tangential forces between nearest neighbours and radial forces between next nearest neighbours with electron gas modification has been obtained. This has the following form:

$$(1+2\lambda)(1-C_{1}C_{2}C_{3}) \quad (1-\lambda)S_{1}S_{2}C_{3} \quad (1-\lambda)S_{1}C_{2}S_{3}$$

$$+\frac{3}{2}\mu S_{1}^{2}+\xi_{p}R_{1}-\Omega_{B}^{2} +\xi_{q}R_{1} +\xi_{r}R_{1}$$

$$(1-\lambda)S_{1}S_{2}C_{3}+\xi_{p}R_{2} \quad (1+2\lambda)(1-C_{1}C_{2}C_{3}) \quad (1-\lambda)C_{1}S_{2}S_{3}$$

$$+\frac{3}{2}\mu S_{2}^{2}+\xi_{q}R_{2}-\Omega_{B}^{2} +\xi_{r}R_{2}$$

$$(1-\lambda)S_{1}C_{2}S_{3}+\xi_{p}R_{3} \quad (1-\lambda)C_{1}S_{2}S_{3}+\xi_{q}R_{3} \quad (1+2\lambda)(1-C_{1}C_{2}C_{3})$$

$$+\frac{3}{2}\mu S_{3}^{2}+\xi_{r}R_{3}-\Omega_{B}^{2}$$

$$(1-\lambda)S_{1}C_{2}S_{3}+\xi_{p}R_{3} \quad (1-\lambda)C_{1}S_{2}S_{3}+\xi_{q}R_{3} \quad (1+2\lambda)(1-C_{1}C_{2}C_{3})$$

$$+\frac{3}{2}\mu S_{3}^{2}+\xi_{r}R_{3}-\Omega_{B}^{2}$$

In Eq. (1) the quantities p, q and r are the direction cosines of the wave propagation vector  $\vec{k}$  while

$$C_i = \cos \pi a k_i \quad \text{and} \quad S_i = \sin \pi a k_i, \tag{2}$$

where a is the lattice parameter and  $k_{\rm i}$  are the three components of the wave propagation vector.

The constants  $\lambda,\ \mu$  and  $\xi$  are related to the force constants which have been introduced. Thus

$$\lambda = \beta_1 / \alpha_1; \quad \mu = \alpha_2 / \alpha_1 \quad \text{and} \quad \xi = (\alpha_1' - \alpha_1) / \alpha_1. \tag{3}$$

The force constants are related to the elastic constants by the following relations:

$$\alpha_{1} = \frac{3a}{2} c_{44} - 2\beta_{1}$$

$$\alpha_{1}' = \frac{a}{2} (c_{12} + 2c_{44})$$

$$\alpha_{2} = \frac{a}{2} (c_{11} - c_{12}) - 2\beta_{1}$$

$$\alpha_{2}' = \alpha_{2} + \frac{2}{3} (\alpha_{1}' - \alpha_{1})$$
(4)

while the electron gas bulk modulus K<sub>e</sub> is given by

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$$K_{e} = \frac{2}{a} (\alpha_{1}' - \alpha_{1}) = c_{12} - c_{44} + \frac{4\beta_{1}}{a} .$$
 (5)

 $\Omega_B^2 = \frac{3\pi^2 \nu^2 M}{2\alpha_1}$  where  $\nu$  is the frequency of vibration and M is the mass of the

sodium atoms. The quantities  $\mathrm{R}_1$  ,  $\mathrm{R}_2$  and  $\mathrm{R}_3$  are given by the following expressions:

$$R_{1} = p (1 - C_{1} C_{2} C_{3} + S_{1}^{2}) + qS_{1}S_{2}C_{3} + rS_{1}C_{2}S_{3}$$

$$R_{2} = pS_{1}S_{2}C_{3} + q(1 - C_{1}C_{2}C_{3} + S_{2}^{2}) + rC_{1}S_{2}S_{3}$$
(6)
$$R_{3} = pS_{1}C_{2}S_{3} + qC_{1}S_{2}S_{3} + r(1 - C_{1}C_{2}C_{3} + S_{3}^{2}).$$

We can now express  $\lambda$ ,  $\mu$ ,  $\xi$  and  $\Omega_B^2$  in terms of the elastic constants  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  and the electron gas bulk modulus  $K_e$ . Thus

$$\lambda = \frac{1}{2} \frac{K_{e} - (c_{12} - c_{44})}{c_{12} + 2c_{44} - K_{e}}$$

$$\mu = \frac{c_{11} - c_{44} - K_{e}}{c_{12} + 2c_{44} - K_{e}}$$

$$\xi = \frac{K_{e}}{c_{12} + 2c_{44} - K_{e}}$$

$$\Omega_{B}^{2} = \frac{3p^{2}a^{2}}{8(c_{12} + 2c_{44} - K_{e})}$$
(7)

, where  $\rho$  is the density of the metal.

We can now obtain the dispersion relations for various symmetry directions from the secular Eq. (1). These are given below.

### (a) Direction [pqr] = [100]

(i) Longitudinal branch [p'q'r'] = [100]

$$\omega^{2} = \frac{16(c_{12} + 2c_{44} - K_{e})}{3\rho a^{2}} \left[ 1 + \frac{2K_{e} - (c_{12} - c_{44})}{c_{12} + 2c_{44} - K_{e}} \right] \sin^{2} \frac{\pi ak}{2} + \frac{4}{\rho a^{2}} \left[ 3(c_{11} - c_{44}) - K_{e} \right] \sin^{2} \pi ak$$
(8)

(ii) Transverse branches [p'q'r'] = [010] or [001]

$$\omega^2 = \frac{16c_{44}}{\rho a^2} \sin^2 \frac{\pi a k}{2}$$
(9)

# (b) Direction [pqr] = [110]

$$\omega^2 = \frac{4}{\rho a^2} \left( c_{11} + c_{12} + 2c_{44} \right) \sin^2 \frac{\pi a k}{\sqrt{2}}$$
(10)

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(ii) Transverse branch  $T_1[p'q'r'] = [1\overline{1}0]$ 

$$\omega^{2} = \frac{4(c_{11} - c_{12})}{\rho a^{2}} \sin^{2} \frac{\pi a k}{\sqrt{2}}$$
(11)

(iii) Transverse branch  $T_2[p'q'r'] = [001]$ 

$$\omega^{2} = \frac{8c_{44}}{\rho a^{2}} \sin^{2} \frac{\pi a k}{\sqrt{2}}$$
(12)

### (c) Direction [111]

(i) Longitudinal branch [p'q'r'] = [111]

$$\omega^{2} = \frac{4(c_{12}+2c_{44})}{\rho a^{2}} \sin^{2} \frac{\pi a k \sqrt{3}}{2} + \frac{4}{3\rho a^{2}} (4K_{e} - 3c_{12} + 6c_{44}) \sin^{2} \frac{\pi a k}{2\sqrt{3}} + \frac{4}{3\rho a^{2}} (3c_{11} - 3c_{44} - K_{e}) \sin^{2} \frac{\pi a k}{\sqrt{3}}$$
(13)

# (ii) Transverse branches $(p'q'r'] = [1\overline{10}]$ or $[11\overline{2}]$

$$\omega^{2} = \frac{4}{3\rho a^{2}} \left[ 13c_{44} - c_{12} + K_{e} \right] \sin^{2} \frac{\pi ak}{2\sqrt{3}}$$
$$+ \frac{4}{\rho a^{2}} (c_{11} - c_{44} - K_{e}) \sin^{2} \frac{\pi ak}{\sqrt{3}}$$
$$+ \frac{2}{\rho a^{2}} \left[ K_{e} - (c_{12} - c_{44}) \right] \sin^{2} \frac{\pi ak\sqrt{3}}{2}$$
(14)

### 3. CALCULATION AND RESULTS

The phonon dispersion curves in [100], [110] and [111] symmetry directions have been calculated from the above-given dispersion relations. The elastic constants and other data used are the same as used by SHARMA and JOSHI [9] for sodium at  $90^{\circ}$ K. These are

$$c_{11} = 8.08 \times 10^{10} \text{ dyn/cm}^{2}$$

$$c_{12} = 6.64 \times 10^{10} \text{ dyn/cm}^{2}$$

$$c_{44} = 5.86 \times 10^{10} \text{ dyn/cm}^{2}$$

$$\rho = 1.04 \text{ g/cm}^{3}$$

$$a = 4.24 \text{ Å}$$

The bulk modulus  $K_e$  for sodium, as calculated by one of us using the method of PINES [10] in order to take into account the exchange and correlation energies along with the Fermi energy, has been used. This calculated value for sodium is  $K_e = 0.61 \times 10^{10} \text{ dyn/cm}^2$  and it is not too much different from  $c_{12}-c_{44}$ . The calculated phonon dispersion curves are shown in Figs. 1, 2 and 3. The curve obtained from de LAUNAY's [7] theory using





Dispersion curves for sodium in [100] direction —— Present calculation

----- Calculated from de Launay's secular equation

- O Longitudinal experimental point
  - × Transverse experimental point





Dispersion curves for sodium in [110] direction — Present calculation

- O Longitudinal experimental point
- × Transverse experimental point

only radial force constants between first and second nearest neighbours is also shown in the same figures. The experimental values of WOODS <u>et al.</u> [1] are also given for comparison.



Fig. 3

Dispersion curves for sodium in [111] direction Present calculation

---- Calculated from de Launay's secular equation

Congitudinal experimental point
 X Transverse experimental point

### 4. DISCUSSION

The phonon dispersion curves obtained by us are shown by continuous curves while those obtained from de Launay's secular equation are indicated by dotted curves. The experimental points are indicated by circles for the longitudinal branches and crosses for the transverse branches. It will be seen that adding one more force constant brings out only a very slight change from the phonon dispersion curves obtained from de Launay's secular equation. This is why the dotted curves are seen to be different from the continuous curves only at some places. The shift of the continuous curves is generally in the right direction and this makes the agreement with experiment better. The phonon dispersion curves in [100] direction show greater proximity of the longitudinal and transverse branches at the point ka = 1. At this point the symmetry requires both branches to have identical frequency. Similarly the symmetry requires the longitudinal and transverse branches in the [111] direction to be degenerate at  $ka/\sqrt{3}=1$ . Again the phonon dispersion curves obtained by us show a closer proximity than those obtained from de Launay's theory.

The value of the force constant  $\beta_1$ , obtained from equation  $c_{12} - c_{44} = K_e - 4\beta_1/a$ , equals - 18 dyn/cm while the value obtained from the experimental data of Woods <u>et al</u>. is - 142 dyn/cm. If the values of elastic constants of sodium as reported by HUNTINGTON [11] are used along with our bulk modulus of the electron gas we get  $\beta_1 = -189 \text{ dyn/cm}$ . In any case  $\beta_1$  is much smaller than  $\alpha_1$  and  $\alpha_2$  which have values of 3727 and 341 dyn/cm as compared to the experimental values from the phonon dispersion curves which are 3818 and  $472 \pm 30 \text{ dyn/cm}$ , respectively. The lattice dynamics of sodium and other alkali metals are thus primarily controlled by the force constants  $\alpha_1$  and  $\alpha_2$  and other force constants enter only to improve the finer details of the phonon dispersion curves.

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## LATTICE DYNAMICS OF TRANSITION METALS

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#### Presented by G. Dolling

#### Abstract — Résumé — Аннотация — Resumen

LATTICE DYNAMICS OF TRANSITION METALS. The frequency versus wave-vector  $\nu(\vec{q})$  dispersion relations for the normal modes of vibration of several body-centred cubic transition metal crystals have been measured recently at room temperature. The dispersion curves for niobium, measured by Nakagawa and Woods, displayed some very unusual features, and the results could only be fitted by means of a Born-von Kármán model if interactions out to very distant neighbours (beyond eighth) were included. Subsequent measurements on tantalum by Woods showed very similar results. This is not surprising since niobium and tantalum are in column V of the periodic table and many of their electronic properties are similar.

Measurements of the dispersion curves of molybdenum by Woods and Chen and of tungsten by Chen and Brockhouse showed that although these metals, which are in column VI of the periodic table, had dispersion relations which were similar to each other, these dispersion relations were very different from those of the column V metals, niobium and tantalum. The gross features of the  $\nu(\vec{q})$  for molybdenum and tungsten were very nearly describable by a third neighbour axially symmetric Born-von Kármán force model, although several important features were not reproduced by this model. One of these features is a striking anomaly in the  $[\zeta\zeta\zeta]$  longitudinal (L) branch for molybdenum where the frequency changes from  $\nu = 6.3 \times 10^{12}$  c/s at  $\zeta = 0.92$  to  $\nu = 5.5 \times 10^{12}$  c/s at  $\zeta = 1.0$ . If this and other observed features are Kohn anomalies, their positions are consistent with the dimensions of the Fermi surface of the column V metals proposed by Lomer. Thus it is suggested that the striking differences between the dispersion relation for niobium and that for molybdenum (metals which are believed to have quite similar band structures) reflect differences in the Fermi energies and hence the Fermi surfaces for these materials.

DYNAMIQUE DE RÉSEAU DES MÉTAUX DE TRANSITION. Les relations de dispersion  $\nu(\vec{q})$  (fréquencevecteur d'onde) pour les modes de vibration normaux de plusieurs cristaux de métaux de transition à structure cubique centrée ont fait récemment l'objet de mesures à la température ambiante. Les courbes de dispersion relatives au niobium, établies par Nakagawa et Woods, présentent des particularités très exceptionnelles et on n'a pu faire concorder les résultats obtenus avec la théorie à l'aide d'un modèle Born et von Kármán qu'en tenant compte des interactions englobant des voisins très éloignés (au-delà du huitième). En procédant ultérieurement à des mesures sur le tantale, Woods a obtenu des résultats très semblables, ce qui n'est guère surprenant puisque le niobium et le tantale figurent dans la colonne V du tableau de la classification périodique et qu'ils possèdent des propriétés électroniques analogues sous de nombreux rapports,

Les courbes de dispersion établies par Woods et Chen pour le molybdène et par Chen et Brockhouse pour le tungstène oftémontré que si ces deux métaux qui figurent dans la colonne VI du tableau ont des relations de dispersion semblables l'une à l'autre, ces relations différent sensiblement de celles des métaux de la colonne V, niobium et tantale. Les caractéristiques générales de la relation  $\nu(\vec{q})$  pour le molybdène et le tungstène peuvent être décrites avec une grande précision au moyen d'un modèle Born et von Kármán de forces tenant compte d'une structure à symétrie axiale englobant le troisième voisin, bien que plusieurs caractéristiques importantes ne soient pas reproduites par ce modèle. Pour le molybdène, une de ces caractéristiques est une anomalie frappante de la branche (L) longitudinale [ $\zeta\zeta\zeta$ ] où la fréquence passe de  $\nu = 6,3 \cdot 10^{12}$  c/s pour  $\zeta = 0,92$  à  $\nu = 5,5 \cdot 10^{12}$  c/s pour  $\zeta = 1,0$ . Si cette caractéristique et d'autres, qui ont aussi été observées, sont des anomalies de Kohn, leurs positions sont compatibles avec les dimensions de la surface de Fermi des métaux de la colonne V, proposées par Lomer. On peut donc supposer que les différences nettes entre relations de dispersion pour le niobium et pour le molybdène (métaux dont on admet qu'ils ont des structures de bandes très semblables) correspondent à des différences dans les énergies de Fermi et, partant, dans les surfaces de Fermi de ces matières.

#### A.D.B. WOODS

ДИНАМИКА РЕШЕТКИ ПЕРЕХОДНЫХ МЕТАЛЛОВ. Дисперсионное соотношение частота/волновой вектор  $v(\vec{q})$  для обычных видов колебаний некоторых объемно-центрированных кубических кристаллов переходных металлов было недавно измерено при комнатной температуре. Кривые дисперсии для ниобия, измеренные Накаговой и Вудсом, проявили некоторые очень необычные черты, и результаты можно было привести в соответствие только с помощью модели Борн фон Кармана, если включить взаимодействия с очень отдаленными членами ряда дальше восьмого. Последующие измерения Вудсом тантала дали очень похожие результаты. Это не удивительно, поскольку ниобий и тантал находятся в V группе периодической таблицы и многие из их электронных свойств одинаковы.

Измерения кривых дисперсий молибдена Вудсом и Ченом и вольфрама Ченом и Брокхаузом показали, что, хотя у этих металлов, которые находятся в группе VI периодической таблицы, дисперсионные соотношения являются аналогичными, эти дисперсионные соотношения сильно отличаются от дисперсионных соотношений для ниобия и тантала, находящихся в группе V. Основные черты  $v(\vec{q})$  для молибдена и вольфрама очень близко описываются третьим членом ряда симметричной по осям силовой модели Борн-фон Кармана, хотя некоторые важные черты не воспроизводятся этой моделью. Одной из таких черт является разительная аномалия в продольной [ $\zeta \zeta \zeta$ ] ветви (L) для молибдена, где частота изменяется от  $v = 6,3 \cdot 10^{12}$  гц при  $\zeta = 0,92$  до  $v = 5,5 \cdot 10^{12}$  гц при  $\zeta = 1,0$ . Если эта и другие отмеченные черты представляют собой аномалии Кона, то их положение совместимо с размерами поверхности Ферми для металлов группы V, предложенными Ломером. Таким образом, предполагается, что разительные различия между дисперсионных соотношением для ниобия и дисперсионным соотношением для молибдена (металлы, которые, как предполагают, имеют совершенно одинаковые полосные структуры) отражают различия в величине энергии Ферми и следовательно в величине поверхностей Ферми для этих материалов.

DINAMICA DE LA RED CRISTALINA DE LOS METALES DE TRANSICION. La relación de dispersión frecuencia/vector de onda  $v(\vec{q})$ , correspondiente a los modos normales de vibración de varios cristales cúbicos de metales de transición centrados en el cuerpo, se ha medido recientemente a temperatura ambiente. Las curvas de dispersión del niobio, medidas por Nakagawa y Woods, presentaban algunas particularidades verdaderamente insólitas, y los resultados sólo podían ajustarse por medio de un modelo de Born-von Kármán si se incluían las interacciones que alcancen hasta átomos vecinos muy distantes (más allá del octavo). Las mediciones ulteriores realizadas en el tántalo por Woods dieron resultados análogos. Ello no es sorprendente, puesto que el niobio y el tántalo figuran en la columna V de la clasificación periódica y muchas de sus propiedades electrónicas son análogas.

Las mediciones de las curvas de dispersión del molibdeno, efectuadas por Woods y Chen, y del volframio, por Chen y Brockhouse, mostraron que si bien estos metales, que figuran en la columna VI de la clasificación periódica, presentan relaciones de dispersión comparables, éstas difieren considerablemente de las correspondientes a metales de la columna V como el niobio y el tántalo. Las características generales de  $\nu(\vec{q})$ correspondientes al molibdeno y al volframio se pudieron describir adecuadamente por medio de un modelo de fuerzas axialmente simétrico de Born-von Kármán que alcanza hasta el tercer átomo vecino, aunque dicho modelo no refleja algunas particularidades importantes. Una de éstas es una sorprendente anomalía en la rama longitudinal (L) [ $\zeta \xi \zeta$ ] del molibdeno, en que la frecuencia varía de  $\nu = 6,3 \cdot 10^{12}$  Hz para  $\zeta = 0,92$  a  $\nu = 5,5 \cdot 10^{12}$  Hz para  $\zeta = 1,0$ . Si estas y otras particularidades observadas son anomalías de Kohn, sus posiciones son compatibles con las dimensiones de la superficie de Fermi propuesta por Lomer para los metales de la columna V. Se formula la hipótesis de que las sorprendentes diferencias existentes entre la relación de dispersión del niobio y la del molibdeno (metales que, según se cree, poseen estructuras de banda muy semejantes) reflejan diferencias en las energías de Fermi y, por tanto, en las superficies de Fermi de estos materiales.

#### 1. INTRODUCTION

The transition metals of columns V and VI of the periodic table have extremely interesting electronic, superconducting and lattice vibrational properties. In addition, they are all body-centred cubic with one atom per unit cell; thus interpretation and comparison of their various properties is considerably simplified. The systematic study of the lattice dynamics of these metals [1-4] was undertaken in the hope that some pattern might emerge that could be correlated with their electronic properties. Recent theoretical studies of the Fermi surface [5, 6] and the band structure [7] of these metals provide a framework within which many of the features of the measured dispersion curves can be understood.

### 2. EXPERIMENTAL RESULTS

Measurements of the frequency wave vector ( $\nu(\vec{q})$  dispersion relation for the normal modes of vibration propagating in the high symmetry directions have been made at 296°K for niobium [1], molybdenum [2], tantalum [3], and tungsten [4]. These experiments were all carried out using the tripleaxis crystal spectrometer at Chalk River [8].

The results indicate that a certain pattern does indeed exist. The dispersion curves for niobium and tantalum have many features in common, such as the crossing of the longitudinal (L) and transverse (T) branches in the  $[00\zeta]$  direction. The dispersion curves for molybdenum and tungsten are similar to each other but very different from those for niobium and tantalum. Fourier analysis of  $\nu(\vec{q})$  for these four metals [2] indicates that this pattern is not merely qualitative; Fourier coefficients beyond first are similar for niobium and tantalum on the one hand and molybdenum and tungsten on the other, but may even be of different sign in going from niobium to molybdenum. Table I lists the Fourier components for several branches for all four metals Figures 1 and 2 show the  $[00\zeta]L$  and  $[\zeta\zeta\zeta]L$  branches respectively for niobium and molybdenum and illustrate very strikingly the differences in the lattice dynamical properties and effective interatomic forces in these metals.

### 3. DISCUSSION

The  $[\zeta\zeta\zeta]L$  branch for molybdenum is quite flat beyond  $\zeta = \frac{1}{2}$  until, near the end of the branch  $(\zeta = 1)$  there is a sharp drop in frequency from  $6.30 \times 10^{12}$  c/s at  $\zeta = 0.92$ , to  $5.50 \times 10^{12}$  c/s at  $\zeta = 1$ . The most reasonable explanation for this behaviour is that it is an anomaly of the type predicted by KOHN [9], and corresponds to an abrupt change in the ability of the electrons to screen out the ionic motions. The anomaly occurs wherever the phonon wave vector is equal to an extremal distance across the Fermi surface. (Such anomalies have previously been observed in lead [10, 11].) The Fermi surface dimension corresponding to this anomaly is in excellent agreement with the dimensions of the Fermi surface predicted by LOMER [5, 6] for the chromium group metals. Figure 3 shows Lomer's band structure curves for the [100] and [111] directions and the (110) plane of the corresponding Fermi surface. Other smaller anomalies on this branch at  $\zeta = 0.26 \pm 0.02$  and  $\zeta = 0.78 \pm 0.02$  are also consistent with this picture and lead to values of  $k = 0.45 \text{ Å}^{-1}$  and  $k = 0.29 \text{ Å}^{-1}$  for the radii of the electron and hole surfaces around  $\Gamma$  and H. The shape of the dispersion curves in the vicinity of the anomaly at  $\zeta = 0.26$  is not sufficiently accurate to decide

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#### TABLE I

| [ζζζ]Τ              | $\Phi_1$       | Ф <sub>2</sub> | $\Phi_3$       | $\Phi_4$        | $\Phi_5$ | $\Phi_6$ |
|---------------------|----------------|----------------|----------------|-----------------|----------|----------|
| Nb                  | 11.3           | 0.9            | 1.7            | -1.4            | -0.2     | 0.4      |
| Ta                  | 13.3           | . 0. 5         | 1.7            | -1.0            | -0.1     | 0.4      |
| Мо                  | 11,3           | 8.5            | -0.07          | 2.2             | -1.2     | 0.07     |
| W                   | 18.3           | 9.7            | 0.01           | 1.4             | -0.4     | -0.6     |
| [00ζ]L              | $\Phi_1$       | Φ2             | Φ3             | Ф <sub>4.</sub> |          |          |
| Nb                  | 10,2           | 3.6            | 2.4            | -1.5            |          |          |
| Та                  | 13.1           | 2.7            | 2.1            | -0.7            |          |          |
| Мо                  | 12.2           | 11.6           | -1.2           | 1.7             |          |          |
| W                   | 19.0           | 12, 0          | - 0. 7         | 0.4             |          |          |
| [çç0]T <sub>2</sub> | Ф <sub>і</sub> | Ф <sub>2</sub> | Ф <sub>3</sub> |                 |          |          |
| Nb                  | 7.5            | -2.1           | 0.3            |                 |          |          |
| Та                  | 10.9           | -2.1           | 0.4            |                 |          |          |
| Мо                  | 7.8            | 0.5            | -0.8           |                 |          | -        |
| w                   | 11.5           | 1.0            | -0.5           |                 |          |          |

### COMPARISON OF INTERPLANAR FORCE CONSTANTS FOR FOUR BODY-CENTRED CUBIC TRANSITION METALS (UNITS 10<sup>4</sup> dyn/cm)

on the nature of the anomaly and hence to differentiate between the radii of the electron and hole surfaces. Magnetoacoustic measurements on tungsten [12], however, indicate that the radius of the electron surface in this direction is the larger. The size of the anomaly near H (a 15% change in  $\nu$ ) at  $\zeta = 0.96$  is unusually large. The density of states on this almost flat Fermi surface is high and thus will lead to a discontinuity much stronger than the logarithmic singularity which results from a spherical Fermi surface [13]. The close similarity in size and shape of the electron and hole surface may also contribute to the strength of the anomaly [14].

A striking anomaly is also apparent in the  $[\zeta\zeta\zeta]L$  branch for niobium at  $\zeta = 0.45 \pm 0.03$  and leads to an extremal dimension in this direction of k=1.48 Å<sup>-1</sup>. This extremal dimension is consistent with the intersection of the Fermi level with the band structure curves at ~40% of the distance  $\Gamma P$  as shown in Fig.3. The band structure curves predict an anomaly in the [00 $\zeta$ ] direction near H (intersection of  $E_F$  and  $\Delta_2$ ). The data suggest that such an anomaly may exist near  $\zeta = 0.75$ .



[005]L branch of  $\nu(\vec{q})$  for niobium and molybdenum The solid lines have been drawn freehand through the points.

The shapes of these dispersion curves therefore appear to be influenced to a large extent by the presence of Kohn anomalies and it is postulated that the major differences between the  $\nu(\vec{q})$  for these metals are those due to the Kohn effect, and hence to their different Fermi surfaces. Calculations [7] suggest that the band structures for vanadium and chromium (and thus presumably for niobium and molybdenum) are similar; the differences in their Fermi surfaces therefore arise from their different Fermi energies and hence from the different number of valence electrons.

In a paper discussing the observation of the Kohn effect in sodium and other metals, KOENIG [15], without elaboration, has made a suggestion similar to that discussed above. Koenig has pointed out that the Kohn effect can be observed in the oscillating behaviour of the Fourier coefficients for  $\nu^2$ . The results of the Fourier analysis of the  $[00\zeta]L$  branch for niobium and molybdenum are shown in Fig. 4. The long range oscillatory behaviour is quite striking and is similar to that observed in lead [11]. The oscillations most likely correspond to the "Friedel oscillations" [16] which are a direct consequence of the Kohn effect. The period of oscillation for niobium is  $\sim 3.5$  interplanar spacings and for molybdenum  $\sim 2$  interplanar spacings. These results emphasize the differences in the Fermi surfaces of these metals. Unfortunately, however, it is not possible to extract accurate values for the Fermi surface dimensions from these results for two reasons: (1) values of the oscillating function can only be derived at a few discrete points; considerably higher precision and more determinations on each dispersion curve would be required to extend this significantly, and (2) in complicated metals like these, more than one period may be present; in such a case separation into components is difficult because the damping function (r-3 for transverse modes and a spherical Fermi surface) is not known.







Long-range Fourier coefficients (interplanar force constants) for  $[00\zeta]L$  branch of  $\nu(q)$  for niobium and molybdenum

### 4. CONCLUSIONS

The measured  $\nu(\vec{q})$  for the transition metals of columns V and VI of the periodic table can be qualitatively understood on the assumption that many of the gross features are a consequence of the Kohn effect. This pattern of the electron-phonon interaction, when compared with the corresponding pattern of superconducting transition temperatures [17], suggests that the electron-phonon interaction is the mechanism responsible for superconductivity in these transition metals.

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The author is indebted to many colleagues and visitors who have contributed in many ways to these investigations, in particular to Dr. Y. Nakagawa and Dr. S. H. Chen who collaborated on many of the experiments. He would also like to thank Dr. B. N. Brockhouse, Dr. R. A. Cowley, Dr. G. Dolling, and Dr. R. J. Elliott for assistance, advice and useful discussions on many occasions.

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### DISCUSSION

K.P. SINHA: In the transition metals which have overlapping s- and d-bands we should take into account the effect of s-d mixing. Such a mixing is possible as a result of interaction with phonons also. It is worthwhile examining the effect of such interactions on the phonon dispersion curves of various transition metals. Some of the anomalies pointed out might be correlated with this.

G. DOLLING: I quite agree.

P. EGELSTAFF: Is your explanation of these effects a qualitative one or have you obtained quantitative results?

G. DOLLING: The explanation is qualitative, but Dr. Woods very much hopes that professional theoreticians will rise to the occasion and propose more fundamental explanations.

# INELASTIC SCATTERING OF NEUTRONS IN CHROMIUM

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#### Abstract — Résumé — Аннотация — Resumen

INELASTIC SCATTERING OF NEUTRONS IN CHROMIUM. The phonon spectrum of chromium has been studied by neutron inelastic scattering. The dispersion curves are very similar in form to those of tungsten and molybdenum, indicating similar interionic force constants. The neutron groups broaden but do not shift appreciably when the temperature is raised. No effect has been observed which can be attributed to the interaction between the phonons and the crystal magnetization in the antiferromagnetic phase.

DIFFUSION INÉLASTIQUE DES NEUTRONS DANS LE CHROME. Les auteurs ont étudié le spectre phononique du chrome par la méthode de la diffusion inélastique des neutrons. La forme des courbes de dispersion ressemble beaucoup à celles du tungstène et du molybdène, ce qui indiquerait que les constantes de forces interioniques sont analogues.

On constate un élargissement des groupes de neutrons, mais aucun déplacement important lorsque la température augmente. On n'observe pas d'effet qui puisse être attribué à l'interaction entre les phonons et la magnétisation du cristal dans la phase antiferromagnétique.

НЕУПРУГОЕ РАССЕЯНИЕ НЕЙТРОНОВ НА ХРОМЕ. Фононный спектр хрома был изучен при помощи неупругого рассеяния нейтронов. Дисперсионные кривые очень похожи по форме на дисперсионные кривые вольфрама и молибдена, что говорит о сходстве констант межионных сил. При повышении температуры происходит расширение нейтронных групп, но значительного изменения не наблюдается. Никаких эффектов, которые могли бы быть объяснены взаимодействием между фононами и намагниченностью кристаллов в антиферромагнитной фазе, не наблюдалось.

DISPERSIÓN INELÁSTICA DE NEUTRONES EN EL CROMO. El espectro fonónico del cromo se ha estudiado por dispersión inelástica de neutrones. Las curvas de dispersión presentan una forma muy parecida a las del volframio y del molibdeno, lo que indica la existencia de constantes de fuerza interiónica análogas. Al elevarse la temperatura, los grupos neutrónicos se ensanchan, pero no se desplazan apreciablemente. No se ha observado ningún efecto que pueda atribuirse a la interacción entre los fonones y la magnetización del cristal en la fase antiferromagnética.

The phonon spectrum of chromium has been studied by the inelastic scattering of thermal neutrons. A triple-axis spectrometer situated at the DR3 reactor was used for these experiments and the phonon dispersion curves were studied in symmetry directions, using the constant-Q method, with fixed energy of the scattered neutrons. The specimens were single crystals of pure chromium metal in the approximate form of a cylinder 4 cm long and 1 cm in diameter. They could be placed in a nitrogen cryostat or in an oven whose temperature could be varied over a range between room

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temperature and approximately 600°K. One of these crystals had been used earlier for studies of critical magnetic scattering in chromium [1].

Well-defined neutron groups were observed for most of the  $\vec{Q}$ -values studied. Their intensity was as great as three times the background intensity, which was principally due to incoherent scattering from the crystal. The room background counting rate was approximately 5 cpm.



Fig. 1 Reduced wave vector co-ordinates ζ

The dispersion curves in symmetry directions are shown in Fig.1. Because of poorly formed neutron groups, the phonon energies between P and H are rather uncertain at present. These dispersion curves bear a close resemblance to those of tungsten [2] and molybdenum [3] and can therefore also be fitted quite closely by a force constant scheme extending to third nearest neighbours. The phonon energies scale approximately as the inverse square root of the ionic masses, indicating similar force constants and manifesting the similarity in the electronic structures of the three metals. No anomalies of the type found in molybdenum [3] were observed.

When the crystals were heated from approximately 100 to 400°K, the neutron groups progressively broadened, but no change could be observed in the phonon energies. One of the crystals used in these experiments contained a small uniaxial strain, which produced a large magnetic anisotropy [1]. This anisotropy was not reflected in the phonon spectrum, nor was any change observed in the energies of those phonons with wavelengths near the magnetic periodicity of the crystal, when it was heated through the Néel temperature. The coupling between the magnetization waves and the lattice is therefore presumably small.

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## DISCUSSION

G. DOLLING: It should be pointed out that only one of the anomalies in molybdenum (near the [ $\zeta\zeta\zeta$ ] zone boundary) is really very large, while the others are quite small. The experiments on tungsten are considerably more difficult than those on molybdenum, so that observation of small anomalies is even more difficult. Do you feel that your chromium measurements are as yet sufficiently complete to permit detection of such small anomalies?

A. MACKINTOSH: As far as chromium is concerned, I think that the results presented are still somewhat preliminary. I was not responsible for the work on tungsten which I mentioned. This was done at Chalk River and we can assume that it was done very carefully. At any rate, no anomalies appear to have been found. In terms of Fermi surfaces, we could expect to see a difference between chromium, tungsten and molybdenum. But the surprising thing is that tungsten and molybdenum have always seemed to be very similar in this respect.

## PHONON FREQUENCY DISTRIBUTION OF VANADIUM

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## Abstract — Résumé — Аннотация — Resumen

PHONON FREQUENCY DISTRIBUTION OF VANADIUM. The phonon frequency distribution of vanadium has been measured several times using the beryllium filter time-of-flight method. The results of the various authors agree more or less satisfactorily. But there have been objections against this method; for instance it does not start with monochromatic neutrons, and multiphonon processes are corrected only in a crude way. It seems worth while to determine the frequency distribution of vanadium by a different method.,

In the present work the authors tried to obtain this frequency distribution by a method which covers a larger part of the energy-transfer, momentum-transfer plane. Using the rotating crystal time-of-flight spectrometer at Karlsruhe with incident neutron energies between 0.018 and 0.08 eV energy transfers in the range from 0 to  $2 k_B T$  and Q-values between 0 and 14 Å<sup>-1</sup> (where hQ is the momentum transfer) have been measured.

Scattering-law values have been calculated and the frequency distribution was determined with the extrapolation method proposed by Egelstaff in an iterative way with the help of LEAP calculations.

Taking into account the experimental errors the results agree very satisfactorily with the cold neutron work for energy transfers greater than  $0.5 k_BT$ . Below  $0.5 k_BT$  we have found an additional peak, the origin of which is not yet explained.

Results are discussed and compared with existing theoretical calculations.

DISTRIBUTION DE FRÉQUENCE DES PHONONS DANS LE VANADIUM. La distribution de'fréquence des phonons dans le vanadium a été mesurée, à plusieurs reprises, par la méthode du temps de vol faisant appel à un filtre en béryllium. Les résultats obtenus par les divers auteurs concordent de façon plus ou moins satisfaisante. Cependant, on a élevé des objections contre cette méthode, en faisant valoir notamment que la source de neutrons n'est pas monochromatique et que les processus à plusieurs phonons ne font l'objet que d'une correction approximative. Il semble donc utile d'établir la distribution de fréquence dans le vanadium par une méthode différente.

Les auteurs ont essayé d'appliquer une méthode qui couvre une plus grande partie du plan transfert d'énergie - transfert de quantité de mouvement. En utilisant le spectromètre à temps de vol à cristal tournant de Karlsruhe avec des énergies des neutrons incidents de 0,018 et 0,08 eV, ils ont mesuré des transferts d'énergie entre 0 et  $2k_BT$  et les valeurs de Q entre 0 et 14 Å<sup>-1</sup> (hQ étant le transfert de quantité de mouvement).

Les auteurs ont calculé les valeurs relatives à la loi de diffusion et déterminé la distribution de fréquence par la méthode d'extrapolation d'Egelstaff employée itérativement à l'aide du code LEAP.

Compte tenu des erreurs expérimentales, les résultats concordent de manière très satisfaisante avec ceux que fournit l'étude, par les neutron froids, des transferts d'énergie supérieurs à 0,5 kgT. Au-dessous de 0,5 kgT, les auteurs ont constaté la présence d'un pic supplémentaire dont l'origine n'est pas encore élucidée.

Les résultats obtenus font l'objet d'un examen critique et sont comparés à ceux des calculs théoriques dont on dispose actuellement.

РАСПРЕДЕЛЕНИЕ ФОНОННЫХ ЧАСТОТ ВАНАДИЯ. Распределение фононных частот ванадия измерялось несколько раз при помощи метода измерения по времени пролета с использованием бериллиевого фильтра. Результаты различных авторов согласуются более или менее удовлетворительно. Однако против этого метода имелись возражения, так как он, например, не начинается с монохроматических нейтронов, и многофононные процессы корректируются лишь приблизительно. 11о-видимому, стоит определить распределение частот ванадия каким-то другим методом.

В настоящей работе сделана попытка получить это распределение частот методом, который охватывает большую часть плоскости передачи энергии и передачи импульса. С по-

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мощью спектрометра с врашающимся кристаллом для измерения по времени пролета в Карлсруз были измерены передачи энергии в диапазоне от 0 до 2 kpT и величины Q между 0 и 14 Å -1 (где лQ является передачей импульса) при энергиях бомбардирующих нейтронов между 0,018 и 0,08 эв.

Были вычислены величины для закона рассеяния, и было определено распределение частот с помощью метода экстраполяции, предложенного Эгельштаффом, итерационным путем с помощью расчетов LEAP.

В пределах экспериментальных ошибок эти результаты согласуются вполне удовлетворительно с результатами работы по передаче энергии выше 0,5 k<sub>B</sub>T холодными нейтронами. Ниже 0,5 k<sub>B</sub>T мы обнаружили дополнительный пик, происхождение которого еще не объяснено.

Результаты обсуждаются и сравниваются с существующими теоретическими расчетами.

DISTRIBUCIÓN DE LAS FRECUENCIAS FONÓNICAS EN EL VANADIO. La distribución de las frecuencias fonónicas en el vanadio se ha medido en diversas ocasiones por el método de tiempo de vuelo y filtro de berilio. Los resultados obtenidos por los distintos investigadores concuerdan de una manera relativamente satisfactoria. Ahora bien, se han formulado objeciones al empleo de ese método, ya que, por ejemplo, la fuente neutrónica no es monocromática y, por otra parte, la corrección aplicada a los procesos multifonónicos es poco precisa. Parece justificado, por tanto, determinar la distribución de las frecuencias en el vanadio recurriendo a otro método,

Los autores han procurado determinar la distribución de las frecuencias con ayuda de un método que abarca un sector más amplio del plano de la transferencia de energía en función de la transferencia de impulso (curva de dispersión). Empleando el espectrómetro de cristal giratorio de Karlsruhe y el método de tiempo de vuelo, han medido con energías de los neutrones incidentes comprendidas entre 0,018 y 0,08 eV, transferencias de energía que se extienden de 0 a  $2 k_B T$ , y valores de Q comprendidos entre 0 y 14 Å<sup>-1</sup> (siendo fiQ la transferencia de impulso).

Con ayuda de la clave de cómputo LEAP, se han calculado repetidamente los valores correspondientes de la ley de dispersión y se ha determinado la distribución de las frecuencias por el método de extrapolación propuesto por Egelstaff.

Teniendo en cuenta el margen de error experimental, los resultados obtenidos concuerdan de manera muy satisfactoria con los de los trabajos sobre neutrones fríos para transferencias de energía superiores a  $0.5 k_B T$ . Por debajo de ese valor, los autores han encontrado un pico adicional cuyo origen no ha podido explicarse aún.

Los datos obtenidos se examinan y comparan con los resultados de cálculos teóricos realizados previamente.

#### I. INTRODUCTION

The investigation of inelastic scattering of slow neutrons in solids yields valuable information on dynamic properties of such many-particle systems. If the coherent scattering is dominant, single phonons can be "seen" and, as a result of systematic measurements of phonons in certain directions in single crystals, dispersion curves can be constructed. If the scattering is incoherent, this method is not possible. In this case, however, the frequency distribution of the normal modes can be deduced in a more or less direct way from the measured scattering distribution. A comparison of experimental and theoretical frequency distributions often suggests a more realistic picture of the properties of the scatterer. Unfortunately, only a few substances scatter almost completely incoherently. Of these, vanadium, with a body-centred cubic lattice, has a relatively simple structure. Several workers [1-4] have reported frequency distributions of vanadium obtained by the scattering of beryllium-filtered cold neutrons. In the present paper, a somewhat different method is described in which the scattering law of vanadium is measured for a relatively large range of momentum

transfer, hQ, and energy transfer,  $\hbar\omega (0 < Q < 14 \text{ Å}^{-1}; 0 < \hbar\omega < 2k_BT)$ . Starting with the scattering-law values and using the extrapolation technique proposed by EGELSTAFF [5], values of the frequency distribution function have been obtained. The only assumption made for the purpose of performing the iteration of the extrapolated values is that the motions of the atoms are harmonic. But then the separation of multiphonon processes is straightforward and no previous evaluation of the Debye-Waller factor is necessary.

## II. EXPERIMENTAL ARRANGEMENT AND PROCEDURE

A beam from the Karlsruhe rotating-crystal time-of-flight spectrometer described in detail in Reference [6] provided the incident monoenergetic neutrons in an energy range of 18 to 80 meV. Primary energy resolution was 5% at 18 meV and time resolution about 20  $\mu$ s/m.



Fig.1

Schematic sketch of the rotating-crystal time-of-flight spectrometer at the FR2 reactor

A sketch of the apparatus is shown in Fig. 1. The sample-detector distance was 2 m. Nine detectors at scattering angles between 20 and 140° were used simultaneously. At present, two different types of detectors are in use, namely He<sup>3</sup> counters, 1 in in diameter, forming banks with an effective area of 155 cm<sup>2</sup>, and Li<sup>6</sup>F-ZnS scintillators, 5 in in diameter. For data acquisition and reduction, a multiple input data acquisition system (MIDAS) with a Control Data 160-A computer (8K core memory) as central unit is employed [7]. This computer handles simultaneously on-line four different reactor beam experiments. The events recorded by the time-offlight detectors of the scattering experiment are fed into a multiparameter coding unit which digitizes the experimental number, the particular detector number and the neutron time-of-flight. This unit is connected with the computer by means of a central buffer station.

The scattering sample was a  $7 \text{ cm} \times 4.5 \text{ cm}$  vanadium plate with a thickness of 0.2 cm. The transmission of the sample was 85% for incident neutrons of the smallest energy and about 90% for the highest energy used. For

each of the three incident energies (about 18, 40 and 80 meV) a run of approximately 50-h duration was carried out. This corresponds to a few hundred counts in the significant inelastic channels. For background elimination similar runs without the sample were made. Because of the rotational symmetry of the crystal monochromator, background contributions from fast neutrons and uncorrelated slow neutrons are constant in time and are, therefore, easily corrected.

## III. DATA PROCESSING AND RESULTS

The quantity to be directly calculated from the measured scattering distributions is the scattering law  $S(\alpha, \beta)$ , defined as follows:

$$S(\alpha,\beta) = \frac{4\pi k_{B}T}{\sigma_{f}} \left(\frac{A}{A+.1}\right)^{2} e^{\beta/2} \left(\frac{E_{0}}{E}\right)^{\frac{1}{2}} \frac{d^{2}\sigma}{d\Omega dE}, \qquad (1)$$

where

 $\frac{d^2\sigma}{d\Omega dE}$  is the double differential neutron scattering cross-section,

 $\sigma_{f}$  the free-atom cross-section of the scattering nucleus,

k<sub>B</sub> the Boltzmann constant,

T the absolute temperature of the scatterer,

A the ratio of the mass of the scattering nucleus to the mass of the neutron,

 $d\Omega$  the element of solid angle into which the neutrons are scattered,

 $E_0$ , E the incident and scattered neutron energies, respectively,

$$\beta = \frac{\mathbf{E} - \mathbf{E}_0}{\mathbf{k}_B \mathbf{T}},\tag{2}$$

$$\alpha = \frac{\mathbf{E}_0 + \mathbf{E} - 2(\mathbf{E}_0 \mathbf{E})^{\frac{1}{2}} \cos \theta}{\mathbf{A} \mathbf{k}_{\mathrm{B}} \mathbf{T}},$$
(3)

 $\theta$  the scattering angle.

For incoherently scattering solids a direct relation can be established, in the harmonic approximation, between the phonon frequency distribution of the crystal lattice  $\rho(\beta)$  and the limiting value of  $S(\alpha, \beta)/\alpha$  for  $\alpha = 0$ :

$$\rho(\beta) = 2\beta \, (\sinh \beta/2) \, (S/\alpha)_{\alpha=0}. \tag{4}$$

In a first step a "calibration programme" was run for the purpose of calculating the detector efficiency as a function of energy. Here effects of sample thickness, mainly absorption, are taken into account. The calculation is based on the Placzek heavy-mass expansion [8]. A function of the type proposed by HARRIS et al. [9] was fitted to the calculated efficiency values. The resulting parameters were fed into the computer together with the raw data from sample-in and sample-out runs and a second calculation

was started with the "scattering-law programme", which delivers the  $\alpha$ ,  $\beta$ ,  $S(\alpha, \beta)$ ,  $S(\alpha, \beta)/\alpha$  and the statistical errors of the measurement for each time channel. In this programme the built-in possibility of smoothing the raw data in selected time-channel intervals was used when advisable, namely for the background data and the sample-in data at the lowest energy. A typical result for  $S(\alpha, \beta)/\alpha$  versus time-channel is shown in Fig. 2.



Fig. 2

Typical plot of  $(\alpha, \beta)/\alpha$  values obtained with the "scattering-law programme" ( $\theta = 124.5^{\circ}$ ;  $E_0 = 42.3$  meV)

The calculated  $S(\alpha, \beta)/\alpha$  values are then plotted against  $\alpha$  and extrapolated to  $\alpha = 0$  for  $\beta$ -values at 0.05 intervals (Fig. 3). In the first extrapolation the resolution effects that tend to increase the gradient of the  $S/\alpha$ curves, especially at low  $\alpha$ , have not been corrected for. Then the LEAP programme [10] was run with the first extrapolated values, assuming that the gradient of the LEAP output curves would be approximately correct. Based on this gradient a correction for the elastic peak resolution was performed using the assumption that the peak shape and also the energy resolution for a given time channel and a given incident energy are independent of the scattering angle.

It was further assumed that the  $\alpha$ -dependence of the elastic amplitude in a given channel is described by the Debye-Waller factor. This resolution correction determines a parallel displacement of the curves calculated with LEAP which is of significance only for low  $\beta$ -values.





Typical curves of log  $(S/\alpha)$  versus  $\alpha$ . L indicates the curves from the final LEAP calculation, R 80 and R 40 the curves calculated on the basis of L and the resolution correction sketched in the text for incident energies of 80 and 40 meV, respectively.

β positive and negative

 $\stackrel{\bigcirc}{\bullet} = 20 \text{ meV}$  $\stackrel{\bigcirc}{\bullet} = 40 \text{ meV}$  $\stackrel{\frown}{\bullet} = 80 \text{ meV}$ 

With the new extrapolated values a second LEAP calculation was made and the results were again compared with the measured data; this procedure was repeated until the slope of the L-lines (Fig. 3) and their limit at  $\alpha = 0$ stabilized themselves. Three runs were made,  $\rho(\beta)$  being normalized to one at every run. The variations of the calculated Debye-Waller factor and of the area under the input  $\rho(\beta)$  during the whole process were not greater than 10%. Figures 4 and 5 show the obtained  $(S/\alpha)_{\alpha=0}$  and  $\rho(\beta)$  curves.



Fig. 4 The values of  $(S/\alpha)_{\alpha=0}$  versus  $\beta$ 



Fig. 5  $\rho(\beta)$  deduced from the measurements

#### IV. DISCUSSION OF RESULTS

In Fig. 6 the final frequency distribution  $\rho(\nu)$  extracted from the scattering-law measurements is compared with some of the previously reported measurements using the beryllium-filter technique. The area under each curve is normalized to unity. All of them show roughly the same shape but in details there are disagreements. In curve 3 corrections are made for the energy distribution of the incident neutrons [3]. The decrease in peak height in our curve (curve 4) may be partially due to some extra scattering at higher energies; a decrease may be caused also by resolution effects



A comparison of several experimental frequency distributions for wanadium The number on the curve gives the reference number. Curve 4 is the result of the present work.

in the inelastic spectrum. But another possible explanation is the effect of multiple scattering; in our measurements we used much thinner samples than the other workers did.

The present curve (No.4) has a small bump at  $\nu = 2.4 \times 10^{12} \text{ s}^{-1}$ . The existence of such a peak has been predicted previously at about  $\nu = 2 \times 10^{12} \text{ s}^{-1}$  and attributed to the Kohn effect [11].

Although vanadium has a high transition temperature for the superconducting state indicating a strong electron-phonon interaction which favours a strong Kohn effect, such a peak, in principle, can be expected also on the basis of the Born-von Kármán theory. Using a model with noncentral nearest-neighbour and central next-neighbour interactions SINGH and BOWERS [12] calculated a frequency spectrum showing three peaks. Unfortunately they did not use the correct elastic constants. After the elastic constants of vanadium had been measured by ALERS [13], calculations using the Born-von Kármán and the de Launay models were made [14]. None of the models, however, gives a satisfactory representation of the measured frequency distributions.

From the LEAP calculations the Debye-Waller coefficient  $\lambda = 2 W/\alpha$ is found to be 4.22±0.42. In the Debye approximation a Debye temperature  $\theta_0 = 354 \pm 15^{\circ}$ K can be deduced from this value. Starting from the measured frequency distribution we calculated the specific heat as a function of temperature. The results are well described by the above Debye temperature and are, within the experimental errors, in agreement with the low temperature specific heat measurements by CORAK et al. [15].

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## DISCUSSION

P. EGELSTAFF: Measurements on vanadium made with the scatteringlaw apparatus at Chalk River confirm the existence of the low-energy peak which Mr. Gläser reports.

K.-E. LARSSON: Using the extrapolation technique of Egelstaff to obtain  $f(\omega)$ , we often get one series of experimental points for  $S(\alpha, \beta)/\alpha$  but quite another extrapolated curve, sometimes disagreeing markedly with these experimental points. What is the reason for this? Also, what is the uncertainty caused by this technique at small  $\beta$ -values?

W.GLÄSER: In most of the work we have done, the differences between sets of experimental points  $S/\alpha$  for different incident energies and the final extrapolation curves were mainly due to resolution. By making corrections for the finite widths of the elastic peaks, we were able to explain these differences; in particular, the change in slopes versus  $\alpha$  was found to be reasonable. The uncertainty at small  $\beta$ -values depends on the magnitude of this correction.

## PHONONS IN WHITE TIN

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## (Presented by S.K.Sinha)

## Abstract — Résumé — Аннотация — Resumen

PHONONS IN WHITE TIN. Phonons have been studied in white tin with slow neutrons on a time-offlight apparatus. The frequencies of about 700 phonons in the (100) and (001) planes have been measured at room temperature. Dispersion curves along symmetry directions are compared with those predicted from a model of Musgrave and with predictions from other models.

PHONONS DANS L'ÉTAIN. L'auteur a étudié les phonons dans l'étain à l'aide de neutrons lents et d'un dispositif à temps de vol. Il a mesuré, à la température ambiante, les fréquences de 700 phonons environ dans les plans (100) et (001). Il compare les courbes de dispersion le long des directions de symétrie à celles qui ont été établies sur la base du modèle de Musgrave et aux prévisions fondées sur d'autres modèles.

ФОНОНЫ В БЕЛОМ ОЛОВЕ. Изучены фононы в белом олове с помощью медленных нейтронов на устройстве для отбора частиц по времени пролета. При комнатной температуре измерены частоты приблизительно 700 фононов в плоскостях (100) и (001). Кривые дисперсии по направлениям симметрии сравниваются с кривыми, предсказанными с помощью модели Мусграве, и с предсказаниями, полученными на основе других моделей.

LOS FONONES EN EL ESTAÑO BLANCO. El autor ha realizado un estudio de los fonones en el estaño blanco empleando neutrones lentos en un aparato de tiempo de vuelo. Ha medido las frecuencias, a la temperatura ambiente, de unos 700 fonones en los planos (100) y (001). El autor compara las curvas de dispersión correspondientes a direcciones de simetría con las previstas tomando como base un modelo Musgrave y con previsiones basadas en otros modelos.

## 1. INTRODUCTION

Two models have recently been proposed for the lattice dynamics of white tin and used to predict the phonon dispersion relations from the measured elastic constants. MUSGRAVE [1] has introduced a model capable of representing grey and white tin in order to study the transition between the two phases. WOLFRAM, LEHMAN and De WAMES [2-4] have applied an axially symmetric force-constant model and calculated a Debye-Waller factor to compare with Mössbauer experiments. Musgrave's theory predicts stationary points ( $\nabla \omega = 0$ ) in the dispersion curves which are in good agreement with the superconducting tunnelling experiments recently reported by ROWELL et al. [5].

This paper describes measurements of phonon frequencies in the (100) and (001) planes of white tin. A comparison is made with the models mentioned, but no attempts to fit a theoretical model to these measurements are described at this stage.



Time-of-flight apparatus used by Cambridge University at Harwell

## 2. EXPERIMENT

Phonons are measured with slow neutrons by studying events in which a neutron creates or destroys a single phonon in a crystal. This experiment was done on the Cold Neutron Apparatus on the reactor DIDO at Harwell (Fig. 1). A liquid hydrogen source in the reactor provides a beam of cold neutrons which is passed through a rotor to give a monoenergetic beam of 4-Å neutrons. These may be scattered by the crystal into 24 detectors which lie in a plane also containing the incident beam, called the "scattering plane". The energy of the scattered neutrons is found by measuring their time of arrival at the detectors. The crystal symmetry plane under consideration is aligned with the scattering plane and observations are made in all counters simultaneously for each position of the crystal. In this method phonons are measured at general positions in the plane, i.e. without reference to symmetry points or directions.

Measurements were made in this way at 16 positions for the (001) plane and 24 positions for the (100) plane.

Approximately 700 phonons were found in the two planes. For conciseness results are given only for those phonons with wave vectors near symmetry directions. The (100) plane is equivalent to the (010) plane, the designation which is used henceforward.

## 3. RESULTS

The unit cell of the white tin lattice is shown in Fig.2. The Bravais lattice is body-centred tetragonal with c/a = 0.55. The basis consists of two atoms at (0, 0, 0) and (a/2, 0, c/4). Consequently the dispersion relations





Unit cell and Brillouin zone of white tin



Fig. 3 Dispersion curves in (001) plane

have six branches. Figure 2 also shows the first Brillouin zone. The section with the (001) plane can be reduced to the triangle  $\Gamma MX$ . The section with the (010) plane can be reduced to the quadrilateral  $\Gamma HH^{1}M$ . H<sup>1</sup>M is the continuation of  $\Gamma H$  from the point of view of the reciprocal lattice point (0,1,1), and so  $\Gamma HM$  can be taken as a whole to be the symmetry direction [001].

Phonons with wave vectors lying within 5° of one of the symmetry directions are shown in Figs. 3 and 4. The frequency  $\nu$  is plotted against the length of the wave vector  $|\vec{q}|$ . Figure 3 also has phonons within 0.0707 of the zone boundary MX. Figure 3 shows the triangle  $\Gamma MX\Gamma$  of the (001)plane; for the direction  $\Gamma M$ , phonons measured in both planes are plotted together. Figure 4 shows the direction [001].



Dispersion curves in [001] direction

The unusual symmetry of white tin means that the usual classification in terms of longitudinal, transverse, acoustic, and optic branches is not meaningful except at  $\vec{q} = 0$ . CHEN [6] has performed a group-theoretical analysis of the white tin lattice and it is convenient to use his notation to label the branches. Each symbol refers to a particular symmetry which in the symmetry directions may be possessed by one branch or by a pair of branches together. The points in the figures are the results of this experiment. The lines refer to Musgrave's theory, which are discussed subsequently.

Where branches are close together it is necessary to consider intensities in order to assign phonons to the correct branch. The one -phonon crosssection contains a factor  $|S|^2$ , where S is the structure factor

$$S = \sum_{K} \vec{Q} \cdot \vec{e}_{K} e^{-i \vec{G} \cdot \vec{R}_{K}}, \qquad (1)$$

where

$$S = \vec{G} + \vec{q}$$
(2)

and  $\vec{e}_K$  are the polarization vectors depending on the branch and wave vector of the phonon in question.

The situation is particularly complicated for the (001) plane since it is not a mirror plane, and in general all six branches have components of polarization vectors in the plane. However these fall into two symmetry types with three branches in each. These have identical frequencies at the zone boundary. In a given zone the structure factor is zero for one of the symmetry types. In zones about even reciprocal lattice points for example the symmetry type, which becomes  $\Sigma_2$ ,  $\Sigma_4$ ,  $\Delta_2$ ,  $\Delta_3$  in the symmetry directions, has zero structure factors, and so phonons observed in symmetry directions in these zones must be  $\Sigma_1$ ,  $\Sigma_3$ ,  $\Delta_1$  or  $\Delta_4$ . In the [100] direction it can be seen that  $\Sigma_1$  and  $\Sigma_3$  are well separated and identification between the two is no problem; likewise  $\Sigma_2$  and  $\Sigma_4$  are well separated, except for the degeneracy at  $\vec{q} = 0$ . The situation is not so good in the [110] direction, where  $\Delta_2$  is close to  $\Delta_3$  and  $\Delta_1$  to  $\Delta_4$ . However  $\Delta_1$  and  $\Delta_2$  are pure longitudinal,  $\Delta_3$  and  $\Delta_4$  pure transverse, and in some directions of reciprocal space the structure factor for one of the branches may be zero or very small, indicating that the phonon found belongs to the other branch. Only phonons for which this is the case have been retained. At the zone boundary the two longitudinal branches as well as the two transverse are degenerate. The two degeneracies are close together and these results are not adequate to decide which is higher. In particular there are two close points near the zone boundary which have been assigned on intensity considerations to  $\Delta_1$  and  $\Delta_4$ . There is of course the possibility of a Bragg reflection preceding or following a phonon event which would result in a different structure factor for that event. This has been observed in lead by BROCKHOUSE et al. [7] and of course throws doubt on all assignments made on intensity considerations.

The (010) plane is a mirror plane and so two branches are polarized perpendicular to the plane. In the [100] direction  $\Sigma_1$  and  $\Sigma_2$  are the branches polarized in the plane, which cannot be simply distinguished. Only those phonons for which branches can be unambiguously assigned by frequency considerations alone have been plotted in Fig. 3. In the [001] direction  $\Lambda_1$ and  $\Lambda_3$  are pure longitudinal and  $\Lambda_5$  is pure transverse. For most of the range however  $\Lambda_1$  and  $\Lambda_3$  are close together. The structure factor depends on the reciprocal lattice point (h, 0, 1) with respect to which  $\vec{q}$  is taken.

If l = 4n, the structure factor is non-zero for  $\Lambda_1$  only; if l = 4n + 2, it is non-zero for  $\Lambda_3$  only; if l is odd, scattering is expected for both branches. Only phonons for which l is even have been retained. With an incident wavelength of 4Å and the range of counter angles in the apparatus, the (000) zone is only accessible for phonons with  $\vec{q}$  between H and M; the (004) zone cannot be reached at all. Consequently results for  $\Lambda_1$  are inadequate.

Measurements in this direction have been made at Chalk River by ROWE [8]. These confirm that  $\Lambda_1$  and  $\Lambda_3$  are very close for most of the range and that  $\Lambda_1$  crosses  $\Lambda_3$  just after H. There is good agreement with the frequencies shown here.

## 4. THEORETICAL COMPARISON

MUSGRAVE [1] has produced a model of white tin which can also be used to describe grey tin. He considers the two types of angles  $\phi$ ,  $\phi'$  subtended at an atom by its four nearest neighbours; in grey tin these take the same value  $\theta$ . The forces between atoms are described by six parameters. Three force constants are taken to be central stiffnesses for first, second and third nearest neighbours; two are angular stiffnesses for  $\phi$  and  $\phi'$ ; the sixth is an interaction constant for deformation of opposite angles  $\phi'$ . The six elastic constants expressed in terms of these force constants are equated to those found experimentally by RAYNE and CHANDRASEKHAR [9]. The solution for the force constants gives negative values for  $k_{\phi'}$  and  $k_{\phi'\phi'}$ . He therefore takes a different value for  $C_{13}$  which still produces negative values for these force constants but renders the lattice stable. The dispersion curves worked out from this set of force constants are plotted in Figs. 3 and 4. Also shown are the slopes of the dispersion curves at  $\vec{q} = 0$ , calculated from the elastic constants.

In the [100] direction agreement with the results looks better than it is. It appears for instance that  $\Sigma_2$  has the same behaviour for theory and experiment. However according to the theory, at M the branch polarized in the (001) plane meets  $\Sigma_3$  at C, a higher point than D where the branch polarized in the [001] direction meets  $\Sigma_1$  at D. The corresponding experimental points A and B show A lower than B: the lowest frequency at M is not the branch polarized in the [001] direction. This would require a much lower value of  $k_0$  in the theory.

Agreement in the [110] direction is better. At the point X the transverse branches meet at G, a slightly higher point than H where the longitudinal branches meet. This separation is similar to that indicated by the experimental points, although as stated in the last section this is not well determined.

In the [001] direction the flatness of  $\Lambda_5$  is adequately represented. The discrepancy at M has been noted.  $\Lambda_1$  and  $\Lambda_3$  are not so close together as the experimental points.

The general shape of the curves is confirmed by the experiment. The experimental frequencies are somewhat lower, as expected from the discrepancy between the specific heat calculated from the theory and that observed experimentally. The theory successfully predicts the existence of low optic frequencies which MUSGRAVE [10] associates with the transition to a body-centred cubic structure observed at 110 kb (room temperature). The low-lying stationary points ( $\nabla \omega = 0$ ) in the acoustic branches, for which the theoretical values agree well with Rowell's superconducting tunnelling results [5], also occur in the measured dispersion curves.

WOLFRAM, LEHMAN and De WAMES [2] have a model of eight parameters, two central force constants per neighbour out to fourth nearest neighbours. Rigorous comparison with elastic constants would imply seven conditions on these, the six elastic constants and the isotropic pressure condition. In the comparison they neglect however the terms to first order in  $\vec{q}$  in the relative motion of the two lattices. This requires a condition to be satisfied by the elastic constants:

$$C_{44} - C_{13} - C_{66} + C_{12} = 0$$
, (3)

which, if satisfied, leaves six experimental conditions to be satisfied by the eight parameters. The parameters are adjusted within these conditions to give the best fit to the observed specific heat and Debye-Waller factor.

Dispersion curves [3] worked out on the basis of Rayne and Chandrasekhar's elastic constants do not predict the low optic modes. Also the values predicted for the two optical frequencies at  $\vec{q} = 0$  are 5.6 and  $5.8 \times 10^{12} \text{ c/s}$  compared with the experimental values of 1.3 and  $3.8 \times 10^{12} \text{ c/s}$ . Rayne and Chandrasekhar's elastic constants definitely do not satisfy Eq.(3). A generalization of the model [4] to obtain consistency with their values yields optical

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frequencies of 2.0 and  $2.2 \times 10^{12}$  c/s. Since the difference of the squares of the optical frequencies is uniquely determined on this model by the elastic constants, the approach does not seem very promising.

## 5. CONCLUSIONS

The results confirm the existence of the low-lying stationary points in the dispersion curves suggested by the super-conducting tunnelling results. There are low optic modes which were predicted by Musgrave and associated by him with the high pressure phase transition. The presence of very flat acoustic modes indicates that a model of interatomic forces will require forces between distant atoms to fit the experimental curves.

## ACKNOWLEDGEMENTS

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# RECENT RESULTS ON THE CRYSTAL PHYSICS OF WHITE TIN

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#### Abstract — Résumé — Аннотация — Resumen

RECENT RESULTS ON THE CRYSTAL PHYSICS OF WHITE TIN. Preliminary measurements of the frequencies of some normal modes of white tin (double body-centred tetragonal) have been made utilizing the three-axis crystal spectrometer of Ispra. Frequency versus wave-vector dispersion relations at room temperature have been obtained for a number of normal modes propagating along the [001] direction. The experimental results are compared with calculations made by Wolfram, Lehman and De Warnes (WLD) using the axially symmetric model. The theoretical values, based on the experimentally determined elastic constants, are not in agreement with our experimental results, since (i) the numerical value of the maximum observed frequency is about one half of the calculated one, and (ii) the shape of the observed dispersion curve for the [001] direction is rather different from the theoretical one and seems to indicate a comparatively strong interaction between first neighbours along the c-axis. This relatively strong interaction suggests an interpretation of the dynamical structure of white tin as a chain-like structure along the c-direction. Force constants giving a more reasonable fit with the preliminary values of the experimental frequencies are evaluated using the WLD model, and a frequency distribution of the normal modes is calculated.

The anomalous behaviour of the anisotropy ratio of the Debye-Waller factor in white tin, revealed by Mössbauer measurements, has been checked using the technique of elastic neutron diffraction by a powder sample. The same technique has been utilized with a single-crystal sample in order to map the anomalous intensity of neutrons diffracted in the surrounding of the (002) reflection, which should be forbidden.

An attempt is made to correlate these anomalous behaviours to a certain amount of static disorder present in the crystal. On the basis of the results available at present, such static disorder is not in contradiction to the chain-like structure proposed for white tin.

NOUVELLES DONNÉES SUR LA PHYSIQUE DES CRISTAUX D'ÉTAIN. Pour les mesures préliminaires des fréquences de quelques modes normaux de l'étain, les auteurs ont utilisé le spectromètre à cristal triaxial d'Ispra. Ils ont obtenu des relations de dispersion (fréquence/vecteur d'onde) à la température ambiante pour plusieurs modes normaux se propageant selon la direction [001]. Les résultats expérimentaux font l'objet d'une comparaison avec les calculs faits par Wolfram, Lehman et de Wames (WLD) au moyen du modèle à symétrie axiale. Les valeurs théoriques, fondées sur les constantes d'élasticité déterminées par voie expérimentale, ne concordent pas avec les résultats expérimentaux obtenus par les auteurs du mémoire; en effet: a) la valeur numérique de la fréquence maximum observée est d'environ la moitié de la valeur calculée; b) la forme de la courbe de dispersion expérimentale pour la direction [001] est assez différente de celle de la courbe théorique et semble indiquer une interaction relativement forte entre les voisins les plus proches selon l'axe c. Cette interaction suggère une interprétation selon laquelle la structure dynamique de l'étain serait semblable à une chaîne le long de la direction c. Les auteurs évaluent, au moyen du modèle WLD, des constantes de force qui donnent un meilleur ajustement avec les valeurs préliminaires des fréquences expérimentales, et ils calculent la direction c.

Le comportement anormal du rapport d'anisotropie du facteur Debye-Waller pour l'étain, déterminé par l'effet Mössbauer, a été vérifié par la méthode fondée sur la diffusion élastique des neutrons par une poudre. La même méthode a été utilisée avec un monocristal afin de déterminer, au moyen de courbes de niveau, l'intensité anormale des neutrons diffusés au voisinage de la réflexion (002) qui devrait être une réflexion interdite.

Les auteurs essaient d'établir une corrélation entre ce comportement anormal et un certain degré de désordre statique existant dans le cristal. Compte tenu des données actuellement disponibles, ce désordre statique n'est pas en contradiction avec la structure en chaîne proposée pour l'étain.

ПОСЛЕЛНИЕ РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЙ ФИЗИКИ КРИСТАЛЛОВ БЕЛОГО ОЛОВА. Были проведены предварительные измерения частот некоторых собственных колебаний белого олова (дважды объемно центрир. тетрагональная решетка) с помощью трехосного кристаллического спектрометра, имеющегося в Испре. Для ряда собственных колебаний, распространяющихся вдоль направления [001] при комнатной температуре, были получены дисперсионные соотношения частота – волновой вектор. Результаты экспериментов сравниваются с расчетами, произведенными Вольфрамом, Леманом и Де Вамесом (ВЛД) с помощью оксиально симметричной модели. Теоретические величины, основанные на константах упругости, полученных экспериментальным путем, не согласуются с нашими экспериментальными результатами, поскольку 1) цифровая величина максимума наблюдаемой частоты составляет около половины расчетной, и 2) форма наблюдаемой дисперсионной кривой для направления [001] несколько отличается от теоретической и, по-видимому, указывает на довольно сильное взаимодействие между первыми соседними атомами вдоль оси с. Такое относительно сильное взаимодействие дает возможность рассматривать динамическую структуру белого олова как цепную структуру в направлении с. Константы силы, наиболее соответствующие предварительным величинам экспериментальных частот, рассчитываются с помощью модели ВЛД; рассчитываются собственные колебания распределения частоты.

Аномальное поведение степени анизотропии фактора Дебая Уоллера в белом олове, вскрытое измерениями Мессбауэра, было проверено с помощью метода дифракции нейтронов на порошковом образце. Тот же самый метод использовался с монокристаллическим образцом для того, чтобы зафиксировать аномальную интенсивность нейтронов, дифрагированных вблизи отражения (002), что должно быть запрещено.

Делается попытка установить соотношение между этим аномальным поведением и некоторым статическим разупорядочением, имеющим место в этом кристалле. Имеющиеся в настоящее время результаты говорят о том, что такое статическое разупорядочение не противоречит цепной структуре, предложенной для белого олова.

RESULTADOS DE ESTUDIOS RECIENTES SOBRE LA FISICA DE CRISTALES DE ESTAÑO BLANCO. Los autores han realizado mediciones preliminares de las frecuencias de algunos modos normales en el estaño blanco (tetragonal doblemente centrado en el cuerpo) utilizando para ello el espectrómetro triaxial de cristal de Ispra. Han obtenido las relaciones de dispersión de los vectores de onda en función de la frecuencia, a la temperatura ambiente, para diversos modos normales que se propagan en la dirección [001]. Comparan los datos experimentales con los resultados de los cálculos realizados por Wolfram, Lehman y De Wames con ayuda de un modelo axialmente simétrico. Los valores teóricos, basados en las constantes elásticas determinadas experimentalmente, no concuerdan con los resultados experimentales a que llegan los autores, ya que; a) el valor numérico de la frecuencia máxima observada es aproximadamente la mitad del valor calculado. y b) la forma de la curva de dispersión observada para la dirección [001] difiere bastante de la curva teórica, y parece indicar la existencia de una interacción relativamente intensa entre átomos vecinos a lo largo del eje c. Esta interacción sugiere la posibilidad de interpretar la estructura dinámica del estaño blanco como una estructura de tipo cadena según la dirección c. Empleando el modelo de Wolfram, Lehman y De Wames, los autores determinan constantes de fuerza que permiten lograr una concordancia más razonable con los valores preliminares de las frecuencias experimentales, calculando seguidamente una distribución de frecuencias de los modos normales.

El comportamiento anômalo de la razón de anisotropía del factor de Debye-Waller en el estaño blanco, puesto de manifiesto por las mediciones del efecto Mossbauer, se ha comprobado mediante el método de la difracción elástica de neutrones en una muestra pulverulenta. Este mismo método ha sido aplicado a una muestra monocristalina a fin de determinar, mediante curvas de nivel, la intensidad anómala de los neutrones difractados en las proximidades de la reflexión (002), que se supone prohibida.

Los autores procuraron relacionar estos comportamientos anómalos con un cierto grado de desorden estático presente en el cristal. Con arreglo a los resultados de que se dispone en la actualidad, ese desorden estático no está en desacuerdo con la estructura de tipo cadena propuesta para el estaño blanco.

## I. INTRODUCTION

Preliminary results on the lattice dynamics of the anisotropic tetragonal white tin are reported. The results have been obtained at room temperature using the techniques of elastic [1 - 3] and inelastic scattering of neutrons [4], and the data have been taken with the three-axis spectrometer [5] at the Ispra-1 reactor.

Two different approaches to the problem have been followed. The usual constant- $\overline{Q}$  method for looking at phonon peaks has been used to determine frequency versus wave vector relations. Elastic diffraction has been used to study the anisotropy of the Debye-Waller factor and the anomalous intensity around the reciprocal lattice point (0, 0, 2), which should correspond to a forbidden reflection. Careful examination of the Renninger effect at the (002) reflection has been made, in order to eliminate the principal part of the intensity, which comes from parasitic reflections.

The results are interpreted in terms of a certain amount of static disorder present in white tin. The observations seem to be consistent with those of PRASAD and WOOSTER [6] using the X-ray technique.

## II. STRUCTURE OF WHITE TIN AND DYNAMICAL MODELS

White tin has a structure which can be described in terms of two interpenetrating tetragonal body-centred sub-lattices, centred at points (0, 0, 0)and (a/2, 0, c/4), respectively. The lattice constants at 25°C are a = 5.8314 Å and c = 3.1815 Å [7]. The tetragonal cell of white tin and the Brillouin zone in reciprocal space are shown in Fig. 1.



Fig. 1

A: Tetragonal unit cell of white tinB: Brillouin zone for white tin

(The irreducible part is delimited by the heavy line.)

The Born-von Kármán theory of lattice vibrations has been applied in different ways to calculate the dispersion relations and the frequency spectrum of the normal modes.

An application has been made by WOLFRAM, LEHMAN and De WAMES [8], who calculated the coefficients of the dynamical matrix using the axially symmetric (A - S) model, and subsequently by De WAMES and LEHMAN [9] using a modified A-S model which includes an anisotropy factor.

Another calculation of the dynamical matrix has been made by MUSGRAVE [10] who introduces force constants to account specifically for the variations of certain angles.

The model of Wolfram, Lehman and De Wames (WLD) takes into account forces up to fourth neighbours, in order to get elastic consistency. The force constants are deduced from the elastic constants measured in a large range of temperature by RAYNE and CHANDRASEKHAR [11]. Since in white tin one can choose a unit cell containing two atoms, one expects of course to find acoustic as well as optic branches.

It may be observed that the [001] direction (along the c-axis) is a highsymmetry direction. The frequency of transverse modes propagating along this axis is independent of the direction of vibration, and the eigenfrequencies of the dynamical matrix correspond to pure longitudinal and transverse degenerate modes.

## III. THE ANISOTROPY IN THE DEBYE-WALLER FACTOR

Since white tin is a highly anisotropic substance, one expects that the Debye-Waller factor consists of two distinct components, one along the c-axis and the other in the basal plane.

Accordingly, the Debye-Waller factor can be expressed in the following way:

$$2W = H_{xx} \frac{h^2 + k^2}{a^2} + H_{zz} \frac{l^2}{c^2} , \qquad (1)$$

where h, k and l are the Miller indices of a reflecting plane.

The quantity  $\epsilon = H_{xx}/H_{zz}$ , i.e. the ratio of the mean square atomic displacements along the xy-crystal planes and along the c-axis, is the anisotropy ratio of the Debye-Waller factor.

There is a striking discrepancy between the theoretical and the experimental values for  $\epsilon$ . All the calculations done so far, using dynamical models, give for  $\epsilon$  a value which is larger than unity, while the experimental values of  $\epsilon$  are systematically smaller than unity.

The calculation made by KAGAN [12] neglecting the contribution of the optical modes, the calculation of De WAMES <u>et al.</u> [13] using the A-S model and the calculation of De WAMES <u>et al.</u> [9] using the modified A-S model give values of  $\epsilon$  which are larger than one. In the last paper De Wames and Lehman point out that the anisotropy ratio depends essentially on the elastic constants C<sub>33</sub> and C<sub>11</sub>, since  $2W \propto 1/\omega^2$ , so that any dynamical model based on the values of elastic constants will always give  $\epsilon > 1$ .

The experimental value of the anisotropy ratio in white tin is due to ALEKSEYEVSKY et al. [14] who found that at room temperature  $\epsilon = 0.88$ , using Mössbauer absorption experiments. Another measurement of Mössbauer absorption is that of MEECHAN et al. [15] which confirms that  $\epsilon < 1$ .

We used neutron elastic diffraction to evaluate  $\epsilon$ . The intensities of seven diffraction peaks from a powder sample were used, after the usual corrections, to evaluate the Debye-Waller factor. The result of a fit of the



Fig. 2

Behaviour of the Debye-Waller factor for white tin The points correspond to experimentally determined integrated intensities of peaks of elastic diffraction. The straight lines are the result of a fit using the least square method.

intensity data to an expression of type (1), using the least square method, is shown in Fig.2. The anisotropy ratio which comes from our data is 0.64, which is still < 1.

Physically, the discrepancy shows that the mean displacement of the atoms in the c-direction is larger than that implied from the dynamical properties of the crystal.

If one calculates from our data the mean square displacements within the basal plane and along the c-axis, one gets respectively

$$\mu_{x} = 0.074 \text{ Å and } \mu_{z} = 0.093 \text{ Å}$$
 (2)

A tentative explanation of the discrepancy is the following. Let us suppose that there is in the crystal a certain amount of static disorder along the c-axis. This means that we can separate the mean square displacement along the c-axis in two components in the following way:

$$\mu_{z}^{2} = \mu_{z \, dyn}^{2} + \mu_{z \, st}^{2} , \qquad (3)$$

where the contribution  $\mu_{z \, dyn}$  is due to thermal disorder induced by the lattice vibrations and is governed by the elastic properties, and the contribution  $\mu_{z,s}$  is due to static disorder.

If we assume for the dynamical part of the anisotropy ratio the value 1.2, which comes from calculations using the WLD model [13], we find

$$\mu_{z \, dyn}^2 = \mu_x^2 / 1.2 \tag{4}$$

which gives, taking into account Eq. (2),

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$$\mu_{z,dyn} = 0.067 \text{ Å} \text{ and } \mu_{z,st} = 0.064 \text{ Å}$$
. (5)

The hypothesis of static disorder along the c-axis in white tin at room temperature can be supported by the temperature behaviour of the anisotropy ratio. Since the static part of the displacement should not be affected by temperature,  $\epsilon$  should decrease with decreasing temperature and this agrees with Mössbauer experiments of ALEKSEYEVSKY <u>et al.</u> [14] at 77°K.

## IV. THE ANOMALOUS INTENSITY AT THE (002) REFLECTION

PRASAD and WOOSTER [6], using X-ray technique, observed anomalies in the distribution of the background scattering intensity from white tin. They observed:

(a) That the intensity in the reciprocal lattice along a line passing through a reciprocal lattice point was strongly dependent on the line.

(b) That the intensity was distributed in plates normal to the crystallographic axes.

(c) That there was scattered intensity at points corresponding to forbidden reflections.

Prasad and Wooster concluded that these effects can probably be due to some static disorder connected with the phase transformation.

In our experiment we detected an abnormally high intensity at the point (0,0,2), which corresponds to a forbidden reflection and we decided to investigate the origin of this intensity.

First of all it must be noted that a great contribution is given by the Renninger effect [16, 17].

It is very well known that, when the conditions for Bragg scattering are satisfied for two different planes, a third plane, whose indices are given by the difference of the indices of the previous planes, is also in a reflecting position. In our case it is possible to find many couples of planes, having non-zero structure factor, able to simulate the forbidden reflection (002). To study the effect, two different crystal specimens of white tin were successively mounted on the spectrometer table with the [001] axis parallel to the scattering vector, and rotated around this axis.

The result of  $45^{\circ}$  of azimuthal rotation around the [001] direction is shown in Fig. 3. The zero of the azimuthal angles corresponds to a situation where the [100] direction is parallel to the scattering plane, and the arrows indicate the calculated positions at which the parasitic reflections are active, while looking at the (002) reflection. One will notice the tremendous variation of the intensity with the azimuthal angle. What is more interesting here is the constant level over which the peaks of multiple Bragg scattering rise.

This level is made with the following contributions:

 $I_{\lambda \text{ el. inc.}}$  incoherent elastic scattering of neutrons of wavelength  $\lambda$ 

 $I_{\lambda \ inel} \qquad \text{inelastic scattering of neutrons of wavelength } \lambda$ 

coherent elastic scattering of neutrons of wavelength  $\lambda/2$  $I_{\frac{\lambda}{2} el. coh.}$ I,

The four contributions are summed as follows:

level = 
$$I_{\lambda \text{ el. inc.}} + I_{\lambda \text{ inel.}} + I_{\frac{\lambda}{2} \text{ el. coh.}} + I_{x}$$
. (6)

The background has also been measured rotating the tin crystal out of the Bragg position. We assume that

background = 
$$I_{\lambda \text{ el. inc.}} + I_{\lambda \text{ inel.}}$$
 (7)

The assumption that  $I_{\lambda \text{ inel}}$  in the two cases is the same is rather arbitrary.

The multiple Bragg scattering measurement has been done in three different ways:

- (a) With the spectrometer set in the conventional way.
- (b) Filtering the outcoming white beam with a 8-cm quartz single crystal to reduce the  $\lambda/2$ -component.
- (c) With the spectrometer set for elastic diffraction, the analyser crystal being set to reflect the first order of  $\lambda$ .

The intensities measured in the different ways are recorded in Table I.

We can use the intensities of the multiple Bragg peak, which is essentially due to coherent elastic scattering of the  $\lambda$ -component, to normalize the intensities in the three ways of operation.

The numbers in brackets in Table I are the intensities after normalization. We can write for the three ways of operation the following equations:

$$\begin{cases} \text{level} = I_{\lambda \text{ el. inc.}} + I_{\lambda \text{ inel.}} + I_{\lambda} \text{ el. coh.} + I_{x} \\ \hline 2 \\ \text{background} = I_{\lambda \text{ el. inc.}} + I_{\lambda \text{ inel.}} \end{cases}$$
(8)

$$\int \text{level} = I_{\lambda \text{ el. inc.}} + I_{\lambda \text{ inel.}} + I_{x}$$
(9)

 $\lfloor$  background =  $I_{\lambda el. inc.} + I_{\lambda inel.}$ 

$$level = I_{\lambda el. inc.} + I_{x}$$
(10)  
background = I<sub>\label el. inc.</sub>

## TABLE I

|  | Conventional<br>diffraction | Quartz-filtered<br>beam |        | Elastic<br>diffraction |        |
|--|-----------------------------|-------------------------|--------|------------------------|--------|
| Background   | 82                          | 35                      | (74)   | 6                      | (28)   |
| Typical peak<br>of multiple<br>Bragg<br>scattering | 4000.                       | 1900                    | (4000) | 850                    | (4000) |
| Level  | 450                         | 160                     | (337)  | 45                     | (211)  |

## CONTRIBUTIONS TO THE INTENSITY AT THE (002) FORBIDDEN REFLECTION

Equations (8), (9) and (10) refer to the conventional diffraction, the conventional diffraction with quartz-filtered beam and the elastic diffraction assuming that the  $\lambda/2$ -component is negligible after reflection over the analyser crystal, respectively. Introducing the values from Table I, normalized at 4000 as indicated, into these equations, it is possible to evaluate I<sub>x</sub>, i.e. the coherent elastic disorder scattering. One obtains from Eq. (9) (quartz-filtered beam)

and from Eq. (10) (elastic diffraction)

$$I_x = 183.$$
 (10')

Though what we actually get at present is only an order of magnitude, it is important to note that, after having eliminated the multiple Bragg component, the  $\lambda/2$ -component and the inelastic component, a coherent elastic component, which disappears if the crystal is rotated out of the Bragg position, still remains at the (002) reflection. The amount of this component is found experimentally to be about 0.001 of that in a permitted reflection at the same angle.

A map of the intensity distribution around the point (0, 0, 2) is presented in Fig.4. The spectrometer was set for elastic diffraction and the tin single crystal was oriented with the [100] and [001] axis lying in the scattering plane. In this orientation, corresponding to the zero of the azimuthal angles, no parasitic reflections appear. One can see that the intensity distribution is steeper along the [001] direction, confirming the plate shape observed by Prasad and Wooster.

The anomalous <u>elastically</u> diffracted intensity observed at the (002) reflection can be attributed to a static disorder along the c-axis. This disorder might be due, for instance, to defects or vacancies along any indivi-



Fig.3

Intensity of neutrons diffracted from the (002) reflection of white tin at different azimuthal angles The zero of the azimuthal angles corresponds to the [100] direction lying in the scattering plane. The arrows correspond to the calculated positions at which parasitic reflections appear.



Map of intensity of neutrons elastically diffracted from white tin around the (0, 0, 2) reciprocal lattice point, in the (100, 001) reciprocal lattice plane.

dual atomic chain parallel to the c-axis, to irregular mutual displacements of neighbouring chains, etc. It is possible to account for the <u>static</u> component of the mean square atomic displacement along the c-axis (see Eq. (5)) by any of the above-mentioned reasons. More detailed information on the pattern of the density of the nuclear scattering amplitude around the equilibrium positions would require the study of other forbidden reflections of tin.

## V. INELASTIC SCATTERING EXPERIMENTS

A number of frequencies of normal modes of vibration has been measured at room temperature using the three-axis crystal spectrometer in the constant- $\vec{Q}$  way of operation.

Since the beginning of the measurements it appeared that some of the phonon peaks, especially the [001] L, were rather broad and weak, making difficult a precise determination of the dispersion curves.

Here we are presenting only results in the [001] direction, but measurements in other directions are pursued.

Figure 5 shows the experimental points in the [001] direction for the longitudinal optic and transverse acoustic branches. In Fig. 5 one can also see (a) a sketch of the reciprocal lattice plane (100, 001) and (b) the behaviour of the inelastic structure factor for the [001] L branches. The structure factor for these particular branches does not depend on the model, and it is represented by straight lines.

The measurements for the longitudinal branch have been done between the points (0, 0, 2) and (0, 0, 4). The measurements for the transverse acoustic branch have been done between the reciprocal lattice points (4,0,0) and (4,0,1). The transverse optical vibrations have not been found at the moment.

The wavelength of the neutrons used was 1.501 and 1.800 Å; also in these experiments two different crystal specimens were used as a sample. One was a sphere of 2-in diameter and the other was a cylinder of 1-in diameter and 4 in in length. The important features of the dispersion relations observed are the following.





Dispersion curves for the [001] direction in white tin

Experimental points

[001] LA
[001] LO
[001] LO
[001] TA

The solid lines are the dispersion curves calculated according to a simplified A-S model, as explained in the text. The reciprocal lattice plane (100, 001) and the behaviour of the inelastic structure factor for the [001]L branches are also shown.

The maximum frequency is about twice lower than the frequency calculated by WLD in the first A-S model. The modified A-S model [9] gives frequencies which are nearer, by an order of magnitude, to the frequencies we observed.

The shape of the dispersion curves we observed is rather different from the calculated one. For the [001] branches we notice that the shape is similar to that of an acoustic dispersion relation in a linear chain having an interatomic distance c. This seems to indicate that the most important unit in the tin structure is the chain of atoms in the c-direction. The hypothesis of a "chain-like structure" can be confirmed by the values of the force constants which are necessary to fit the experimental data.

The lines in Fig. 5 are calculated using the WLD model, considering only interactions up to second neighbours, and imposing the condition that the curves should pass through some special points. Elastic consistency and better agreement with the experimental points could very easily be obtained by introducing more constants; in particular the dip at  $q/q_{max} = 0.5$  could be explained introducing a force constant between second neighbours along the c-axis (these are not taken into account in the WLD model).

In Table II A-S force constants corresponding to the lines plotted in Fig.5 are given. One must notice that the largest value is that of  $K_1(2, 11)$ 





Frequency spectrum of white tin evaluated by the root sampling method The frequencies have been calculated in 2250 points equally spaced within the irreducible part of the Brillouin zone (see Fig. 1B) using the simplified A-S model.

## TABLE II

# A-S FORCE CONSTANTS\* $(10^4 \text{ dyn/cm})$

| $K_{1}(1, 12) = 0.543$ | $C_2(1, 12) = 0.125$ . |
|------------------------|------------------------|
| $K_1(2, 11) = 1.557$   | $C_{2}(2, 11) = 0.157$ |
| $K_{1}(3, 12) = 0_{1}$ | $C_{2}(3, 12) = 0$     |
| $K_{1}(4, 11) = 0$     | $C_{2}(4, 11) = 0$     |
|                        |                        |

\*  $K_1(s, ab) = C_1(s, ab) - C_2(s, ab)$ , where  $C_1(s, ab)$  and  $C_2(s, ab)$  are the "bond-stretching" force constant and "bond-bending" force constant, respectively, for the interaction of the b-th atom of the s-th shell with the a-th atom in the cell at the origin.

which corresponds to first neighbours along the c-axis. This confirms obviously the previous idea of the chain-like structure.

We did not try to obtain a better fit because it is not worth while until one has more precise data.

We want to point out that the difference between the acoustic and optic part of the [001]L branch is very small and almost negligible for  $q/q_{max} > 0.3$ .

This can probably result from the static disorder in the c-direction, which should be present in the crystal.

A sketch of the frequency distribution of the normal modes of vibration, calculated using the WLD model and the constants given in Table II, is shown in Fig.6. This frequency distribution is obtained by sampling the frequency values at 2250 points within the irreducible volume of the Brillouin zone.

#### VI. CONCLUSIONS

Measurements on this subject are still being carried out to get more details on the dispersion relations. At present the idea we have of the dynamical structure of white tin is that of a chain-like structure along the c-axis with a certain amount of static disorder along the same axis.

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## DISCUSSION

P.K.IYENGAR: Earlier this year we, too, made some measurements on white tin, particularly on the TA branch in the [001] direction. Our values are in agreement with the data provided by Dr.Caglioti. We also found the forbidden reflection due to disorder.

G. CAGLIOTI: I would merely reiterate the point made in the paper that particular care was paid to discrimination between the anomalous (002) intensity and the very significant influence of the multiple Bragg reflections (the Renninger effect). B. BURAS: It seems to me that if you have some imperfections in the c-direction you should also have them in other directions, e.g. in the a-direction. In the paper, however, you take into account only those in the c-direction.

G. CAGLIOTI: The shape of the elastic intensity pattern around the (002) forbidden reflection supports the suggestion of disorder along the c-axis. Nevertheless, we are going to measure the forbidden reflections in order to detect the amount of disorder in other crystal directions.

H. HAHN (Chairman): Could you indicate which atoms move where in the phase transition from white to grey tin?

G. CAGLIOTI: It can be said that the phase transformation consists in an enormous compression along the c-axis, by a factor of almost 2. As pointed out by PRASAD and WOOSTER[6], the transition from the  $\alpha$ -phase to the  $\beta$ -phase of tin should be accompanied by a noteworthy homogeneous contraction of the c-axis (from a = 6.42 A to c = 3.18Å).

# О СПЕКТРЕ КОЛЕБАНИЙ РЕШЕТКИ БЕЛОГО ОЛОВА

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## Доклад представлен М.Г. Земляновым

#### Abstract — Résumé — Аннотация — Resumen

THE VIBRATION SPECTRUM OF THE WHITE TIN LATTICE. The authors consider the dynamic problem of vibration in white tin, using the Born-von Kármán model.

They use all force constants entering into the full dynamic matrix for the first three co-ordination spheres and interaction with the fourth co-ordination sphere is assumed to be central. In determining the elements of the dynamic matrix, they use both modules of elasticity and experimental data for the isotropy of the Mössbauer effect.

The resulting dispersion curve displays marked anomalies.

The frequencies of one of the optical branches, at the terminal value, are very low, with the minimum lying on the [001] axis. This results in peculiar behaviour of the distribution function for  $g(\omega)$  frequencies at small values of  $\omega$ , of the heat capacity at low temperatures, and of other spectrum integral characteristics.

The results obtained explain the anisotropy sign of the Mössbauer effect observed in experiments at temperatures of 300 and  $77^{\circ}$ K and point to an inversed anisotropy sign at lower temperatures.

SPECTRE DES OSCILLATIONS DU RÉSEAU DE L'ÉTAIN. Le mémoire présente une étude approfondie du rôle dynamique des oscillations de l'étain dans le cadre du modèle de Born et von Kármán. On a utilisé toutes les constantes de force qui interviennent dans une matrice dynamique complète pour les trois premières sphères de coordination, tandis que l'interaction avec la quatrième sphère de coordination est supposée être centrale. Pour déterminer les éléments de la matrice dynamique, on a eu recours non seulement aux modules d'élasticité mais encore aux données expérimentales touchant l'anisotropie de l'effet de Mössbauer.

Les courbes de dispersion ainsi établies présentent une forte anomalie.

Les fréquences de l'une des branches optiques accusent une valeur terminale très peu élevée, le minimum se situant sur l'axe [001]. Il en résulte un comportement spécifique de la fonction de distribution des fréquences  $g(\omega)$ , lorsque  $\omega$  est petit, de la capacité thermique pour de basses températures et des autres caractéristiques intégrales révélées par le spectre.

Les résultats obtenus permettent d'expliquer le signe de l'anisotropie de l'effet de Mössbauer, qui a été observé expérimentalement aux températures de 300 et 77°K, et de prévoir une inversion du signe de l'anisotropie à des températures plus basses.

О СПЕКТРЕ КОЛЕБАНИЙ РЕШЕТКИ БЕЛОГО ОЛОВА. Последовательно рассматривается динамическая задача колебаний для белого олова в рамках Борн-Кармановской модели.

Используются все силовые постоянные, входящие в полную динамическую матрицу для первых трех координационных сфер, а взаимодействие с 4-й координационной сферой предполагается центральным. Для определения элементов динамической матрицы, помимо модулей упругости, привлечены экспериментальные данные по анизотропии Мессбауэра.

Найденные дисперсионные кривые обладают резкой аномалией.

Частоты одной из оптических ветвей при конечном значении имеют весьма малую величину, причем минимум лежит на оси [001]. Это приводит к своеобразному поведению функции распределения частот g(ω) при малых ω, теплоемкости при низких температурах и других интегральных по спектру характеристик. Полученные в работе результаты позволяют объяснить знак анизотропии эффекта Мессбауэра, наблюдавшийся экспериментально при температурах 300° и 77°К, и предсказывают инверсию знака анизотропии при более низких температурах.

ESPECTRO DE LAS OSCILACIONES DE LA RED DEL ESTAÑO BLANCO. En la memoria se estudia detenidamente la dinámica de las oscilaciones de la red cristalina del estaño blanco con arreglo al modelo de Bornvon Kármán.

Se han utilizado todas las constantes de fuerza que participan en una matriz dinámica completa para las tres primeras esferas de coordinación, en tanto que la interacción con la cuarta esfera de esa índole se considera de carácter central. Para determinar los elementos de la matriz dinámica, además del módulo de elasticidad, se han tenido en cuenta los datos experimentales relativos a la anisotropía del efecto Mössbauer.

Las curvas de dispersión obtenidas presentan fuertes anomalías.

Las frecuencias de una de las ramas ópticas acusan valores terminales muy reducidos; el mínimo se encuentra en el eje [001]. De ello resulta un comportamiento característico de la función de distribución de las frecuencias  $g(\omega)$ , cuando el valor  $\omega$  es pequeño, de la capacidad térmica a bajas temperaturas y de otras características integrales reveladas por el espectro.

Los resultados obtenidos permiten explicar el signo de la anisotropía del efecto Mössbauer, observado experimentalmente a temperaturas comprendidas entre 300 y 77°K, y predecir su inversión a temperaturas más bajas.

## 1. ВВЕДЕНИЕ

Исследование динамических свойств решетки олова представляет большой интерес. В первую очередь, это связано с тем обстоятельством, что наличие двух атомов в элементарной ячейке олова приводит к появлению оптических ветвей, которые сильно перекрываются с акустическими. Возникающая сложная картина колебаний заметно отличается от случая одноатомных решеток и традиционных двухатомных решеток типа NaC1. Как следствие, даже такая интегральная характеристика спектра, как зависимость теплоемкости от температуры, оказывается существенно отличающейся от той, которая получается на основе использования однопараметрической дебаевской модели [1].

С другой стороны, проводившиеся в последнее время исследования эффекта Мессбауэра на ядрах изотопа Sn<sup>119</sup> в решетке белого олова позволили определить другую интегральную по спектру характеристику, а именно, зависимость среднего квадрата смещения атомов от температуры [2-5].

Более того, тетрагональная симметрия решетки белого олова обусловливает появление анизотропии вероятности эффекта Мессбауэра [6]. И, действительно, такая анизотропия экспериментально обнаружена в работах [7-10]. Эти измерения позволяют определить изменения с температурой совершенно новых интегральных характеристик, которые зависят уже не только от частот фононного спектра, но и в существенной степени от векторов поляризации.

Как оказывается, и в случае олова это проявилось очень четко, эти величины весьма чувствительны к характеру колебаний решетки. Поэтому учет их дает возможность сразу резко продвинуться в решении общей динамической задачи.

Наконец, следует обратить внимание на проведенные в последнее время измерения туннельного эффекта для олова в сверхпроводящем состоянии, которые позволяют, по-видимому, получить положение особенностей функции распределения частот фононного спектра [11].
При теоретическом анализе динамических свойств кристаллической решетки олова мы можем воспользоваться обычной теорией Борна-Кармана. Эта возможность связана, главным образом, с превалирующей ролью ковалентных связей в решетке. Сильная асимметрия расположения атомов в элементарной ячейке, к сожалению, обусловливает необходимость знания большого числа силовых констант. Поэтому даже наличие экспериментальных значений для 6 модулей упругости не дает возможности выбрать сколько-нибудь однозначным образом совокупность силовых констант для ближайших координационных сфер. Оказывается, что в случае олова остающийся при этом произвол столь существенен, особенно в той части, которая касается оптических ветвей, что спектр колебаний может резко меняться, если произвольно распорядиться свободными силовыми константами.

Именно это обстоятельство нашло свое отражение в результатах недавно опубликованных теоретических работ, которые при расчете в качестве независимых параметров использовали только шесть модулей упругости [12,13].

Авторам не удалось получить результатов, хорошо согласующихся даже с температурным ходом экспериментально измеренной теплоемкости. Что же касается анизотропии эффекта Мессбауэра, то во всех трех работах [12] знак анизотропии оказывался противоположным наблюдаемому экспериментально [7-10]. Более того, авторы пришли к заключению, что совокупность экспериментальных значений модулей упругости находится в противоречии с результатами измерений по анизотропии эффекта Мессбауэра.

Следует сделать несколько замечаний и о моделях, использованных при расчетах в работах [12-13].

Как уже отмечалось самим автором, принятая в работе [13] весьма искусственная модель для силовых взаимодействий между атомами, оказалась внутренне противоречивой, поскольку она привела к появлению мнимых частот, т.е. к заведомо неустойчивой решетке. Поэтому автору пришлось чисто волевым образом взять один из модулей упругости отличным от наблюдаемого на эксперименте.

В работах [12] была использована т.н. аксиально-симметричная модель для парных взаимодействий между атомами. Нам представляется, что эта модель при сильно асимметричном расположении атомов в элементарной ячейке и ярко выраженной ковалентности взаимодействия не может дать полностью адекватного описания динамической задачи.

Следует также отметить, что в работах [12] были произвольно опущены квадратичные по силовым постоянным члены, входящие в уравнения, связывающие скорости звука с силовыми постоянными. Однако, как это видно, в частности, из результатов нашей работы, эти члены весьма существенны.

В настоящей работе приводятся результаты последовательного рассмотрения динамической задачи в рамках Борн-Кармановской схемы с использованием всех силовых постоянных, входящих в динамическую матрицу для первых трех координационных сфер и при предположении, что взаимодействие с 4-й координационной сферой может рассматриваться как центральное.

Для определения элементов динамической матрицы, помимо модулей упругости, были привлечены экспериментальные данные по анизотропии эффекта Мессбауэра.

#### 2. НЕКОТОРЫЕ ОБЩИЕ СООТНОШЕНИЯ

В принципе задача колебаний кристаллической решетки полностью описывается системой уравнений типа Борна-Кармана.

$$\omega^{2} \mathbf{e}_{\alpha}(\tilde{\mathbf{k}}) = \Sigma_{\mathbf{k}'} \mathbf{D}_{\alpha\beta}(\tilde{\mathbf{k}}') \mathbf{e}_{\beta}(\tilde{\mathbf{k}}'), \qquad (1)$$

$$D_{\alpha\beta}(\hat{k}'_{kk'}) = \frac{1}{\sqrt{m_k m_{k'}}} \Sigma_{\ell} \Phi_{\alpha\beta}(\ell_{kk'}) e^{-i\tilde{f}\ell(\ell)}$$
(2)

где приняты стандартные обозначения.

Для случая решетки Бравэ динамическая матрица всегда действительна, что объясняется наличием центра инверсии в такой решетке.

Для двухатомной решетки с двумя атомами в элементарной ячейке центр инверсии не совпадает ни с одним из узлов решетки. Поэтому динамическая матрица, а следовательно и вектора поляризации, комплексны. Однако наличие центра инверсии, хотя и не совпадающего с узлами, приводит к условию

$$D_{\alpha\beta}(\frac{\tilde{f}}{11}) = D_{\alpha\beta}^{*}(\frac{\tilde{f}}{22}),$$
$$D_{\alpha\beta}(\frac{\tilde{f}}{12}) = D_{\alpha\beta}^{*}(\frac{\tilde{f}}{21})$$



Рис.1. Кристаллическая структура белого олова.

по той же причине

$$|\mathbf{e}_{\alpha}(\bar{f}_{1})|^{2} = |\mathbf{e}_{\alpha}(\bar{f}_{2})|^{2}.$$
(3)

Легко видеть, что поэтому динамическая матрица без труда приводится к действительной с помощью унитарного преобразования (приложение II).

#### 3. ДИНАМИЧЕСКАЯ МАТРИЦА РЕШЕТКИ БЕЛОГО ОЛОВА

Белое олово ( $\beta$  — модификация олова) кристаллизуется в тетрагональную решетку с пространственной группой  $D_{4h}^{19}$ . Его кристаллическая структура может быть представлена как две объемноцентрированные тетрагональные решетки Бравэ, вложенные друг в друга с базисным вектором  $\vec{\rho}_{12} = (0, a/2 c/4)$  и ребрами а и с (рис.1).

В табл.1 даны координаты 18 атомов, являющихся соседями 0 атома и расположенных в 4 координационных сферах.

Построим силовые матрицы взаимодействия 0 атома со всеми остальными. Не будем предполагать специального вида этого взаимодействия, а учтем лишь требования симметрии. Используя элементы пространственной группы симметрии решетки, найдем вид всех 18 матриц, описывающих взаимодействия (прилож.1). Как оказывается, необходимо 4 + 2 + 4 + 6 = 16 силовых постоянных для описания колебаний. Не все силовые постоянные, однако, независимы. Мы должны учесть условия инвариантности энергии относительно вращения кристалла как целого и так называемые условия Борна-Хуана, соответствующие отсутствию анизотропных компонент напряжения в равновесном состоянии кристалла.

Математически эти условия выражаются в виде тождеств [14]

$$\sum_{\substack{k'\\k'}} \Phi_{\alpha\beta}(\ell_{kk'}) X_{\gamma}(\ell_{kk'}) = \sum_{\substack{\ell'\\k'}} \Phi_{\alpha\gamma}(\ell_{kk'}) X_{\beta}(\ell_{kk'}), \qquad (4)$$

$$X_{\alpha}(\ell_{kk}^{\ell}) = X_{\alpha}(\ell_{k}) - X_{\alpha}(\ell_{k}),$$

$$\sum_{\substack{\ell'\\k'}} \Phi_{\alpha\beta} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix} X_{\gamma} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix} X_{\delta} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix} = \sum_{\substack{\ell'\\k'}} \Phi_{\gamma\delta} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix} X_{\alpha} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix} X_{\beta} \begin{pmatrix} \ell\ell'\\kk' \end{pmatrix}$$
(5)

Используя табл.1 и прилож.1, получим для нашего случая соответственно

2a [
$$\delta_1 - \delta_3 + 2\delta_4 - 2\epsilon_4$$
] = c [ $\alpha_1 - \beta_1 - 3\alpha_3 + 3\beta_3$ ], (4 a)

$$c^{2}[9\alpha_{3}+9\beta_{3}+\alpha_{1}+\beta_{1}+16\beta_{2}+16\alpha_{2}] = 4a^{2}[\gamma_{1}+\gamma_{3}+4\beta_{4}].$$
 (5 a)

где

#### координаты атомов, расположенных в 4-х координационных сферах

|         |       | 1 сфера  | 1 сфера — З сфера — |  | 4 сфера   |  |  |  |  |
|---------|-------|--|---------------------|--|---|--|--|--|--|
|         |       | (12)<br>$\rho_1 = \frac{1}{4}\sqrt{4a^2 + c^2}$        | $(11)$ $\rho_2 = c$ | (12)<br>$\rho_3 = \frac{1}{4}\sqrt{4a^2 + 9c^2}$           | (11)<br>$\rho_4 \doteq \frac{1}{2}\sqrt{2a^2 + c^2}$  |  |  |  |  |
| Nº a1   | гомов | 1 2 3 4  | 56                  | 7 8 9 10   | 11 12 13 14 15 16 17 18   |  |  |  |  |
| PI      | x     | $0  0  \frac{a}{2}  -\frac{a}{2}$                      | 0 0                 | $0 \qquad 0 \qquad \frac{a}{2} \qquad -\frac{a}{2}$        | $-\frac{a}{2}$ $-\frac{a}{2}$ $\frac{a}{2}$ $\frac{a}{2}$ $\frac{a}{2}$ $\frac{a}{2}$ $-\frac{a}{2}$ $-\frac{a}{2}$       |  |  |  |  |
| ординас | у     | $\frac{a}{2} - \frac{a}{2} = 0 = 0$                    | 0 0                 | $-\frac{a}{2}$ $\frac{a}{2}$ 0 0                           | $-\frac{a}{2}$ $\frac{a}{2}$ $\frac{a}{2}$ $-\frac{a}{2}$ $-\frac{a}{2}$ $-\frac{a}{2}$ $-\frac{a}{2}$ $\frac{a}{2}$      |  |  |  |  |
| Koc     | z     | $\frac{c}{4}  \frac{c}{4}  -\frac{c}{4}  -\frac{c}{4}$ | c -c                | $-\frac{3c}{4}  -\frac{3c}{4}  \frac{3c}{4}  \frac{3c}{4}$ | $\frac{c}{2}  \frac{c}{2}  \frac{c}{2}  \frac{c}{2}  \frac{c}{2}  -\frac{c}{2}  -\frac{c}{2}  -\frac{c}{2}  -\frac{c}{2}$ |  |  |  |  |

Е.Г. БРОВМАН и

Ю.КАГАН

Далее, переходя к пределу длинных волн, т.е. f → 0, мы получим связь между модулями упругости и силовыми постоянными. Используя обычные методы [14], получаем:

$$cc_{11} = \alpha_{1} + \alpha_{3} + 4\alpha_{4} - \frac{1}{2(\gamma_{1} + \gamma_{3})} (\delta_{1} - \delta_{3} + 2\epsilon_{4} - 2\delta_{4})^{2},$$

$$cc_{13} = -(\gamma_{1} + \gamma_{3} + 4\beta_{4}) + 4\nu(\epsilon_{4} + \delta_{4}) + \nu(\delta_{1} + 3\delta_{3}),$$

$$cc_{66} = \beta_{1} + \beta_{3} + 4\alpha_{4},$$

$$\frac{2cc_{33}}{\nu^{2}} = \gamma_{1} + 9\gamma_{3} + 8\beta_{4} + 8\alpha_{2},$$

$$cc_{44} = \gamma_{1} + \gamma_{3} + 4\beta_{4} - \frac{1}{\alpha_{1} + \alpha_{3} + \beta_{1} + \beta_{3}} (\delta_{1} - \delta_{3} + 2\delta_{4} - 2\epsilon_{4})^{2},$$
(6)

$$cc_{12} = \frac{1}{2(\gamma_1 + \gamma_3)} \left( \delta_1 - \delta_3 + 2\epsilon_4 - 2\delta_4 \right)^2 + 4(\gamma_4 + \sigma_4) - (\beta_1 + \beta_3 + 4\alpha_4) ,$$

где  $\nu = \frac{c}{a}$  ·

Отметим сразу же, что в выражения для упругих постоянных входят квадратичные члены, вызванные одновременным отсутствием центра инверсии, совпадающего с одним из узлов и некубичностью кристалла. Квадратичные члены сильно усложняют расчет. В следующих разделах будет показано, каким образом можно регулярным способом учесть их. Наконец, используя определение динамической матрицы (2) и приведенные в прилож.1 матрицы силового взаимодействия, можно построить динамическую матрицу колебаний (прилож.II).

Диагонализация полученной матрицы не может быть произведена в общем виде для произвольного волнового вектора  $\overline{f}$ , и поэтому решение этой задачи осуществляется с помощью численных методов на вычислительной машине. Однако для трех симметричных направлений в кристалле матрица несколько упрощается. Оказывается, что, используя методы теории групп, можно не только найти характер вырождения ветвей по этим направлениям, но и определить соответствующие частоты. Результаты такого исследования приведены в прилож.III.

### 4. ВЫБОР МОДЕЛИ КОЛЕБАНИЙ

В предыдущем параграфе были получены выражения для динамической матрицы при весьма общих предположениях. Само по себе ограничение взаимодействия четырьмя координационными сферами в ковалентных кристаллах типа олова весьма разумно, и такая модель должна довольно хорошо схватывать все особенности динамической задачи. Однако полное использование этой модели требует знания 16 независимых элементов динамической матрицы, тогда как без привлечения дополнительных экспериментальных данных мы имеем лишь восемь независимых условий для их определения (см. (6) и (4a, 5a)). Обычно, когда хотят уменьшить число независимых постоянных, идут на сокращение числа учитываемых координационных сфер и на уменьшение числа независимых констант, характеризующих взаимодействие с данной координационной сферой.

В последнем случае, как правило, вводятся специальные предположения о характере нецентрального взаимодействия.

К сожалению, мы не можем отказаться от учета четвертой координационной сферы (8 соседей), ибо в противном случае связь внутри одной и той же подрешетки осуществлялась бы только за счет двух соседей во второй координационной сфере. Как следствие, неправомерно завышались бы взаимодействия между обеими подрешетками и тем самым частоты оптических ветвей.

С другой стороны, в силу ярко выраженной ковалентности, мы не можем изменить число независимых констант в первых трех координационных сферах, используя различные физические объяснения.

Приведенные соображения заставили нас выбрать модель, в рамках которой сохраняются все силовые константы, относящиеся к первым трем координационным сферам, а взаимодействие с четвертой координационной сферой предполагается центральным. Поэтому взаимодействие с четвертой координационной сферой описывается одной постоянной, через которую прежние константы выражаются следующим образом

$$\alpha_4 = \gamma_4 = \sigma_4 = \lambda ,$$
  
$$\beta_4 = \nu^2 \lambda ,$$
  
$$\delta_4 = \epsilon_4 = \nu \lambda .$$

В этой модели число независимых констант сокращается до 11. Для нахождения недостающих трех независимых условий можно воспользоваться результатами измерений анизотропии вероятности эффекта Мессбауэра [7-10].

Вернемся к соотношению (6). Если зафиксировать константы взаимодействия с 4-й координационной сферой, то легко непосредственно показать, что при этом оказываются однозначно определенными некоторые комбинации констант, относящиеся к 1-й и 3-й координационным сферам.

Так, в частности, в нашей модели:

$$\beta_1 + \beta_3 = \operatorname{cc}_{66} - 4\lambda , \qquad (7 a)$$

$$\alpha_1 + \alpha_3 = c(c_{66} + c_{12} + c_{11}) - 12\lambda, \qquad (7 6)$$

$$\gamma_1 + \gamma_3 = \frac{1}{c(c_{11} - c_{12})} (cc_{44} - 4\nu^2 \lambda) [c(2c_{66} + c_{12} + c_{11}) - 16\lambda], \qquad (7 \text{ B})$$

$$(\delta_1 - \delta_3)^2 = 2(\gamma_1 + \gamma_3)[c(c_{66} + c_{12}) - 8\lambda],$$
 (7 r)

$$\delta_1 + 3\,\delta_3 = \frac{1}{\nu} \left[ c c_{13} + (\gamma_1 + \gamma_3) - 4\,\nu^2 \lambda \right] \,. \tag{7 a}$$

Существенно, что именно комбинации 7а — 7г вместе с  $\lambda$  однозначно определяют дисперсионные кривые по направлениям (100) и (110) и фиксируют частоты на границах зоны Бриллюэна по направлению (001) (прилож.III). Заметим, что тем самым фиксируются и величины частот точек Ван-Хова, которые лежат на пересечении этих трех направлений с гранями зоны Бриллюэна и при  $\overline{f} = 0$ . Интересно, что одна из этих частот – оптическая частота для волнового вектора вдоль оси (100) на границе зоны Бриллюэна, в рамках приближения с 4-мя координационными сферами определяется однозначно вне зависимости от модели (IIIа).

$$\omega_3^2 = \omega_5^2 = \frac{4cc_{66}}{m}$$

Если обратиться к выражениям (IIIв), определяющим закон дисперсии для фононов с волновым вектором вдоль оси (001), то легко убедиться, используя (7а-7д), что для определения четырех ветвей, вектора поляризации которых лежат в плоскости ху, достаточно знать два параметра  $\lambda$  и  $\beta_2$ .

Таким образом, все ветви колебаний по симметричным направлениям, дающие вклад в смещения атомов в плоскости ху, зависят только от двух параметров λ и β<sub>2</sub>.

Аналогичный анализ показывает, что вклад ветвей по симметричным направлениям в смещения атомов вдоль оси z снова определяется только двумя параметрами, а именно λ и β<sub>2</sub>.

Хотя эти результаты и не будут строго справедливы при произвольном значении волнового вектора, однако непосредственные расчеты четко показывают, что смещения атомов в плоскости ху остаются слабо чувствительными к значению параметра  $\alpha_2$ , а смещения вдоль оси z к параметру  $\beta_2$  во всем фазовом объеме.

Это обстоятельство делает крайне заманчивым использование анизотропии эффекта Мессбауэра для раздельного определения этих групп параметров. Действительно, вероятность эффекта Мессбауэра при вылете  $\gamma$ -кванта в направлении оси с (f<sub>c</sub>) зависит только от смещения атомов вдоль оси z, а при направлении вдоль оси a (f<sub>a</sub>) только от смещения атомов в плоскости xy.

Подробные численные расчеты (см. следующий раздел) показали, что постоянная  $\beta_2$  имеет весьма малую величину и очень слабо влияет (по сравнению с  $\lambda$ ) на величину  $f_a$  (напомним, что  $\beta_2$  является константой нецентрального взаимодействия для 2 атомов, расположенных вдоль оси с, в силу чего малость ее величины кажется физически вполне разумной).

Поэтому в окончательных вариантах расчетов мы положили  $\beta_2 = 0$  и из сравнения вычисленных и измеренных значений для  $f_a$  и  $f_c$  получили возможность определить значения соответственно  $\lambda$  и  $\alpha_2$  и, как следствие, всю совокупность силовых констант, фигурирующих в нашей модели.

#### 5. ЧИСЛЕННЫЕ РАСЧЕТЫ

Диагонализация динамической матрицы при произвольном значении волнового вектора производилась с помощью численных методов на быстродействующей счетной машине. При этом находились как собственные значения, так и собственные вектора задачи.

Если воспользоваться соображениями симметрии, то легко показать, что неприводимой является 1/16 часть полной зоны Бриллюэна (1-я зона Бриллюэна изображена на рис.2). При проведении численных расчетов использовались пробные точки, равномерно расставленные в этой области. Расстояния до ближайших узлов по трем ребрам параллелепипеда в обратной решетке делились на одно и то же число, равное 20. В результате в 1/16 части зоны Брюллиэна было размещено 198 точек, что в полной зоне оказывается эквивалентным 2000 точек.

В целях более тщательного определения низкотемпературной части теплоемкости и вероятности эффекта Мессбауэра, область фазового пространства вблизи f = 0, соответствующая 1/125 от объема 1-й зоны Бриллюэна и подобная ей, в свою очередь бала разбита на 2000 частей.

Найденные значения частот и векторов поляризации для всего фазового объема могли быть использованы для получения таких интегральных характеристик, как функция распределения частот фононного спектра  $g(\omega)$ , зависимость теплоемкости от температуры, вероятности эффекта Мессбауэра для неэквивалентных направлений. При этом знание векторов поляризации необходимо только для определения последних величин. Действительно, для одноосных кристаллов типа олова имеем  $f_{a,c} = \exp(-z_{a,c})$ 

$$z_{c} = \frac{R}{N} \sum_{\hat{f}, \alpha} \frac{\left| e_{z} \left( \bar{f}_{1} \alpha \right) \right|^{2}}{\hbar \omega (\bar{f}, \alpha)} [2\bar{n}(\omega) + 1],$$

$$z_{a} = \frac{R}{N} \sum_{\bar{f}, \alpha} \frac{\left| e_{x} \left( \bar{f}, \alpha \right) \right|^{2}}{\hbar \omega (\bar{f}, \alpha)} [2\bar{n}(\omega) + 1], \qquad (8)$$

где R - энергия отдачи для свободного ядра,

**n** - бозевское распределение для фононов,

N - число элементарных ячеек в кристалле.

Подчеркнем, что в силу свойств (3) вероятности эффекта для обоих атомов в элементарной ячейке имеют одно и то же значение.

Необходимо отметить, что хотя 1/16 часть 1-й зоны Бриллюэна является достаточной для определения всего спектра частот, при учете векторов поляризации следует принимать во внимание их поворот, возникающий при преобразовании одной неприводимой части зоны в другую. В нашем случае, если воспользоваться соображениями симметрии, это обстоятельство может быть учтено при расчетах с 1/16 частью зоны Бриллюэна путем замены в выражении (8)

 $|\mathbf{e}_{\mathbf{x}}\left(\overline{f}_{1}^{}\alpha\right)|^{2} \quad \mathbf{ha} \quad \frac{1}{2}\left\{\left|\mathbf{e}_{\mathbf{x}}\left(\overline{f}_{1}^{}\alpha\right)\right|^{2}+\left|\mathbf{e}_{y}\left(\overline{f}_{1}^{}\alpha\right)\right|^{2}\right\}$ 



Рис.2

Первая зона Бриллюэна решетки белого олова.

Таблица 2

# ЗНАЧЕНИЯ УПРУГИХ ПОСТОЯННЫХ И ПАРАМЕТРОВ БЕЛОГО ОЛОВА

| C <sub>11</sub> | C 33 | C <sub>12</sub> | C <sub>13</sub> | C 44  | C <sub>66</sub> | С·10 <sup>8</sup> см | а·10 <sup>8</sup> см |
|-----------------|------|-----------------|-----------------|-------|-----------------|----------------------|----------------------|
| 7,23            | 8,84 | 5,94            | 3,578           | 2,208 | 2,400           | 3,183                | 5,832                |

С<sub>ік</sub> — даны в единицах 10<sup>11</sup> дин/см<sup>2</sup>

При проведении конкретных расчетов использовались данные для упругих постоянных при T = 300°K, полученные в работе [15]. Значения этих постоянных, а также параметры решетки приведены в табл.2.

Далее, мы воспользовались результатами измерения вероятности эффекта Мессбауера  $f_c$  и  $f_a$  также при комнатной температуре, найденными в работе [10]. При этом в качестве независимых величин брались данные по  $f_a$  и  $f_c/f_a$ .

Следует отметить, что эти два параметра на опыте определяются с существенно различной точностью: отношение  $f_c/f_a$  с весьма большой точностью, а абсолютные величины с существенно меньшей. Именно поэтому отношение  $f_c/f_a$ , фигурирующее в работах [9,10], имеет практически одно и то же значение:  $f_c/f_a \approx 0,67$ . Это значение и было принято в наших расчетах. Что же касается абсолютного значения эффекта Мессбауэра, то оно существенно различается у разных авторов (см., например, помимо цитированных, также работы [2-5]). В настоящей работе мы использовали значение  $f_a = 0,085$ , полученное в наиболее поздней из них [10].

Таблица З

## значения силовых постоянных

| α <sub>1</sub> | β1     | $\gamma_1$ | δ1    | α2   | α3     | β <sub>3</sub> | γ <sub>3</sub> | δ3    | λ   |
|----------------|--------|------------|-------|------|--------|----------------|----------------|-------|-----|
| 2562           | -5,140 | -5,777     | 2,410 | 8,28 | 10,990 | 0,78           | 13,478         | 8,672 | 3,0 |

Все константы даны в единицах 10<sup>3</sup> дин/см.

#### 6. ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ

1. В табл.3 приведены полученные в результате численных расчетов значения 10 независимых силовых постоянных, входящих в матрицы взаимодействия (прилож.1).

В связи с ограниченной точностью экспериментального определения использованных в расчетах параметров фигурирующие в табл.З значения их не могут рассматриваться как абсолютно точные. Действительно, если менять в рамках нашей модели параметры в пределах экспериментальной точности, то приближенно можно установить границы колебаний силовых констант.

Непосредственные расчеты показывают, что хотя количественно спектр колебаний и интегральные по спектру величины при этом несколько меняются, все качественные особенности этих величин остаются весьма устойчивыми.

В этом смысле следует относиться и к приводимым ниже результатам, полученным на основе силовых параметров табл.3. Сделаем еще одно замечание. Как видно из полученных результатов, роль квадратичных по силовым постоянным членов в уравнениях (6) весьма существенна. В силу этого, в нашей модели возникает вопрос о двузначности решения. Однако, как показали непосредственные расчеты, одно из решений приводит к мнимым частотам, т.е. к неустойчивости решетки. Таким образом, это решение автоматически исключается.

2. На рис.3 приведены дисперсионные кривые для трех симметричных направлений, соответствующие шести ветвям колебаний\*. Как видно, спектр частот в олове имеет весьма своеобразный характер.

Так максимальной частотой для симметричных направлений оказывается максимум одной из акустических ветвей. (Более того, эта частота совпадает и с абсолютным максимумом спектра).

В силу этого обстоятельства, оптическая полоса находится внутри акустической. Частным следствием этого является наличие большого числа точек случайного вырождения.

Акустические ветви демонстрируют чрезвычайно резкую анизотропию. Обращает на себя внимание также низкое положение двух акустических ветвей по направлению (110).

<sup>\*</sup> При стандартном характере выбора зоны Бриллюэна (рис.2) для построения закона дисперсии фононов с волновыми векторами вдоль (001) мы вынуждены выйти за пределы 1-й зоны. Это связано с тем, что расстояние до границы зоны в этом направлении меньше чем половина расстояния до ближайшего в этом направлении узла обратной решетки.



Кривые дисперсии для направлений - [001], [100] и [110].

Что касается оптических ветвей, то они не имеют каких-либо качественных особенностей, за исключением совершенно неожиданного поведения продольной оптической ветви при направлении волнового вектора вдоль (001). Как видно из рис.4, продольная оптическая ветвь имеет глубокий минимум при  $f \sim 0,7 \ 2\pi/c$ . Хотя значение частоты в минимуме может меняться при изменении исходных параметров в пределах ошибок измерения, однако резко выраженный минимум остается всегда.

Благодаря тому, что эта точка лежит по симметричному направлению, она является точкой Ван-Х ововского типа и, таким образом, приводит к появлению особой точки у функции распределения частот фононного спектра  $g(\omega)$ , лежащей в аномально низкой области частот. По всей видимости, именно эта точка была обнаружена в работе Роуэлла и др. [11], исследовавших туннельный эффект для сверхпроводящего олова. Как известно, авторы нашли особенность функции  $g(\omega)$ , лежащую при частотах  $2-2,5\cdot10^{12}$ рад/сек, аномально низких по сравнению с границей фононного спектра. Заметим, что найденная в этой работе граница фононного спектра весьма близка к значению  $26\cdot10^{12}$  рад/сек., полученному в наших расчетах (абсолютное сравнение экспериментального и теоретического значений частоты в минимуме затруднено также и тем, что приведенные кривые вычислены на основе упругих постоянных, соответствующих  $300^{\circ}$ K).

Следует отметить, что наличие в системе низких частот фононов при больших значениях волнового вектора должно привести к целому ряду аномалий в термодинамических и кинетических величинах. Кроме того, наличие таких частот может привести к тому, что уже при относительно слабом



Спектр фононов для белого олова.

изменении параметров появляется неустойчивость и, как следствие, фазовый переход.

3. На рис.4 приведена функция распределения частот фононного спектра. На оси абсцисс стрелками указаны те положения точек Ван-Хововского типа, которые следуют из кривых закона дисперсии по трем главным направлениям (рис.3).

4. На рис.5 приведена теоретическая кривая зависимости теплоемкости от температуры и одновременно нанесены экспериментальные точки [1]. Видно, что имеет место хорошее согласие между вычисленными и экспериментальными результатами. Очень интересно, что наблюдается хорошее согласие в области низких температур, для которой существенно поведение  $g(\omega)$  в малом по сравнению с  $\omega_{max}$  интервале частот. Но именно в этом интервале частот, функция  $g(\omega)$ , как это непосредственно видно из рис.4, имеет весьма своеобразный характер.

5. На рис.6 приведена кривая зависимости f<sub>c</sub>/f<sub>a</sub> от T, то есть температурная зависимость анизотропии эффекта Мессбауэра в монокристалле олова. В широком интервале температур ниже комнатной анизотропия эффекта Мессбауера имеет энак, совпадающий с наблюденным экспериментально. Однако при достаточно низких температурах возникает интересный эффект инверсии анизотропии. Сам факт инверсии устойчив к точности используемых экспериментально параметров, но температура инверсии может в некоторой степени "плавать".

При T = 0 знак анизотропии совпадает с предсказанным ранее в работе одного из авторов на основе весьма упрощенной модели [6].



Температурная зависимость теплоемкости.



Рис.6

Температурная зависимость коэффициента анизотропии.

Надо сказать, что этот же знак сохранился бы и во всей области температур, если вклад в анизотропию был бы связан, главным образом, с акустическими ветвями, поведение которых в значительной степени схватывается уже модулями упругости. Это нашло свое отражение в работах [12], где анизотропия устойчиво получалась одного знака  $f_c/f_a > 1$  во всем интервале температур в противоречии с экспериментальными результатами [7-10]. Как показывают наши расчеты, истинный знак анизотропии в существенной степени связан с наличием области фазового пространства, где оптические частоты, принадлежащие одной из ветвей, имеют весьма низкие значения.

Таким образом, характер анизотропии эффекта Мессбауэра в олове в значительной степени связан с оптическими ветвями, для последовательного описания которых значения только модулей упрутости оказываются недостаточными.

## Приложение I

При нахождении силовых матриц решетки белого олова могут быть использованы следующие четыре элемента симметрии:

| $\sigma_{\mathbf{x}} = \left( \begin{array}{ccc} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right)$ | - отражение в плоскости x = 0,  |
|--|---|
| $\sigma_{y} = \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array} \right)$          | - отражение в плоскости у = 0,  |
| $\bar{\sigma}_{g} = \left( \begin{array}{ccc} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{array} \right)$    | - отражение в плоскости x = y<br>+ инверсия,  |
| $\tilde{\mathbf{I}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$                | <ul> <li>инверсия в одном из углов</li> <li>+ трансляция на базисный вектор.</li> </ul> |

Первые три преобразования совмещают каждую из подрешеток саму с собой последнее меняет подрешетки местами.

Приведем сами силовые матрицы (везде  $\Phi(01) = \Phi(1)$  и т.д.). Нумерация атомов дана в табл.1 и на рис.1.

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1-я координационная сфера

$$\Phi(1) = -\begin{pmatrix} \beta_1 & 0 & 0 \\ 0 & \alpha_1 & \delta_1 \\ 0 & \delta_1 & \gamma_1 \end{pmatrix} \qquad \Phi(2) = -\begin{pmatrix} \beta_1 & 0 & 0 \\ 0 & \alpha_1 - \delta_1 \\ 0 & -\delta_1 & \gamma_1 \end{pmatrix}$$
$$\Phi(3) = -\begin{pmatrix} \alpha_1 & 0 & -\delta_1 \\ 0 & \beta_1 & 0 \\ -\delta_1 & 0 & \gamma_1 \end{pmatrix} \qquad \Phi(4) = -\begin{pmatrix} \alpha_1 & 0 & \delta_1 \\ 0 & \beta_1 & 0 \\ \delta_1 & 0 & \gamma_1 \end{pmatrix}$$

2-я координационная сфера

 $\Phi(5) = \Phi(6) = -\begin{pmatrix} \beta_2 & 0 & 0\\ 0 & \beta_2 & 0\\ 0 & 0 & \alpha_2 \end{pmatrix}$ 

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## 3-я координационная сфера

$$\Phi(7) = -\begin{pmatrix} \beta_3 & 0 & 0 \\ 0 & \alpha_3 & \delta_3 \\ 0 & \delta_3 & \gamma_3 \end{pmatrix} \qquad \Phi(8) = -\begin{pmatrix} \beta_3 & 0 & 0 \\ 0 & \alpha_3 & -\delta_3 \\ 0 & -\delta_3 & \gamma_3 \end{pmatrix}$$
$$\Phi(9) = -\begin{pmatrix} \alpha_3 & 0 & \delta_3 \\ 0 & \beta_3 & 0 \\ \delta_3 & 0 & \gamma_3 \end{pmatrix} \qquad \Phi(10) = -\begin{pmatrix} \alpha_3 & 0 & -\delta_3 \\ 0 & \beta_3 & 0 \\ -\delta_3 & 0 & \gamma_3 \end{pmatrix}$$

4-я координационная сфера

 $\Phi(11) = -\begin{pmatrix} \alpha_4 & \gamma_4 & -\epsilon_4 \\ \sigma_4 & \alpha_4 & -\delta_4 \\ -\delta_4 & -\epsilon_4 & \beta_4 \end{pmatrix} \qquad \Phi(12) = -\begin{pmatrix} \alpha_4 & -\gamma_4 & -\epsilon_4 \\ -\sigma_4 & \alpha_4 & \delta_4 \\ -\delta_4 & \epsilon_4 & \beta_4 \end{pmatrix}$  $\Phi(13) = -\begin{pmatrix} \alpha_4 & \gamma_4 & \epsilon_4 \\ \sigma_4 & \alpha_4 & \delta_4 \\ \delta_4 & \epsilon_4 & \beta_4 \end{pmatrix} \qquad \Phi(14) = -\begin{pmatrix} \alpha_4 & -\gamma_4 & \epsilon_4 \\ -\sigma_4 & \alpha_4 & -\delta_4 \\ \delta_4 & -\epsilon_4 & \beta_4 \end{pmatrix}$ 

$$\Phi(15) = -\begin{pmatrix} \alpha_4 & \sigma_4 & -\delta_4 \\ \gamma_4 & \alpha_4 & -\epsilon_4 \\ -\epsilon_4 & -\delta_4 & \beta_4 \end{pmatrix} \qquad \Phi(16) = -\begin{pmatrix} \alpha_4 & -\sigma_4 & -\delta_4 \\ -\gamma_4 & \alpha_4 & \epsilon_4 \\ -\epsilon_4 & \delta_4 & \beta_4 \end{pmatrix}$$
$$\Phi(17) = -\begin{pmatrix} \alpha_4 & \sigma_4 & \delta_4 \\ \gamma_4 & \alpha_4 & \epsilon_4 \\ \epsilon_4 & \delta_4 & \beta_4 \end{pmatrix} \qquad \Phi(18) = -\begin{pmatrix} \alpha_4 & -\sigma_4 & \delta_4 \\ -\gamma_4 & \alpha_4 & -\epsilon_4 \\ \epsilon_4 & -\delta_4 & \beta_4 \end{pmatrix}$$

$$\Phi(0) = -\sum_{n} \Phi(n) = \begin{pmatrix} 8\alpha_4 + 2\beta_2 + & 0 & 0 \\ + 2(\alpha_1 + \alpha_3 + \beta_1 + \beta_3) & 0 & 0 \\ 0 & 8\alpha_4 + 2\beta_2 + & 0 \\ + 2(\alpha_1 + \alpha_3 + \beta_1 + \beta_3) & 0 \\ 0 & 0 & 8\beta_4 + 2\alpha_2 + \\ + 4(\gamma_1 + \gamma_3) \end{pmatrix}$$

#### Приложение II

Элементы динамической матрицы D<sub>αβ</sub>( $\frac{1}{2k}$ ) можно получить, используя выражения (2) и (3), а также табл.1 и прилож. I.

$$\mathbf{D}_{\alpha\beta}\begin{pmatrix}\mathbf{f}\\\mathbf{ik}\end{pmatrix} = \begin{pmatrix} \mathbf{D}_{\alpha\beta}\begin{pmatrix}\mathbf{f}\\\mathbf{11}\end{pmatrix} & \mathbf{D}_{\alpha\beta}\begin{pmatrix}\mathbf{f}\\\mathbf{12}\end{pmatrix} \\ \mathbf{D}_{\alpha\beta}^{*}\begin{pmatrix}\mathbf{f}\\\mathbf{12}\end{pmatrix} & \mathbf{D}_{\alpha\beta}^{*}\begin{pmatrix}\mathbf{f}\\\mathbf{11}\end{pmatrix} \end{pmatrix}$$

$$\begin{split} m \ D_{xx} \ (11) &= 2(\alpha_1 + \alpha_3 + \beta_1 + \beta_3) + 2\beta(1 - C_{2z}) + 8\alpha_4 \left(1 - C_x C_y C_z\right), \\ m \ D_{yy} \ (11) &= m \ D_{xx} \ (11) \ , \\ m \ D_{zz} \ (11) &= 4(\gamma_1 + \gamma_3) + 2\alpha_2 \left(1 - C_{2z}\right) + 8\beta_4 \left(1 - C_x C_y C_z\right), \\ m \ D_{xy} \ (11) &= 4S_x S_y \left[\gamma_4 g_z + \sigma_4 g_z^*\right], \\ m \ D_{xz} \ (11) &= -4iS_x C_y \left[\epsilon_4 g_z - \delta_4 g_z^*\right], \\ m \ D_{yz} \ (11) &= -4iS_y C_x \left[\delta_4 g_z - \epsilon_4 g_z^*\right], \\ m \ D_{xx} \ (12) &= -2C_y g_y^* g_z^* \left[\beta_1 g_z + \beta_3 g_z^*\right] - 2C_x g_y^* \left[\alpha_1 g_z^* + \alpha_3 g_z\right], \end{split}$$

$$m D_{yy} (12) = -2C_{y}g_{y}^{*}g_{z}^{*}[\alpha_{1}g_{z} + \alpha_{3}g_{z}^{*}] - 2C_{x}g_{y}^{*}[\beta_{1}g_{z}^{*} + \beta_{3}g_{z}],$$
  

$$m D_{zz} (12) = -2C_{y}g_{y}^{*}g_{z}^{*}[\gamma_{1}g_{z} + \gamma_{3}g_{z}^{*}] - 2C_{x}g_{y}^{*}[\gamma_{1}g_{z}^{*} + \gamma_{3}g_{z}],$$
  

$$m D_{xy} (12) = 0$$
  

$$m D_{xz} (12) = 2iS_{x}g_{y}^{*}[\delta_{1}g_{z}^{*} - \delta_{3}g_{z}],$$
  

$$m D_{yz} (12) = -2ig_{y}^{*}g_{z}^{*}S_{y}[\delta_{1}g_{z} - \delta_{3}g_{z}^{*}].$$

Везде приняты обозначения

 $C_{k} = \cos f_{k} a_{k}/2,$   $S_{k} = \sin f_{k} a_{k}/2,$  $g_{k} = \exp (i f_{k} a_{k}/2).$ 

Что касается действительной матрицы, то она может быть получена из матрицы  $D_{\alpha\beta}({f \atop ik})$  путем унитарного преобразования  $T = {1 \over \sqrt{2}} \begin{vmatrix} 1 & i \\ i & 1 \end{vmatrix}$ , где под элементами понимаются трехрядные подматрицы.

Отметим, что в силу общего характера соотношений (3), это унитарное преобразование будет приводить к действительному виду динамическую матрицу любой двухатомной решетки с одинаковыми атомами.

#### Приложение III

Для волновых векторов, лежащих в симметричных направлениях, динамическая матрица (2) может быть диагонализована в общем виде. Используя "малую группу симметрии" каждого из таких векторов, получим, применяя методы теории групп (см. например [16]), следующие результаты.

а) Направление (100)  $f_y = f_z = 0$  ( $f_x = f_z = 0$ )

Малая группа симметрии 2 mm, частоты ветвей:

$$\begin{split} &m\omega_{1,2}^{2} = \frac{1}{2}(A_{1} + B_{1}) \pm \frac{1}{2} \left\{ (A_{1} - B_{1})^{2} + 4 \left| C_{1} \right|^{2} \right\}^{\frac{1}{2}}, \\ &m\omega_{3,4}^{2} = \frac{1}{2}(A_{2} + B_{2}) \pm \frac{1}{2} \left\{ (A_{2} - B_{2})^{2} + 4 \left| C_{2} \right|^{2} \right\}^{\frac{1}{2}}, \\ &m\omega_{5}^{2} = (1 - C_{x}) \left[ 8\alpha_{4} + 2(\beta_{1} + \beta_{3}) \right], \\ &m\omega_{6}^{2} = 4(\alpha_{1} + \alpha_{3}) + 2(\beta_{1} + \beta_{3})(1 + C_{x}) + 8\alpha_{4}(1 - C_{x}) \right], \end{split}$$

$$\begin{aligned} \mathbf{r}_{\text{A}e} & A_1 = 2(\alpha_1 + \alpha_3)(1 - C_x), \\ B_1 &= 8\beta_4 (1 - C_x) + 2(\gamma_1 + \gamma_3)(3 + C_x), \\ C_1 &= -2i(\delta_1 - \delta_3)S_x, \\ A_2 &= 4(\beta_1 + \beta_3) + 2(\alpha_1 + \alpha_3)(1 + C_x) + 8\alpha_4 (1 - C_x), \\ B_2 &= 2(\gamma_1 + \gamma_3)(1 - C_x), \\ C_2 &= 2i(\delta_1 - \delta_3)S_x. \end{aligned}$$

б) Направление (110)  $f_x = f_y; f_z = 0$ 

Малая группа симметрии 2 mm, частоты ветвей:

$$\begin{split} \mathbf{m}\omega_{1,2}^{2} &= \frac{1}{2}(\mathbf{A}_{1} + \mathbf{B}_{1}) \pm \frac{1}{2}\left[(\mathbf{A}_{1} - \mathbf{B}_{1})^{2} + 4\left|\mathbf{C}_{1}\right|^{2}\right]^{\frac{1}{2}},\\ \mathbf{m}\omega_{3,4}^{2} &= \frac{1}{2}(\mathbf{A}_{2} + \mathbf{B}_{2}) \pm \frac{1}{2}\left[(\mathbf{A}_{2} - \mathbf{B}_{2})^{2} + 4\left|\mathbf{C}_{2}\right|^{2}\right]^{\frac{1}{2}},\\ \mathbf{m}\omega_{5,6}^{2} &= 2(\alpha_{1} + \alpha_{3} + \beta_{1} + \beta_{3})(1 \pm \mathbf{C}_{x}) + 8(\alpha_{4} + \gamma_{4})\mathbf{S}_{x}^{2}, \end{split}$$

где 
$$\begin{aligned} A_1 &= 4(\gamma_1 + \gamma_3)(1 + C_x) + 8\beta_4 S_x^2, \\ B_1 &= 2(\alpha_1 + \alpha_3 + \beta_1 + \beta_3)(1 - C_x) + 8S_x^2(\alpha_4 - \gamma_4), \\ C_1 &= 2\sqrt{2}i(\delta_1 - \delta_3)S_x^*, \\ A_2 &= 4(\gamma_1 + \gamma_3)(1 + C_x) + 8\beta_4 S_x^2, \\ B_2 &= 2(\alpha_1 + \alpha_3 + \beta_1 + \beta_3)(1 + C_x) + 8S_x^2(\alpha_4 - \beta_4), \\ C_2 &= -2\sqrt{2}i(\delta_1 - \delta_3)S_x. \end{aligned}$$

в) Направление (001) 
$$f_x = f_y = 0$$

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Малая группа симметрии 4 mm, частоты ветвей:

$$\begin{split} \mathbf{m}\omega_{1,2}^{2} &= \mathbf{m}\omega_{3,4}^{2} = 8\alpha_{4}(1-\mathbf{C}_{z}) + 2(\alpha_{1}+\alpha_{3}+\beta_{1}+\beta_{3}) + 2\beta_{2}(1-\mathbf{C}_{2z}) \pm \\ \pm 2\left\{ \left[ (\alpha_{1}+\beta_{1})\mathbf{C}_{z/2} + (\alpha_{3}+\beta_{3})\mathbf{C}_{3z/2} \right]^{2} + \left[ (\alpha_{1}-\beta_{1})\mathbf{S}_{z/2} - (\alpha_{3}-\beta_{3})\mathbf{S}_{3z/2} \right]^{2} \right\}^{\frac{1}{2}}, \\ \mathbf{m}\omega_{5,6}^{2} &= 8\beta_{4}(1-\mathbf{C}_{z}) + 4(\gamma_{1}+\gamma_{3}) + 2\alpha_{2}(1-\mathbf{C}_{2z}) \pm 4\gamma_{1}\mathbf{C}_{z/2} + 4\gamma_{3}\mathbf{C}_{3z/2} \right]. \end{split}$$

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#### DISCUSSION

G. CAGLIOTI: If I understood correctly, the authors of this paper utilized the experimental value of the anisotropy ratio of the Debye-Waller factor of white tin in certain relations connecting the elastic constants and the interatomic force constants. As I mentioned during the presentation of my paper<sup>\*</sup>, there is experimental evidence that the behaviour of the anisotropy factor  $\epsilon$  ( $\epsilon_{\text{exptl}} < 1$ ,  $\epsilon_{\text{theor}} > 1$ ) is not due to dynamical considerations, but most likely to static disorder present in the crystal, especially along the [001] symmetry direction. Perhaps these are the reasons for the discrepancy in dispersion relations between this theoretical work you presented and the independent experimental findings of the Italian, British and Canadian groups.

M.G. ZEMLYANOV: Your comment is very interesting. Unfortunately I have not yet been able to acquaint myself with the experimental work to which you refer.

<sup>\*</sup> BORGONOVI, G., CAGLIOTI, G. and ANTONINI, M., "Recent results on the crystal physics of white tin", these Proceedings I.

## LATTICE DYNAMICS OF MAGNESIUM

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#### Abstract — Résumé — Аннотация — Resumen

LATTICE DYNAMICS OF MAGNESIUM. A group theoretical analysis of modes of vibrations in hexagonal close-packed lattices has been made. The results have been used to classify the phonons at some special points in the Brillouin zone and factorize the secular determinant. Dispersion relations for phonons in magnesium along the two symmetry directions [0001] and [0110] have been measured (at room temperature) more accurately than reported earlier. The measurements have been made using a triple-axis spectrometer and a "window filter" spectrometer, both operated in the "constant- $\vec{Q}$ " mode. The results are compared with calculations based on three- and four-neighbour axially symmetric models. It is observed that the four-neighbour tensor force model. The force constants derived from the experiment have been used to compute the frequency distribution.

DYNAMIQUE DE RÉSEAU DU MAGNÉSIUM. Les auteurs ont procédé à une analyse théorique par groupe des modes de vibration dans les réseaux à structure hexagonale compacte. Ils ont utilisé les résultats pour classer les phonons en des points particuliers de la zone de Brillouin et analyser mathématiquement le déterminant séculaire. Afin d'établir les relations de dispersion pour les phonons du magnésium dans les deux directions de symétrie [0001] et [0110] (à la température ambiante), ils ont fait des mesures plus précises que celles qui ont été signalées jusqu'à présent. A cet effet, ils ont utilisé un spectromètre triaxial et un spectromètre avec «filtre à fenêtre», l'un et l'autre dans le mode de « Q constant ». Ils ont comparé les résultats aux calculs fondés sur des modèles à symétrie axiale faisant intervenir les troisième et quatrième voisins. Ils ont constaté que le deuxième de ces modèles fournit une assez bonne description des données. Un modèle de forces tensorielles englobant le quatrième voisin assure une concordance encore meilleure. Les auteurs ont utilisé les constantes de force déduites de l'expérience pour calculer la distribution de fréquence.

ДИНАМИКА РЕШЕТКИ МАГНИЯ. Был произведен групповой теоретический анализ видов колебаний в гексагональной решетке с плотной упаковкой. Результаты были использованы для классификации фононов в некоторых специальных точках зоны Бриллоуина и разложения векового детерминанта. Дисперсионные соотношения для фононов в магнии в двух симметричных напралениях [0001] и [0110] были измерены (при комнатной температуре) более точко, чем сообщалось ранее. Измерения были произведены с помощью трехосного спектрометра и спектрометра с "оконным фильтром". Оба эти спектрометра работали при колебании с "постоянным Q". Результаты измерений сопоставляются с результатами расчетов, основанных на трех- и четырехчленных аксиально симметричных моделях. Установлено, что четырехчленная модель дает довольно хорошее описание этих данных. Еще более хорошее согласие получено с четырехчленной моделью тензорной силы. Константы силы, полученые в результате экспериментов, были использованы для вычисления распределения частот.

DINÁMICA RETICULAR DEL MAGNESIO. Los modos de vibración de las redes hexagonales compactas se han analizado sobre la base de la teoría de los grupos. Los resultados se han utilizado para clasificar los fonones de algunos puntos especiales de la zona de Brillouin y para factorizar el determinante secular. Se han medido, con mayor precisión que la alcanzada hasta el presente, las relaciones de dispersión de los fonones en el magnesio en dos direcciones de simetría [0001] y [0110], a la temperatura ambiente. Las mediciones se han efectuado utilizando un espectrómetro triaxial y un espectrómetro con « filtro de ventana », funcionando ambos según el modo de « $\vec{Q}$  constante». Los resultados se comparan con cálculos basados en modelos axialmente simétricos que abarcan hasta el tercer o el cuarto átomo vecino. Se ha comprobado que este último modelo se ajusta adecuadamente a los datos obtenidos. Con un modelo de fuerzas tensoriales que alcanzan hasta el cuarto átomo, se obtiene una concordancia aún más satisfactoria. Para calcular la distribución de frecuencias se han utilizado las constantes de fuerza deducidas del experimento.

#### I. INTRODUCTION

Magnesium is a divalent element belonging to group II of the periodic table. It has a hexagonal close-packed (hcp) structure and shares this with two other elements in the group, namely beryllium and zinc, though with some differences in packing. Zinc has a c/a ratio of 1.855, the highest known. For beryllium the value is 1.58, one of the lowest. Magnesium with a value of 1.622 approaches the ideal packing, for which c/a is 1.633. This difference in the c/a ratio among these metals, manifests itself in several properties including the elastic one. It is therefore interesting to compare the lattice vibration spectrum of these three substances and look for systematics, if any, with respect to the c/a ratio. The phonon spectrum in both beryllium [1] and zinc [2, 3] has been studied by other groups. In this paper we give a complete account of our investigations of the lattice dynamics of magnesium by neutron inelastic scattering. The following section gives an account of the application of group theory to the dynamics of hcp lattices. A brief account of the theoretical considerations pertaining to neutron scattering is also given. The experimental techniques used and the results obtained are described in section III. The analysis of the experimental results and a comparison with those of beryllium and zinc is presented in section IV. Parts of this work have been reported earlier [4, 5].

#### **II. THEORETICAL CONSIDERATIONS**

#### Lattice dynamics

The space group of magnesium is  $D_{6h}^4$ . In the primitive unit cell there are two atoms whose positions with reference to the hexagonal axes (see Fig.1) are

$$\left(000, \frac{a_1}{3} \frac{2a_2}{3} \frac{a_3}{2}\right)$$

where  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_3$  are the primitive translational vectors. The lattice parameters are  $|\vec{a}_1| = |\vec{a}_2| = a = 3.2028$  Å and  $|\vec{a}_3| = c = 5.196$  Å. The reciprocal lattice is also hexagonal and belongs to the space group  $D_{6h}^1$ .

The dynamics of hcp lattices have been discussed by several authors within the framework of the Born-von Kármán formalism, using different models for the interatomic forces and including interactions up to different distances [1, 5, 6-10]. Some preliminary considerations can, however, be obtained purely from the symmetry of the lattice using the methods of group theory.

Group theory has been widely used in the study of molecular vibrations [11,12]. Its application to lattice vibrations, however, has not been so extensive. As in the case of molecular vibrations, group theory can be useful in two ways: (1) in classifying the modes of vibration and (2) in factorizing the secular determinant.

Consider a crystal having N unit cells with n atoms per unit cell, satisfying the periodic boundary conditions. Let  $\{\vec{a} | \vec{r}(1)\}$  denote a symmetry oper-



The top figure shows the Cartesian axes and the crystallographic axes for the hcp lattice The bottom figure shows the first Brillouin zone.

ation which, when performed on the crystal with all the atoms in their equilibrium, leaves it invariant. Here  $\vec{\alpha}$  stands for the rotational part of the operation and  $\vec{r}(1)$  for the lattice translation. The set of elements  $\{\vec{\alpha} \mid \vec{r}(1)\}$ constitute the space group G. The N elements  $\{\vec{e} \mid \vec{r}(1)\}$  ( $\vec{E}$  representing the identity operation) form the translational sub-group T, which is an invariant sub-group of G. In the study of lattice dynamics, we consider the elements  $\{\vec{\alpha} \mid \vec{r}(1)\}$  to be acting not on the equilibrium crystal, but on the atomic displacements.

Now the displacement vectors of the atoms in the crystal span a 3nN- dimensional space. However, this space is reducible into N sub-spaces each of dimension 3n and it is well known that Bloch-type functions [13, 14]

$$\mathbf{u}_{\alpha} \begin{pmatrix} \mathbf{\vec{q}} \\ \mathbf{k} \end{pmatrix} = \sum_{\mathbf{l}} \exp[-2\pi i \mathbf{\vec{q}} \cdot \mathbf{\vec{r}}(\mathbf{l})] \mathbf{u}_{\alpha} \begin{pmatrix} \mathbf{l} \\ \mathbf{k} \end{pmatrix}$$

form a suitable basis for this reduction\*. These functions are also termed translational symmetry co-ordinates. Upon expressing the vibrational energy in terms of these translational symmetry co-ordinates, one easily obtains the familiar secular determinant.

<sup>\*</sup> We shall follow the same notation as in our earlier paper [5].

The 3n-dimensional sub-space is further reducible if the wave vector  $\vec{q}$  lies along a symmetry direction in reciprocal space or, to put it differently, if the group of the wave vector  $G\vec{q}$  contains rotational elements, mirror planes, etc., in addition to the translational elements. The functions which form the basis for this additional reduction are called symmetry co-ordinates. They transform according to the various allowable or small representations [15] of  $G\vec{q}$ . If the dynamical matrix is developed in terms of these symmetry co-ordinates, then automatically it will be block-diagonalized. These considerations show that, for enumerating the symmetry modes and factorizing the secular determinant, it is sufficient to have a knowledge of the allowable representations of  $G\vec{q}$ . The representations of the complete space group are not necessary.

The allowable representations for the points  $\Gamma$ , A, M, T, K,  $\Sigma$  and  $\Delta$ in the Brillouin zone (see Fig. 1) have been obtained by employing methods developed earlier by RAGHAVACHARYULU [14, 16] in a study of the diamond lattice. For convenience in constructing the symmetry co-ordinates, the complete matrix representation has been obtained. A typical table of allowable matrix representations corresponding to the point  $\Delta$  is shown in Table I. The charactertables constructed from such matrix representations corresponding to the different points in the Brillouin zone which we have considered are listed in the Appendix. (The notation used is also explained there.) They are in agreement with those obtained earlier by HERRING [17] by a different method Using the character tables in the Appendix, it is a simple matter to obtain the number of modes belonging to the various allowable representations. One first calculates the character  $\chi(\mathbf{R})$  of the 3ndimensional reducible representation corresponding to the element R according to the formula [14]

$$\chi(R) = N_{R}(\pm 1 + 2 \cos \phi_{R}),$$
 (1)

where  $N_R$  is the number of atoms in the unit cell which are left in an equivalent position as a result of the operation R, and  $\phi_R$  is the angle implied in the rotation. The positive and negative signs apply to proper and improper rotations, respectively. The number  $n_j$  of modes belonging to a particular allowable representation  $\Gamma_j$  is then given by the relation

$$n_{j} = \frac{1}{N(G_{q}^{2}/T)} \sum_{R \in (G_{q}^{2}/T)} [\chi^{\Gamma_{j}}(R)] * \chi(R), \qquad (2)$$

where  $N(G_{\vec{q}}/T)$  is the order of the factor group  $(G_{\vec{q}}/T)$  and  $\chi^{\Gamma_j}(R)$  is the character of the element R in the allowable representation  $\Gamma_j$ . The results of such a classification are also shown along with the character tables.

We now consider the factorization of the secular determinant: This, as we remarked earlier, requires a knowledge of the symmetry co-ordinates. If the translational symmetry co-ordinates are represented by a column vector  $\vec{u}$  and the normalized symmetry co-ordinates by another column vector  $\vec{v}$ , then the two are related by the matrix equation

$$\vec{v} = \vec{S}\vec{u}$$
, (3)

| TA | BL | E | I |
|----|----|---|---|
|----|----|---|---|

ALLOWABLE REPRESENTATIONS FOR  $\Delta$ 

| Rep.       | {E 0} | $\left\{ c_{2}(z)   \vec{t} \right\}$ | {c <sub>3</sub> (z) 0} | {c <sub>3</sub> -l(z) 0} | $\left\{ c_{6}^{}(z)   \vec{t} \right\}$ | $\left\{c_{6}^{-1}(z)\left \vec{t}\right\}\right\}$ | {od(1)   t} | $\left\{ \sigma_{d}(2)   \vec{t} \right\}$ | {o <sub>d</sub> (3)/t} | {o <sub>v</sub> (4) 0} | {σ <sub>v</sub> (5) 0} | {¤ <sub>v</sub> (6) 0} | nj  |
|------------|-------|---------------------------------------|------------------------|--------------------------|--|---|-------------|--|------------------------|------------------------|------------------------|------------------------|-----|
| Δ,         | 1     | e(z)                                  | 1                      | 1                        | e(z)                                     | e(z)  | e(z)        | e(z)                                       | e(z)                   | 1                      | 1                      | 1                      | 1   |
| $\Delta_2$ | 1     | -e(z)                                 | 1                      | 1                        | -e(z)                                    | -e(z)   | -e(z)       | -e(z)                                      | -e(z)                  | 1                      | 1                      | 1                      | 1   |
| Δ3         | 1     | e(z)                                  | 1                      | 1                        | e(z)                                     | e(z)  | -e(z)       | -e(z)                                      | -e(z)                  | -1                     | -1                     | -1                     | 0   |
| $\Delta_4$ | 1     | -e(z)                                 | 1                      | 1                        | -e(z)                                    | -e(z)   | e(z)        | e(z)                                       | e(z)                   | -1                     | -1                     | -1                     | 0   |
| $\Delta_5$ | а     | a∙e(z)                                | b <sub>.</sub>         | .c                       | c · e(z)                                 | b · e(z)  | d∙e(z)      | g·e(z)                                     | f∙e(z)                 | <b>8</b> .             | f                      | d                      | 1   |
| $\Delta_6$ | a     | -a∙e(z)                               | Ъ                      | c                        | -c∙e(z)                                  | -b∙e(z)   | -d∙e(z)     | -g∙e(z)                                    | -f∙e(z)                | g                      | f -                    | đ                      | - 1 |
| χ(R)       | 6     | 0                                     | 0                      | 0                        | 0  | 0   | 0           | 0  | 0                      | 2                      | 2                      | 2                      |     |

Note:  $\mathbf{e}(\mathbf{z}) = \exp(i\pi cq_{\mathbf{z}}); \ \mathbf{a} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \ \mathbf{b} = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix}; \ \mathbf{c} = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix}; \ \mathbf{d} = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix}; \ \mathbf{f} = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix}; \ \mathbf{g} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ 

where  $\vec{S}$  is the transformation matrix. Expressed in terms of  $\vec{v}$ , the dynamical matrix  $\vec{D}$  becomes  $\vec{S}\vec{D}\vec{S}^{\dagger}$  and will be block-diagonalized. The problem therefore is essentially to determine the symmetry co-ordinates and the transformation matrix  $\vec{S}$ . Once this is done the block-diagonalization is trivial.

The symmetry co-ordinates are best constructed by employing the projection operator technique [18]. The projection operator belonging to the i-th row of the j-th irreducible representation of a group  $\mathscr{G}$  is defined as  $\sum_{R \in \mathscr{G}} [R_{ii}^j] * R$ , where  $R_{ii}^j$  refers to the i-th diagonal element in the matrix representation of R in the j-th irreducible representation. If this projection operator is applied to any arbitrary function F, then it can be shown that the resultant function belongs to the i-th row of the j-th irreducible representation. In our case we require the projection operators corresponding to the allowable representations of  $G_{\vec{q}}$ . As noted by Raghavacharyulu, the construction may be limited to the elements of  $G_{\vec{q}}$  mod T.

We will illustrate the application of the projection operator technique to the construction of the symmetry co-ordinates and subsequent blockdiagonalization of the dynamical matrix by considering the case of the point  $\Delta$ . Using the definition of the projection operator given above in conjunction with the matrix representations listed in Table I, the operators corresponding to the various allowable representations relevant for phonons propagating along  $\Delta$  are easily constructed and these are shown in Table II. The pro-

jection operators are then allowed to act on the Bloch functions  $u_{\alpha} \left( \begin{matrix} \vec{q} \\ \mathbf{k} \end{matrix} \right)$  (of

which there are six in magnesium), and the linearly independent members of the resultant set selected and normalized. This gives the symmetry coordinates transforming according to the relevant allowable representations. The results for the point  $\Delta$  are included in Table II.

Using the results of Table II, the transformation matrix is easily given by

| $\frac{1}{2}$ | $-\frac{i}{2}$ | 0                    | $-\frac{1}{2}e(-z)$ | <u>ie(-z)</u><br>2  | 0                          |
|---------------|----------------|----------------------|---------------------|---------------------|----------------------------|
| $\frac{1}{2}$ | $\frac{i}{2}$  | 0                    | $-\frac{1}{2}e(-z)$ | $-\frac{ie(-z)}{2}$ | 0                          |
| $\frac{1}{2}$ | $-\frac{i}{2}$ | 0                    | $-\frac{1}{2}e(-z)$ | $-\frac{ie(-z)}{2}$ | • 0                        |
| $\frac{1}{2}$ | $\frac{i}{2}$  | 0                    | $-\frac{1}{2}e(-z)$ | <u>ie(-z)</u><br>2  | 0                          |
| 0             | 0              | $\frac{1}{\sqrt{2}}$ | 0                   | 0                   | $\frac{1}{\sqrt{2}}$ e(-z) |
| 0             | 0              | $\frac{1}{\sqrt{2}}$ | 0                   | 0                   | $-\frac{1}{\sqrt{2}}e(-z)$ |

 $e(z) = exp(i\pi cq_z)$ 

**s**=

| Allowable<br>rep. | Projection operators  | Symmetry co-ordinates   |
|-------------------|---|---|
| Δ <sub>1</sub>    | $P(\Delta_1) = E + c_3(1) + c_3(2) + a_v(4) + a_v(5) + a_v(6)$ $+ e(-z)[c_2(z) + c_6(1) + c_6(2) + a_d(1) + a_d(2) + a_d(3)]$     | $\left[u_{3}\left(\overrightarrow{q}\right)+u_{3}\left(\overrightarrow{q}\right)e(-z)\right]$   |
| Δ2                | $P(\Delta_2) = E + c_3(1) + c_3(2) + a_v(4) + a_v(5) + a_v(6)$<br>- e(-z)[c_2(z) + c_6(1) + c_6(2) + a_d(1) + a_d(2) + a_d(3)]    | $\left[u_{3}\left(\overrightarrow{q}^{\dagger}_{1}\right)-u_{3}\left(\overrightarrow{q}^{\dagger}_{2}\right)e(-z)\right]$   |
|                   | $P_{11}(\Delta_{g}) = E + \omega^{2}c_{g}(1) + \omega c_{g}(2) + e(-z)[c_{2}(z) + \omega c_{6}(1) + \omega^{2}c_{6}(2)]$          | $\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} - iu_2 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} \end{bmatrix}$ $- \begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} - iu_2 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} \end{bmatrix} e(-z)$ |
| Δ5                | $P_{22} (\Delta_{5}) = E + \omega c_{3} (1) + \omega^{2} c_{3} (2) + e(-z) [c_{2} (z) + \omega^{2} c_{6} (1) + \omega c_{6} (2)]$ | $\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} + iu_2 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} \end{bmatrix}$ $- \begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} + iu_2 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} \end{bmatrix} e(-z)$ |

## PROJECTION OPERATORS AND SYMMETRY CO-ORDINATES FOR $\Delta$

TABLE II

| Allowable<br>rep. | Projection operators  | Symmetry co-ordinates  |
|-------------------|---|--|
|                   | $P_{11}(\Delta_{6}) = E + \omega^{2}c_{3}(1) + \omega c_{3}(2) - e(-2)[c_{2}(2) + \omega c_{6}(1) + \omega^{2}c_{6}(2)]$    | $\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} - i u_2 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} \end{bmatrix}$ $-\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} + i u_2 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} \end{bmatrix} e(-z)$ |
| Δ.                | $P_{22}(\Delta_{6}) = E + \omega c_{3}(1) + \omega^{2} c_{3}(2) - e(-2) [c_{2}(2) + \omega^{2} c_{6}(1) + \omega c_{6}(2)]$ | $\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} + iu_2 \begin{pmatrix} \vec{q} \\ 1 \end{pmatrix} \end{bmatrix}$ $-\begin{bmatrix} u_1 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} - iu_2 \begin{pmatrix} \vec{q} \\ 2 \end{pmatrix} \end{bmatrix} e(-z)$   |

TABLE II (cont.)

when the components of the column matrix  $\vec{u}$  are arranged in the order  $u_1\begin{pmatrix}\vec{q}\\1\end{pmatrix}$ ,  $u_2\begin{pmatrix}\vec{q}\\1\end{pmatrix}$ ,  $u_3\begin{pmatrix}\vec{q}\\1\end{pmatrix}$ ,  $u_1\begin{pmatrix}\vec{q}\\2\end{pmatrix}$ ,  $u_2\begin{pmatrix}\vec{q}\\2\end{pmatrix}$  and  $u_3\begin{pmatrix}\vec{q}\\2\end{pmatrix}$ . Upon applying this transformation matrix to the dynamical matrix, the latter assumes the form



where

$$A = \frac{1}{2} \left\{ D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + \operatorname{Re} \left[ D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right] \cos \pi cq_z$$
$$- \operatorname{Im} \left[ D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right] \sin \pi cq_z \right\}$$
$$B = \frac{1}{2} \left\{ D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} - \operatorname{Re} \left[ D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right] \cos \pi cq_z$$
$$+ \operatorname{Im} \left[ D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right] \sin \pi cq_z \right\}$$
$$C = D_{33} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + \operatorname{Re} D_{33} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \cos \pi cq_z - \operatorname{Im} D_{33} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \sin \pi cq_z$$
$$D = D_{33} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} - \operatorname{Re} D_{33} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \cos \pi cq_z + \operatorname{Im} D_{33} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \sin \pi cq_z$$

We thus find the dynamical matrix to be completely diagonalized and the dispersion relations for the different branches may be separately computed. Table III summarizes the results of such an analysis for the other points we have considered. Group theory, therefore, offers a method of systematically classifying the modes and factorizing the secular determinant purely from symmetry considerations. It must be remembered, of course, that in some cases, factorization beyond that predicted from symmetry arguments is possible if the interatomic forces assume a very simple form. As an example of the usefulness of group theory, we might quote our experience with the secular determinant for the point T. Conventional calculations based on a simple model by SLUTSKY and GARLAND [8] showed that the  $(6 \times 6)$  determinant could be factorized into a  $(4 \times 4)$  and a  $(2 \times 2)$  determinant. Further reduction was not easy. On the other hand, using group theoretical methods alone, we see that the  $(6 \times 6)$  determinant can be factorized into two  $(2 \times 2)$  determinants and two  $(1 \times 1)$  determinants.

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## TABLE III

| Symmetry line<br>or point | Allowable<br>representation                                 | Dynamical matrix  |
|---------------------------|---|---|
|                           | Γ_2   | $D_{33}\left(\overrightarrow{q}\right) + \operatorname{Re} D_{33}\left(\overrightarrow{q}\right)$   |
|                           | Г <mark>*</mark>  | $D_{33}\left(\stackrel{\rightarrow}{11}\right)$ - Re $D_{33}\left(\stackrel{\rightarrow}{12}\right)$  |
| Г                         | Г <sup>+</sup> 5  | $D_{11}\left(\overrightarrow{q}\right) - \operatorname{Re} D_{11}\left(\overrightarrow{q}\right)$   |
|                           | Γ_6   | $D_{11}\left(\overrightarrow{q}\right) + \operatorname{Re} D_{11}\left(\overrightarrow{q}\right)$   |
|                           | $A_1 \begin{pmatrix} LO \\ LA \end{pmatrix}$                | $D_{33} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix}$  |
| A                         | $A_{3} \begin{pmatrix} TOI, TOI \\ TAI, TAI \end{pmatrix}$  | $D_{11}\left( \overrightarrow{q} \right)$   |
|                           | $\Sigma_1 \begin{pmatrix} LA \\ LO \end{pmatrix}$           | $\left( D_{22} \begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} D_{22} \begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix} \right)$  |
|                           |   | $\left  \begin{array}{c} \left\langle \mathbf{D}_{22}^{*} \begin{pmatrix} \vec{\mathbf{q}} \\ 12 \end{pmatrix} \mathbf{D}_{22} \begin{pmatrix} \vec{\mathbf{q}} \\ 11 \end{pmatrix} \right\rangle$                                      |
| Σ                         | $\Sigma_{3} \begin{pmatrix} TA_{1} \\ TO_{1} \end{pmatrix}$ | $\left( D_{33} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} D_{33} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right)$  |
|                           |   | $\left  \begin{array}{c} \left\langle \mathbf{D}_{33}^{\#} \left( \begin{array}{c} \vec{\mathbf{q}} \\ 12 \end{array} \right) \mathbf{D}_{33} \left( \begin{array}{c} \vec{\mathbf{q}} \\ 11 \end{array} \right) \right\rangle \right $ |
|                           | $\Sigma_4 \begin{pmatrix} TAH \\ TOH \end{pmatrix}$         | $\left( D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right)$  |
|                           |   | $ \sqrt{ D_{\mu}^{*} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} D_{\mu} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} } $  |

# REDUCED MATRICES AT SYMMETRY POINTS

| Symmetry line<br>or point | Allowable representation         | Dynamical matrix   |  |  |
|---------------------------|----------------------------------|--|--|--|
| · · ·                     | M <sup>+</sup> <sub>1</sub> (LA) | $D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} - \text{Re } D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix}$   |  |  |
|                           | м <mark>*</mark> (тоі)           | $D_{33}\left(\overrightarrow{q}\right) - \text{Re } D_{33}\left(\overrightarrow{q}\right)$   |  |  |
|                           | M <sup>+</sup> (TA  )            | $D_{11}\left(\overrightarrow{q}\right) - \operatorname{Re} D_{11}\left(\overrightarrow{q}\right)$  |  |  |
| М                         | M <sub>2</sub> (LO)              | $D_{22} \begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} + \text{Re} D_{22} \begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix}$  |  |  |
|                           | м <b>-</b> (то <u>  </u> )       | $D_{II}\left(\vec{q} \atop 11\right) + \text{Re } D_{II}\left(\vec{q} \atop 12\right)$   |  |  |
|                           | M <sub>4</sub> (TA1)             | $D_{33}\left(\stackrel{\overrightarrow{q}}{11}\right)$ + Re $D_{33}\left(\stackrel{\overrightarrow{q}}{12}\right)$   |  |  |
|                           | T <sub>1</sub>                   | $\begin{pmatrix} D_{11}\begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} + \operatorname{Re} D_{11}\begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix} - i \operatorname{Im} D_{12}\begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix} \\ i \operatorname{Im} D_{12}\begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix} D_{22}\begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} - \operatorname{Re} D_{22}\begin{pmatrix} \overrightarrow{q} \\ 12 \end{pmatrix} \end{pmatrix}$ |  |  |
|                           | T <sub>2</sub> (TO1)             | $D_{33}\left(\overrightarrow{q}\right) - \text{Re } D_{33}\left(\overrightarrow{q}\right)$   |  |  |
| Т                         | Т <sub>3</sub> (ТА⊥)             | $D_{33}\left(\overrightarrow{q}\right) + \text{Re } D_{33}\left(\overrightarrow{q}\right)$   |  |  |
|                           | . Т <sub>4</sub>                 | $\begin{pmatrix} D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} - \operatorname{Re} D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \operatorname{IIm} D_{12} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \\ - \operatorname{IIm} D_{12} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + \operatorname{Re} D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \end{pmatrix}$   |  |  |
| ĸ                         | K1                               | $\frac{1}{2} \left\{ D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} \right\}$   |  |  |
|                           |                                  | + Re $D_{11}\begin{pmatrix} 4\\12 \end{pmatrix}$ - Re $D_{22}$ + Im $D_{12}\begin{pmatrix} 4\\12 \end{pmatrix}$  |  |  |

TABLE III (cont.)

| Symmetry line<br>or point | Allowable<br>representation  | Dynamical matrix  |
|---------------------------|--|---|
|                           | K <sub>2</sub>   | $\frac{1}{2} \left\{ D_{11} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} + D_{22} \begin{pmatrix} \vec{q} \\ 11 \end{pmatrix} - \operatorname{Re} D_{11} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} + \operatorname{Re} D_{22} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} - \operatorname{Im} D_{12} \begin{pmatrix} \vec{q} \\ 12 \end{pmatrix} \right\}$ |
| K<br>(cont.)              | K۵   | $\frac{1}{2} \left( D_{11} \begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} + D_{22} \begin{pmatrix} \overrightarrow{q} \\ 11 \end{pmatrix} \right)$  |
|                           | $K_{6} \begin{pmatrix} TO \downarrow \\ TA \downarrow \end{pmatrix}$ | $D_{33}\left( \overrightarrow{q} \atop 11 \right)$  |

TABLE III (cont.)

An actual evaluation of the frequencies for phonons propagating in the symmetry directions, using the results of Table III, demands a knowledge of the interatomic force constants. In the absence of accurate knowledge of the force constants from first principles, they must necessarily be left as parameters to be determined by experiment, making at best assumptions about the symmetry of the forces. As remarked earlier, several force constant models of this type have been considered in the past for hcp lattices. These include a simplified central force model [1, 8], axially symmetric (A-S) force model [5, 7, 10], and tensor force (T-F) model [5, 6, 9]. In view of the extensive discussions available in the literature, we will not go into the dynamics of hcp lattices here. It is sufficient to remark that calculations according to any desired model are easily made using the simplifications suggested in Table III.

#### Neutron scattering

The nuclear properties of magnesium are quite favourable for a study of the phonon spectrum by the technique of coherent inelastic scattering of slow neutrons. It is well known that when slow neutrons are scattered coherently by phonons in a single crystal, distinct groups occur in the scattered neutron distribution governed by the conservation conditions

$$\vec{k}_0 - \vec{k}' = \vec{Q} = 2\pi \vec{\tau} - 2\pi \vec{q}$$
 (4a)

$$|\mathbf{E}_0 - \mathbf{E}'| = \mathbf{h}\nu_i(\vec{\mathbf{q}}). \tag{4b}$$

Here  $\vec{k}_0$  and  $\vec{k}'$  denote the incident and scattered neutron wave vectors, re-

spectively;  $E_0$  and E' the incident and scattered neutron energies, respectively;  $\vec{\tau}$  a reciprocal lattice vector and  $\nu_j(\vec{q})$  and  $\vec{q}$  are the frequency and the wave vector, respectively of the phonon of the j-th branch participating in the scattering process.

The cross-section for the neutron-phonon interaction is given by [19, 20]

$$\sigma_{j}(\vec{k}_{0} \rightarrow \vec{k}') = \frac{\hbar}{4\pi} \frac{k'}{k_{0}} {N_{j} \choose N_{j+1}} e^{-2W} \frac{g_{j}^{2}(\vec{q}, \vec{\tau})}{|J_{j}|}$$
(5)

per steradian per unit cell. Here  $N_j = [exp(h\nu_j/k_BT)-1]^{-1}$  is the population factor for the phonon annihilation case and  $N_{j+1}$  the corresponding factor for the phonon creation case;  $e^{-2W}$  is the familiar Debye-Waller factor.  $J_j$  is a Jacobian introduced in connection with certain transformations during the calculation of the cross-section and effectively sums over the different normal modes which can contribute to the observed neutron group. For a fixed incident neutron energy  $E_0$ ,  $J_j$  is given by [19]

$$J_{j} = 1 + \frac{\epsilon \hbar}{2E^{\prime}} [\vec{k}^{\prime} \cdot \operatorname{grad}_{\vec{q}} \nu_{j}]$$
(6)

with  $\epsilon = \pm 1$  for neutron energy loss and -1 for neutron energy gain. In the "constant- $\vec{Q}$ " mode of observing the neutron group  $|J_j| = 1$  [21]. The same holds for "constant- $\vec{Q}$ " experiments in which the scattered neutron energy is fixed. The intensity of the scattering process is therefore predominantly controlled by the quantity  $g_j^2(\vec{q}, \vec{\tau})$ , often referred to as the dynamical structure factor. It can be expressed as [20]

$$g_{j}^{2}(\vec{q},\vec{\tau}) = \left| \sum_{k} \frac{b_{k}\vec{Q}\cdot\vec{\xi}_{jk}(\vec{q})}{[M_{k}\nu_{j}(\vec{q})]^{1/2}} \exp\left(i\vec{Q}\cdot\vec{r}(k)\right) \right|^{2}.$$
(7)

In this equation,  $\vec{\tau}(k)$  is the position of the k-th atom in the unit cell,  $M_k$  its mass,  $b_k$  its bound scattering length and  $\vec{\xi}_{jk}(\vec{q})$  the polarization vector. The summation runs over all the atoms in the primitive unit cell. To help in choosing proper lattice points for making observations, we have mapped the behaviour of  $g_1^2(\vec{q},\vec{\tau})$  in reciprocal space for  $\vec{q}$  lying along [0110] and [0001]. For these directions the structure factor (Eq. (7)) is related in a simple manner to the elements of the dynamical matrix and is therefore easily calculated. Our calculations were made assuming a simplified model by Slutsky and Garland involving central forces and interactions up to three neighbours. The results are shown in Fig. 2. The structure factor is periodic in reciprocal space and the region bounded by the dark lines in Fig. 3 shows the unit over which the structure factor repeats.

#### III. EXPERIMENTS

The scattering experiments were perfored with the crystal spectrometers at the Canada-India Reactor (CIR) using the "constant- $\vec{Q}$ " method.



Inelastic scattering structure factors for magnesium calculated on the SG model plotted in units of  $[(b\vec{\xi}_i \cdot \vec{Q})^2/2M\nu_i)$ 

As is well known, in this technique [21], the phonon wave vector and the lattice point for making the observation are first selected, thereby fixing  $\vec{Q}$ ;  $\vec{k}_0$  and  $\vec{k}'$  are then varied suitably keeping  $\vec{Q}$  constant until the two conservation conditions are simultaneously satisfied as indicated by a peak in the scattered neutron intensity. The peak position thus defines the phonon frequency using Eq. (4).

Two variations of the "constant- $\vec{Q}$ " technique were used in the present experiments. In the first  $\vec{k}_0$  was kept fixed and  $\vec{k}$ , the scattering angle  $\phi$ and the crystal orientation  $\psi$  were varied to realize "constant- $\vec{Q}$ " operation. A conventional triple-axis spectrometer, using an aluminium single crystal as a monochromator and the (111) planes of a second aluminium crystal as the analyser, was employed for this purpose. In the later stages a copper crystal reflecting from the (111) planes was substituted for the aluminium analyser. In the second method,  $\vec{k}$  was kept fixed and  $\vec{k}_0$ ,  $\phi$  and  $\psi$  were varied. As has been pointed out by BROCKHOUSE [21], it is possible to







Sections of the reciprocal lattice for the hcp lattice in the  $b_1 b_2$  plane and  $b_2 b_3$  plane The region bounded by the solid lines is the unit over which the structure factor  $g_1^2(\vec{q}, \vec{\tau})$  repeats.

use a triple-axis spectrometer for this method also. We have, however, adapted a beryllium detector spectrometer for this purpose as this gave greater intensity. Monochromatic neutrons were obtained by reflection off the (111) planes of an aluminium crystal and the scattered neutrons selected by a "window filter" [22] in place of the conventional beryllium filter. The "window filter" serves to define  $\vec{k}$  within the limits of Be and BeO edges. The "window filter" technique of observing phonons has been discussed in detail by IYENGAR [23].

The magnesium single crystal used in the experiments was in the form of a square slab 5 cm $\times$ 5 cm $\times$ 1 cm with the hexad axis nearly parallel to one of the long sides. The crystal was mounted on a goniometer and oriented using neutrons. Most of the low frequency phonons were studied using the triple-axis spectrometer. Both energy gain and energy loss processes were used. The "window filter" observations necessarily involve energy loss processes and were confined to the higher frequency





Typical neutron groups observed during the experiment The groups shown in (a) and (b) were observed by conventional crystal spectrometry methods while that in (c) was obtained by the "window filter" method.

phonons as the technique works best here. Specimen neutron groups obtained by the two techniques are shown in Fig.4. Nearly sixty phonons propagating in the two principal symmetry directions  $\Sigma$  and  $\Delta$  were observed and their frequencies are listed in Table IV. The errors quoted are due to counting statistics alone and do not include any possible systematic errors.
# LATTICE DYNAMICS OF MAGNESIUM

## TABLE IV

# FREQUENCY OF PHONONS PROPAGATING IN SYMMETRY DIRECTIONS $\Sigma$ AND $\Delta$ (10<sup>12</sup> c/s)

.

| q/q <sub>max</sub> | [0001] LO       | q/q <sub>max</sub> | [0001] LA       | q/q <sub>max</sub> | [0110] TA      |
|--------------------|-----------------|--------------------|-----------------|--------------------|----------------|
|                    | <u> </u>        | <u> </u>           |                 |                    |                |
| 0.00               | 7.3 ±0.15       | i i                |                 | 1                  |                |
| 0.10               | 7.34 ±0.16      |                    |                 |                    |                |
| 0.20               | 7.13 ±0.14      |                    |                 |                    |                |
| 0.30               | 7.07 ±0.14      |                    |                 |                    | {              |
| 0.40               | 7.03 ±0.14      |                    |                 | 1                  |                |
| 0.50               | 6.78 ±0.13      | 0.50               | 2.70±0.08       | 0.50               | 2.56±0.0       |
| 0.60               | 6.56 ±0.13      | 0.60               | 3.20±0.09       | 0.60               | 2.96 ± 0.0     |
| 0.70               | 6.20 ±0.12      | 0.70               | 3.70±0.11       | 0.65               | 3.28 ± 0.0     |
| 0.80               | 5.92 ±0.12      |                    |                 | 0.70               | 3.40±0.0       |
| 0.90               | 5.615±0.11      | [                  |                 | 0.90               | 3.82±0.0       |
| 1.00               | 5.2 ±0.10       | 1.00               | 5.20±0.10       | 1.00               | 3.71±0.0       |
| q/q <sub>max</sub> | [0001] TO       | q/q <sub>max</sub> | [0001] TA       | q/q <sub>max</sub> | [0110] T.      |
|                    |                 | <u> </u>           | · · ·           | <u> </u>           |                |
| 0.00               | $3.75 \pm 0.08$ |                    |                 |                    |                |
| 0.30               | $3.83 \pm 0.08$ | 1                  |                 |                    |                |
| 0.40               | $3.60 \pm 0.07$ |                    |                 |                    |                |
| 0.50               | $3.71 \pm 0.07$ | 0.50               | 1.55±0.02       | 0.50               | $2.80 \pm 0.0$ |
| 0.60               | $3.58 \pm 0.06$ | 1                  |                 | 0,60               | 3.30±0.0       |
| 0.70               | 3.46±0.05       | 0.70               | 2.03±0.02       | 0.70               | 3.58±0.0       |
| 0.80               | 3.34±0.03       | 0.80               | $2.29 \pm 0.02$ | 0.80               | 3.90±0.0       |
| 0.90               | 3.15±0.03       | 0.85               | $2.66 \pm 0.03$ | 0.90               | 4.10±0.0       |
|                    |                 | 0.95               | 2.82±0.03       |                    |                |
| 1.00               | 2.94±0.03       | 1.00               | 2.94±0.03       | 1.00               | 4.15±0.0       |
| q/q <sub>max</sub> | [0110] LO       | q/q <sub>max</sub> | [0110] LA       | q/q <sub>max</sub> | [0110] TO      |
|                    |                 |                    |                 |                    |                |
| 0.00               | $3.75 \pm 0.08$ |                    |                 | 0.00               | $7.30\pm0.1$   |
| 0,10               | 3.92±0.08       | 1                  |                 | 0.10               | 7.28±0.1       |
| 0.21               | $4.20 \pm 0.08$ |                    |                 | 0.20               | 7.18 $\pm$ 0.1 |
| 0.30               | 4.70±0.09       | 0.30               | 3.20±0.07       | 0.30               | 7.08±0.1       |
| 0.40               | 5,26±0,11       |                    |                 | }                  | 1              |
| 0.52               | $5.69 \pm 0.12$ | 0.60               | 5.58±0.11       | 0,60               | 6.51±0.1       |
| 0.806              | $6.69 \pm 0.13$ | 0.69               | 5.96±0.06       |                    |                |
|                    |                 | 0.78               | 6.25±0.06       | 1                  | 1              |
|                    |                 |                    |                 |                    |                |
| 0.90               | $6.88 \pm 0.14$ | 0.914              | 6.46±0.13       | 0.90               | 6.25±0.0       |

### IV. DISCUSSION

The near ideal close packing that occurs in magnesium would lead one to expect a considerable degree of isotropy in its properties. Indeed the elastic properties do exhibit such a behaviour. This led Slutsky and Garland to describe the lattice dynamics of magnesium in terms of the model referred to earlier. The model assumes central forces involving only stretching of the interatomic bonds and interactions up to three neighbours. Our preliminary measurements tended to support such a view. With the availability of more data, however, it became clear that the Slutsky-Garland model was not adequate and it seemed that a more sophisticated model was called for. We therefore considered a three-neighbour model based on axially symmetric forces [5, 10]. According to this model the ratio  $\nu^2(q_{max})/\nu^2(q=0)$  for transverse phonons propagating along the [0001] direction should be 0.5. The same is true of the longitudinal phonons also. This, however, is in disagreement with the observed data. A four-neighbour A-S model was therefore tried. The following values (in dyn/cm) were used for the force constants:

| $\alpha_{\rm s} = 9.992 \times 10^3$ | $\alpha_{\rm B} = 0.700 \times 10^3$    |
|--------------------------------------|---|
| $\beta_{\rm s} = 10.789 \times 10^3$ | $\beta_{\rm B}$ = 0.543×10 <sup>3</sup> |
| $\gamma_{\rm s} = 2.149 \times 10^3$ | $\gamma_{\rm B} = -1.650 \times 10^3$   |
| $\theta = 0.614 \times 10^3$         | $\phi = 0.303 \times 10^3$              |

(The notation above is the same as in [5].) The values used for the force constants were derived from neutron data corresponding to some special points in the Brillouin zone and the elastic constants  $C_{13}$  and  $C_{44}$  [23]. Dispersion relations calculated using these values are shown in Fig. 5 as solid lines. It is seen that the four-neighbour A-S model gives a reasonably good description of the observed results. Even better agreement was obtained by extending consideration to a four-neighbour T-F model and making a least square fit to the neutron data. The values of the force constants (in dyn/cm) derived in the notation of [5] were as follows:

|     | $\theta = 0.339$      | $\phi = 0.1$                   | 14×10 <sup>3</sup>           |
|-----|-----------------------|--------------------------------|------------------------------|
| ξ = | -0.372×103            | $\eta = -0.581 \times 10^3$    | $\zeta = -0.124 \times 10^3$ |
| λ=  | 2.396 $\times 10^{3}$ | $\mu$ = -1.381×10 <sup>3</sup> | $\nu = 7.163 \times 10^3$    |
| α = | 5.603 $\times 10^{3}$ | $\beta = 2.028 \times 10^3$    | $\gamma = 0.211 \times 10^3$ |

For evaluating many of thermodynamic properties, it is useful to have a knowledge of the frequency distribution. Towards this end, we have computed this quantity using the four-neighbour A-S model just discussed. In calculating the frequency distribution, it is sufficient to consider the irreducible region of the Brillouin zone which in our case is the prism bounded by the planes  $\Gamma$ ALM,  $\Gamma$ MK,  $\Gamma$ KHA and  $\Gamma$ ALH. It is, however, more convenient to consider a zone of twice this volume. This particular choice makes it easier to divide the zone into exactly equal meshes. The secular





Dispersion relations for phonons in magnesium along  $\Gamma M$  and  $\Gamma A$ . The solid points were obtained using the triple-axis spectrometer while the open points were observed using the "window filter" spectrometer. The broken lines are calculations based on a four-neighbour A-S model. The solid lines are the least squares fit assuming a four-neighbour T-F model.

determinant was solved for 3512 points in this enlarged zone (which is 1/12th the Brillouin zone). The frequencies obtained were then sorted in frequency intervals of  $\Delta \nu = 0.075 \times 10^{12}$  c/s after weighting the surface points appropriately. The calculations were performed in a CDC-3600 computer and the results are shown in Fig. 6. Frequency distribution for magnesium has been computed earlier by SLUTSKY and GARLAND [25] and YOUNG and KOPPEL [26]. The parameters used by these authors do not give a good fit to our neutron data. In particular the cut-off frequency (corresponding to the higher of the two q = 0 frequencies) is not given correctly. We believe, therefore, that our frequency distribution is closer to the actual situation than those calculated by the above-mentioned authors. It should be possible to derive an even more reliable frequency distribution using the fourneighbour T-F model which as we have seen earlier gives a better fit to our data than the four-neighbour A-S model. This unfortunately could not be done as it was not possible to deduce all the force constants from our neutron data.

Consideration will now be given to the comparative features of the dispersion relations in beryllium, magnesium and zinc. It is known from the elasto-kinetic equations that the velocity for the propagation of transverse elastic waves along the c-direction is the same as the velocity for transverse waves propagating in the basal plane having their polarization vector perpendicular to the basal plane. It is interesting to see to what extent this similarity holds in the dispersive region. Figure 7 shows the dispersion relations for the [0001] and [0110] TA branches in beryllium, magnesium and zinc. The results for beryllium were taken from the work of SCHMUNK et al. [1], and those for zinc from the work of BORGONOVI et al.



Frequency distribution for magnesium calculated according to the four-neighbour A-S model.



Fig. 7

Dispersion relations for [0001] and [0110] TA perpendicular branches in beryllium, magnesium and zinc

[2]. In all cases, a smooth line has been drawn through the experimental points. It is observed that in all three metals, the phonons in the two branches considered have similar frequencies, the maximum difference being of the order of 10%. In magnesium the dispersion begins half way to the zone boundary. In beryllium and zinc, however, the dispersion occurs much earlier.

The behaviour of the two transverse branches in the  $[01\overline{1}0]$  direction is also interesting. The dispersion relations for these branches for mag-



Fig. 8

Dispersion relations for TA parallel and TA perpendicular branches along the [0110] direction in magnesium and zinc

nesium and zinc are shown in Fig. 8. In magnesium the velocities of sound for the two transverse modes is very nearly the same. This similarity extends to the dispersive region also, though not quite to the same extent. This is in striking contrast to the situation in zinc. No comparison with beryllium has been made as data for the TA parallel branch is not available. It is clear from this discussion that homology between these metals does not exist. This lack of homology suggests that the nature of the interatomic forces in these substances must be quite different.

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### APPENDIX

The following notation will be used for the symmetry operations:

E - identity operation

 $C_n(\xi)$  - n-fold rotation about the axis

- $S_n(\xi)$  n-fold rotation-inversion axis
- i inversion through the origin
- σ<sub>h</sub> horizontal minor plane

σv(ξ))

- vertical minor planes containing the axis  $\xi$   $\sigma_d(\xi)$ 

 $\vec{t}$  - non-primitive translation.

In terms of the above notation, the basic symmetry operations for the hcp lattice are (cf. Fig. 1 for the various axes)



The Z-axis is perpendicular to the plane of the paper.

| {E 0}                                 | $\{c_2(2) 0\}$                        | {i  <b>ī</b> }                                     | $\{\sigma_{d}(2) \vec{t}\}$                    |
|---------------------------------------|---------------------------------------|--|--|
| $\left\{ c_{2}(z)   \vec{t} \right\}$ | $\{c_2(3) 0\}$                        | {a <sub>h</sub>  0}                                | $\{\sigma_{d}(3) \vec{t}\}$                    |
| $\{c_3(z), c_3^{-1}(z) \mid 0\}$      | $\left\{c_2(4)   \vec{t}\right\}$     | $\left\{S_{6}(z), S_{6}^{-1}(z)   \vec{t}\right\}$ | $\{\sigma_v(4) \mid 0\}$                       |
| $\{c_6(z), c_6^{-1}(z) \vec{t}\}$     | $\left\{ c_{2}(5)   \vec{t} \right\}$ | $\left\{ S_{3}(z), S_{3}^{-1}(z) \mid 0 \right\}$  | $\left\{\sigma_{\mathbf{v}}^{(5)}   0\right\}$ |
| $\{c_2(1) 0\}$                        | $\left\{c_{2}(6) \vec{t}\right\}$     | $\left\{ \sigma_{d}(1) \middle  \vec{t} \right\}$  | $\{\sigma_{\mathbf{v}}^{(6)} 0\}$              |

# CHARACTER TABLE FOR $\Sigma$

| Rep. | {E 0} | $\{c_2(2) 0\}$ | { <b>0</b> } | {σ <sub>v</sub> (4) 0} | n <sub>j</sub> |
|------|-------|----------------|--------------|------------------------|----------------|
| Σ1   | 1     | 1              | 1            | . 1                    | 2              |
| Σ2   | 1     | 1              | - 1          | - 1                    | 0              |
| Σ3   | 1     | - 1            | -1           | • 1                    | 2              |
| Σ4   | 1     | - 1            | . 1          | - 1                    | 2              |
| χ(R) | 6     | - 2            | 2            | 2                      |                |

| Rep.           | {E  0} | $\left\{ c_{2}(4) \middle  \overrightarrow{t} \right\}$ | {ơ <sub>h</sub>   0} | $\{\sigma_{d}^{(2)} \vec{t}\}$ | n <sub>j</sub> |
|----------------|--------|---|----------------------|--------------------------------|----------------|
| T <sub>1</sub> | 1      | 1   | 1                    | 1                              | 2              |
| T <sub>2</sub> | 1      | 1   | -1                   | - 1                            | 1              |
| T <sub>3</sub> | · 1    | - 1   | - 1                  | 1                              | 1              |
| T <sub>4</sub> | 1      | - 1   | 1                    | - 1                            | 2              |
| χ(R)           | 6      | 0   | 2                    | 0                              |                |

CHARACTER TABLE FOR T

CHARACTER TABLE FOR M

| Rep.                        | {E 0} | $\left\{c_{2}(z) \vec{t}\right\}$ | {c <sub>2</sub> (2) 0} | $\left\{ c_{2}(4) \middle  \vec{t} \right\}$ | {i  ī} | {\\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ | {o <sub>d</sub> (2)  t} | $\left\{\sigma_{\mathbf{v}}^{(4)} \middle  0 \right\}$ | nj |
|-----------------------------|-------|-----------------------------------|------------------------|--|--------|---|-------------------------|--|----|
| M <sup>+</sup> <sub>1</sub> | 1     | 1                                 | 1                      | 1  | 1      | 1                                       | 1                       | 1  | 1  |
| M <sup>+</sup> <sub>2</sub> | 1     | - 1                               | 1                      | -1   | 1      | -1                                      | 1                       | - 1  | 0  |
| M <sub>3</sub> <sup>+</sup> | 1     | - 1                               | - 1                    | 1  | 1      | -1                                      | - 1                     | 1  | 1  |
| M <sup>+</sup> 4            | 1     | 1                                 | -1                     | -1   | 1      | 1                                       | -1                      | -1   | 1  |
| M_1                         | 1     | 1                                 | 1                      | 1  | - 1    | - 1                                     | - 1                     | -1   | 0  |
| M_2                         | 1     | - 1                               | 1                      | - 1  | - 1    | 1                                       | -1                      | 1  | 1  |
| M <sub>3</sub>              | 1     | - 1                               | -1                     | 1  | - 1    | 1                                       | 1                       | -1   | 1  |
| M_4                         | 1     | 1                                 | - 1                    | ~1   | - 1    | -1                                      | 1                       | 1  | 1  |
| χ(R)                        | 6     | 0                                 | - 2                    | 0  | 0      | 2                                       | 0                       | 2  |    |

| Rep.           | {E]0} | {c <sub>3</sub> (z) 0} | $\{c_3^{-1}(z) 0\}$ | $\left\{ c_{2}^{}(4) \middle  \overrightarrow{t} \right\}$ | $\left\{ c_{2}^{(5)}   \vec{t} \right\}$ | $\left\{c_2(6) \vec{t}\right\}$ | {o <sub>h</sub>  0} | {S <sub>3</sub> (z) 0} | $\{S_3^{-1}(z) 0\}$ | $\{\sigma_{d}(1) \vec{t}\}$ | $\left\{\sigma_{d}^{(2)} \vec{t}\right\}$ | $\{\sigma_{d}(3) \vec{t}\}$ | n <sub>j</sub> |
|----------------|-------|------------------------|---------------------|--|--|---------------------------------|---------------------|------------------------|---------------------|-----------------------------|---|-----------------------------|----------------|
| к,             | 1     | ω²                     | ω                   | 1  | ω²                                       | ω                               | 1                   | ω                      | ω²                  | ω                           | 1   | ω <sup>2</sup>              | 1              |
| K2             | 1     | ω²                     | ω                   | - 1  | - ω²                                     | - ω                             | 1                   | ω                      | ω²                  | -ω                          | - 1                                       | - ω²                        | 1              |
| Кs             | 1     | ω²                     | ω                   | 1  | ω²                                       | ω                               | - 1                 | - <i>w</i>             | - ω²                | -ω                          | - 1                                       | - ω²                        | 0              |
| к₄             | 1     | $\omega^2$             | ω                   | - 1  | - ω²                                     | - <i>w</i>                      | - 1                 | <b>-</b> ω             | - ω²                | ω                           | 1   | ω²                          | 0              |
| Кs             | 2     | -ω²                    | - ω                 | 0  | o  | 0                               | 2                   | -ω                     | - ω²                | 0                           | 0   | 0                           | 1              |
| K <sub>6</sub> | 2     | - ω²                   | ΄-ω                 | 0  | o  | o                               | - 2                 | ω                      | ω²                  | . 0                         | 0   | 0                           | 1              |
| X(R)           | 6     | 0                      | 0                   | 0  | 0  | 0                               | 2                   | - 4                    | - 4                 | 0                           | 0   | 0                           |                |

# CHARACTER TABLE FOR K

# LATTICE DYNAMICS OF MAGNESIUM

| Rep.           | {E 0} | $\left\{ c_{2}(z) \middle  \overrightarrow{t} \right\}$ | $c_{3}(z) 0\}$<br>$c_{3}^{-1}(z) 0\}$ | $\left\{ c_{6}\left(z\right) \middle  \vec{t} \right\}$ $\left\{ c_{6}^{-1}(z) \middle  \vec{t} \right\}$ | $ \{c_{2}(1) \mid 0\} \\ \{c_{2}(2) \mid 0\} \\ \{c_{2}(3) \mid 0\} $ | $ \{c_{2}(4)   \vec{t}\} $ $ \{c_{2}(5)   \vec{t}\} $ $ \{c_{2}(6)   \vec{t}\} $ | {i   t} | {o <sub>h</sub>  0} | $ \{S_6(z)   \vec{t} \} $ $ \{S_6^{-1}(z)   \vec{t} \} $ | $ \{ S_{3}(z)   0 \} \\ \{ S_{3}^{-1}(z)   0 \} $ | $\begin{aligned} & \left\{ \sigma_{d}(1)  \middle   \vec{t} \right\} \\ & \left\{ \sigma_{d}(2)  \middle   \vec{t} \right\} \\ & \left\{ \sigma_{d}(3)  \middle   \vec{t} \right\} \end{aligned}$ | $\{\sigma_{v}(4)  0\}$<br>$\{\sigma_{v}(5)  0\}$<br>$\{\sigma_{v}(6)  0\}$ | nj |
|----------------|-------|---|---------------------------------------|---|---|--|---------|---------------------|--|---|---|--|----|
| A1.            | 2     | 0   | 2                                     | 0 .   | 0   | 0  | 0       | 0                   | 0  | 0   | 0   | 2  | 1  |
| A <sub>2</sub> | 2     | 0   | 2                                     | 0   | 0   | 0  | 0       | 0                   | 0  | 0   | 0   | - 2  | 0  |
| Å <sub>3</sub> | A     | .0  | - 2                                   | 0   | 0   | 0  | 0       | 0                   | 0  | 0   | 0   | 0  | 1  |
| χ(R)           | 6     | 0   | 0                                     | . 0   | - 2   | 0  | 0       | 2                   | 0  | - 4   | 0   | 2  |    |

CHARACTER TABLE FOR A

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<u>.</u>

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### DISCUSSION

G. DOLLING: Contrary to your statement in the oral presentation, there appears to be no experimental basis for rejecting the A-S model of Wolfram et al. on the grounds that the TA parallel and TA perpendicular curves fail to become degenerate until very small wave vectors are reached. The "elastic constant" region of degeneracy need not extend beyond  $q \approx 0.01$ , say, and the neutron results are confined to  $q \ge 0.6$ . After all, no one knows what happens in the intermediate region. Your other reasons for rejecting the A-S model are more convincing.

A.P. ROY: I agree that departure from the velocity-of-sound slope is a secondary consideration. However, in magnesium one expects the dispersion to start for rather larger values of q, as is clearly the case with propagation in the c-direction.

R. SRINIVASAN: Collins has measured the dispersion relations in magnesium and has found that forces up to fourth neighbours give a good fit to experimental data. The forces between the first twelve neighbours are predominantly central. How do Collins' results compare with those you presented?

A.P. ROY: Collins' experimental data are meagre, although they agree with ours within the limits of experimental error. However, the force constants derived by him do not fit all our neutron data.

# LATTICE DYNAMICS OF THE HEXAGONAL CLOSE-PACKED STRUCTURE

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### (Presented by B. Buras)

### Abstract — Résumé — Аннотация — Resumen

LATTICE DYNAMICS OF THE HEXAGONAL CLOSE-PACKED STRUCTURE, Lattice dynamics of hexagonal close-packed (hcp) structures, using the Born-von Kármán approach and assuming interactions with any number of interacting neighbours, were calculated. The general properties of a dynamical matrix, coming from the symmetry of hcp structure, have been established.

Using the operations of a point group of the symmetry group of hcp structure, the families of equivalent, equidistant lattice points and their force matrices have been evaluated. This permitted the calculation of the elements of the Fourier transform of the dynamical matrix,

Using the long waves procedure, the general formulas for elastic constants expressed by elements of a dynamical matrix have been obtained. The phonon dispersion relations have also been evaluated, by a factorization of a secular equation of a problem. In the course of the work a nomenclature convenient for further analysis of formulas obtained has been used.

DYNAMIQUE DE RÉSEAU DES STRUCTURES HEXAGONALES COMPACTES. L'auteur a calculé, par la méthode de Born et von Kármán, la dynamique de réseau des structures hexagonales compactes en supposant que des interactions se produisent avec un nombre quelconque d'atomes voisins. Il a déterminé les propriétés générales d'une matrice dynamique découlant de la symétrie d'une structure très compacte,

En utilisant les opérations d'un groupe ponctuel du groupe de symétrie des structures hexagonales compactes, l'auteur a évalué les familles de points du réseau équivalents et équidistants ainsi que les matrices de forces correspondantes. Ceci a permis d'obtenir les éléments de la transformée de Fourier de la matrice dynamique.

L'auteur a obtenu, par la méthode des grandes ondes, les formules générales des constantes d'élasticité exprimées en fonction d'éléments d'une matrice dynamique. Les relations de dispersion des phonons ont été aussi mesurées, par factorisation d'une équation séculaire d'un problème. Au cours de ces travaux, l'auteur a utilisé une nomenclature destinée à faciliter l'analyse ultérieure des formules obtenues.

ДИНАМИКА РЕШЕТКИ С ГЕКСАГОНАЛЬНОЙ СТРУКТУРОЙ С ПЛОТНОЙ УПАКОВКОЙ. Произведен расчет динамики решетки с гексагональной структурой с плотной упаковкой в приближении Борна-фон Кармана, причем предполагалось, что взаимодействия происходят с любым числом взаимодействующих соседних атомов. Определены общие свойства динамической матрицы, возникающие на основе симметрии гексагональной структуры с плотной упаковкой.

Произведена оценка семейств эквивалентных, эквидистанционных узлов решетки и их силовых матриц с помощью операций точечной группы симметрии гексагональной структуры с плотной упаковкой. Это позволило получить элементы преобразования динамической матрицы по методу Фурье.

С помощью метода длинных волн получены общие формулы для упругих константов, выраженных элементами динамической матрицы. Произведена также оценка фононных дисперсионных соотношений при помощи разложения векового уравнения задачи. В ходе работы использовалась номенклатура, которая подходит для дальнейшего анализа полученных формул.

DINÁMICA RETICULAR DE LA ESTRUCTURA HEXAGONAL COMPACTA. El autor ha calculado, con arreglo al método de Born-von Kármán, la dinámica reficular de la estructura hexagonal, suponiendo interacciones en las que participa cualquier número de átomos vecinos. Seguidamente ha establecido las propiedades generales de una matriz dinámica, derivadas de la simetría de la estructura hexagonal compacta. Mediante operaciones con un sistema puntiforme del grupo de simetría de la estructura hexagonal compacta, ha determinado las familias de puntos reticulares equivalentes y equidistantes, así como sus matrices de fuerza. Ello permitió calcular los elementos de la transformada de Fourier correspondiente a la matriz dinámica.

Ha obtenido, por el procedimiento basado en las ondas largas, las fórmulas generales para las constantes de elasticidad expresadas por elementos de una matriz dinámica. También ha evaluado las relaciones de dispersión fonónica, por factoreo de la ecuación característica de un problema. El autor ha utilizado en su trabajo una nomenclatura apropiada para un análisis más detenido de las fórmulas obtenidas.

### INTRODUCTION

Normal vibrations of the hexagonal close-packed (hcp) structure were first treated by BEGBIE [1], assuming interactions with two nearest neighbours. Afterwards several papers were published, dealing with the subject in the approximation of three, four and five neighbours [2-5].

In this paper the general form of the Fourier transform of the dynamical matrix of the Born-von Kármán theory, assuming interactions of every atom with any number of its neighbours and the form of elastic constants in this case, is elaborated. From the methodological point of view this work is a straightforward generalization of Begbie's procedure. The notation how-ever, for the sake of simplicity, was partly changed from that used by Begbie.

To the best knowledge of the author this kind of general treatment has been carried out only for cubic structures [6].

### GENERAL THEORY

1

ŧ.

Let us consider the lattice-like system of atoms in the adiabatic and harmonic approximation and assume that the motion of the system can be described by a potential  $\phi$ , which is a function of nuclei co-ordinates and has the same symmetry as the system. Under these assumptions the equations of motion are [7]

$$m_{k} \ddot{u}_{\alpha} \begin{pmatrix} l \\ k \end{pmatrix} + \sum_{\beta l' k'} \phi_{\alpha\beta} \begin{pmatrix} l' - l \\ k k' \end{pmatrix} u_{\beta} \begin{pmatrix} l \\ k' \end{pmatrix} = 0, \qquad (1)$$

or in more convenient form (see Table I for notation)

$$\ddot{\mathbf{v}}_{\alpha}\left(\begin{smallmatrix}1\\k\end{smallmatrix}\right) + \sum_{\boldsymbol{\beta}l'k'} \mathbf{D}_{\alpha\boldsymbol{\beta}}\left(\begin{smallmatrix}l'-1\\kk'\end{smallmatrix}\right) \mathbf{v}_{\boldsymbol{\beta}}\left(\begin{smallmatrix}l'\\k\end{smallmatrix}\right) = 0.$$
(2)

The dynamical matrix  $D_{\alpha\beta}(k)$  fulfils the relation

$$D_{\alpha\beta}(\frac{1}{kk'}) = D_{\beta\alpha}(\frac{-1}{k'k'}).$$
(3)

### TABLE I

NOMENCLATURE

| <b>r</b> (1)  | position of a primitive cell   |
|---|--|
| r(k)  | position of atom k in a primitive cell                                       |
| $\vec{r}(^1_k)$   | $=\vec{r}(l)+\vec{r}(k)$ , its Cartesian components - $x_{\alpha}(l_{k})$    |
| <u>u</u> ( <sup>1</sup> <sub>k</sub> )  | displacement vector of an atom in position $\vec{r}(\frac{1}{k})$            |
| √( <sup>1</sup> <sub>k</sub> )  | $=\sqrt{m_k}\vec{u}(\frac{1}{k})$  |
| Φ   | a potential, being a function of nuclei co-ordinates                         |
| $\Phi_{\alpha\beta} \begin{pmatrix} 1'-1\\kk' \end{pmatrix} = \partial^2 \Phi / \partial x_{\alpha} \begin{pmatrix} 1\\k \end{pmatrix} \partial x_{\beta} \begin{pmatrix} 1\\k \end{pmatrix}$ | elements of force matrix (atomic force constants)                            |
| $\mathbb{D}_{\alpha\beta}\left(\frac{l'-1}{kk'}\right) = (m_k m_k \cdot)^{-\frac{1}{2}} \Phi_{\alpha\beta}\left(\frac{l'-1}{kk'}\right)$  | elements of dynamical matrix   |
| <b>ṽ(k),</b> ₩̃(k)  | polarization vectors of the k-th atom  |
| $\omega, \vec{q}$   | angular frequency and wave vector, respectively                              |
| (0) (1) (2)<br>$C_{\alpha\beta}, C_{\alpha\beta}, C_{\alpha\beta}$  | elements of the power expansion of $C_{\alpha\beta}(q \   kk')$ in $\vec{q}$ |
| $(\vec{0})$ $(\vec{1})$ $(\vec{2})$ $W(k)$ , $W(k)$ , $W(k)$  | elements of the power expansion of $\vec{W}(k)$ in $\vec{q}$                 |
| ρ   | density of the crystal   |
| $ ho_{ m N}$ and $ ho_{ m N}$   | weight factors in s and S sub-spaces, respectively                           |

The solutions of Eq.(2), which are expected to be plane waves can be written in two forms

$$v_{\alpha}({}^{l}_{k}) = V_{\alpha}(k) e^{-i\omega t} e^{2\pi i \overrightarrow{qr}(l)}$$
 (4)

$$\mathbf{v}_{\alpha}(\mathbf{k}^{1}) = \mathbf{W}_{\alpha}(\mathbf{k}) \, \mathbf{e}^{\mathbf{i}\,\omega\,\mathbf{t}} \, \mathbf{e}^{2\pi\mathbf{i}\,\overrightarrow{\mathbf{q}\,\overrightarrow{\mathbf{t}}}(\mathbf{k}^{1})}.$$
(5)

Then one obtains

$$\omega^{2} V_{\alpha} (\mathbf{k}) = \sum_{\beta \mathbf{k}'} D_{\alpha\beta} (\mathbf{q} | \mathbf{k} \mathbf{k}') V_{\beta} (\mathbf{k}')$$
(6)

and .

$$\omega^{2} W_{\alpha} (\mathbf{k}) = \sum_{\beta \mathbf{k}'} C_{\alpha\beta} (\mathbf{q} | \mathbf{k}\mathbf{k}') W_{\beta} (\mathbf{k}'), \qquad (7)$$

where

$$C_{\alpha\beta}(q|kk') = D_{\alpha\beta}(q|kk') e^{-2\pi i \vec{q} \cdot [\vec{r}(k) - \vec{t}(k')]}$$
(8)

,

and  $D_{\alpha\beta}(q|kk')$  is the Fourier representation of the dynamical matrix

$$D_{\alpha\beta} \left( q \left| kk' \right) = \sum_{l} D_{\alpha\beta} \left( \frac{l}{kk'} \right) e^{-2\pi i \, \vec{q} \cdot \vec{t} \, (l)} \,. \tag{9}$$

As a condition for the solution of Eq. (6) one has

$$\left| D_{\alpha\beta}(\mathbf{q} | \mathbf{k}\mathbf{k}') - \omega^2 \, \delta_{\mathbf{k}\mathbf{k}'} \delta_{\alpha\beta} \right| = 0 \ . \tag{10}$$

Solutions with respect to  $\omega$  give phonon dispersion relations. The aboveoutlined scheme is quite general and can be used for any structure.

Let us consider a more specific problem, i.e. the dynamics of the hcp structure.

### SYMMETRY PROPERTIES OF THE HCP STRUCTURE

The hcp structure is given by a simple hexagonal lattice with two atoms in the primitive cell. We can look on it as two identical sub-lattices, one shifted with respect to the other. Quite arbitrarily, we fix the origin of the co-ordinate system at one of the atoms. Atoms belonging to the same sublattice as the atom in the origin will be indexed by "1", those belonging to the other sub-lattice by "2". The pattern of the hcp structure and the shape of a primitive cell is shown in Fig.1. Lattice points are given by:

$$\vec{r}(n) = k\vec{a} + l\vec{b} + m\vec{c}$$
(11)

or in the Cartesian co-ordinates

$$\vec{r}(n) = \frac{a}{2} [(21 - k)\vec{i} - \sqrt{3}k\vec{j}] + c m \vec{k}.$$
 (12)

The positions of atoms of the first sub-lattice are just  $\vec{r}$  (n), and positions of atoms of the second sub-lattice are marked  $\vec{R}(N)$ ,

$$\vec{R}(N) = \frac{a}{2} \left[ (2L-K)\vec{i} - \sqrt{3} \left( K + \frac{2}{3} \right) \vec{j} \right] + c(M + \frac{1}{2})\vec{k}.$$
(13)

To find the lattice vectors of the latter, we subtract the vector  $\vec{r}(2, 1)$ , describing the position of an atom 2 in the primitive cell, from the vectors of the first sub-lattice.

The symmetry group of the hcp structure can be generated by three primitive operations. We shall use the symbol  $\{\hat{T} | \vec{t} \}$ , where  $\hat{T}$  is the rotational and  $\vec{t}$  the translational part of an operation. We have

(a) A six-fold axis of rotational inversion - the z-axis.

$$\hat{\mathbf{T}} = \hat{\mathbf{T}}_{\mathbf{r}} = \begin{bmatrix} -1/2 & -3/2 & 0\\ 3/2 & -1/2 & 0\\ 0 & 0 & -1 \end{bmatrix}, \quad \vec{\mathbf{t}} = 0.$$
(14)



The projection of the hexagonal close-packed structure on the basal z=0 plane

k=2 ---- z=0
 k=1 ----- z=±c/2

(b) A two-fold axis of rotation - the y-axis

$$\hat{\mathbf{T}} = \hat{\mathbf{T}}_{u} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \vec{t} = 0.$$
(15)

(c) A glide plane, consisting of reflection in the y = 0 plane and translation with vector  $\vec{r}(2, 1)$ , i.e.

$$\hat{T} = \hat{T}_g = -\hat{T}_u, \ \vec{t} = \vec{r} (2, 1).$$
 (16)

Let us suppose an atom in the position  $\vec{r}$  has the matrix  $\hat{D}$ . If symmetry operation  $\{\hat{T}|\hat{t}\}$  transforms vector  $\vec{r}$  into  $\vec{r'}$ 

$$\vec{r}' = \hat{T}\vec{r} + \vec{t} \tag{17}$$

then matrix  $\hat{D}'$  connected with  $\vec{r}'$  is given by [8]

$$\hat{D}' = \hat{T} \hat{D} \hat{T}$$
. (18)

Let us set up the following symmetry operation:

$$\{\hat{\mathbf{T}}_{i}|\vec{\mathbf{t}}\} = \{\hat{\mathbf{T}}_{u}|\vec{\mathbf{0}}\}\{\hat{\mathbf{T}}_{g}|\vec{\mathbf{r}}(2,1)\} = \{\hat{\mathbf{T}}_{u}\hat{\mathbf{T}}_{g}|\hat{\mathbf{T}}_{u}\vec{\mathbf{r}}(2,1)\} .$$
(19)

As the glide plane transforms the sub-lattice 1 into the sub-lattice 2 and  $\underline{vice}$  versa, we have

$$D_{\alpha\beta}(\frac{1}{kk}) = \hat{T}_{i} D_{\alpha\beta}(\frac{-1}{k'k}) \quad \tilde{T}_{i} = D_{\alpha\beta}(\frac{-1}{k'k})$$
(20)

$$D_{\alpha\beta}\begin{pmatrix}1\\11\end{pmatrix} = D_{\alpha\beta}\begin{pmatrix}-1\\22\end{pmatrix}; \quad D_{\alpha\beta}\begin{pmatrix}1\\12\end{pmatrix} = D_{\alpha\beta}\begin{pmatrix}-1\\21\end{pmatrix}.$$
(21)

Including Eq.(3), one has

$$D_{\alpha\beta}(\frac{1}{12}) = D_{\beta\alpha}(\frac{1}{12}), \qquad (22)$$

i.e. matrices  $D_{\alpha\beta}(12)$  are symmetric.

Let us write the matrix  $D_{\alpha\beta}({}^1_{11})$  as a sum of a symmetric and antisymmetric part

$$D_{\alpha\beta}(\frac{1}{11}) = D_{\alpha\beta}^{s}(\frac{1}{11}) + D_{\alpha\beta}^{a}(\frac{1}{11}).$$
 (23)

Comparing Eqs. (3) and (22) one obtains

$$D_{\alpha\beta}^{s} \begin{pmatrix} 1\\11 \end{pmatrix} + D_{\alpha\beta}^{a} \begin{pmatrix} 1\\11 \end{pmatrix} = D_{\alpha\beta}^{s} \begin{pmatrix} -1\\11 \end{pmatrix} - D_{\alpha\beta}^{a} \begin{pmatrix} -1\\11 \end{pmatrix} = D_{\alpha\beta}^{s} \begin{pmatrix} 1\\22 \end{pmatrix} - D_{\alpha\beta}^{a} \begin{pmatrix} 1\\22 \end{pmatrix} .$$
(24)

Operations { $\hat{T} \mid \vec{0}$ } acting on a vector generate other vectors of the same length. In this way one obtains the family of equidistant structure points. Their force matrices  $\phi_{\alpha\beta}$  ( $_{kk'}$ ) (or  $D_{\alpha\beta}$  ( $_{kk'}$ ) matrices) can be obtained by transformation of the matrix (see Eq.(18)) corresponding to the mentioned vector. In the case of the hcp structure there are 12 vectors of that kind. We know however, that in the sub-lattice 1 for every vector  $\vec{r}$  (n) there exists also a lattice vector  $\vec{r}$  (-n) =  $\vec{r}$  (n) and its matrix is given by Eq.(24). For these reasons we shall formally include the "inversion" points in families of equidistant points in sub-lattice 1, i.e. we shall treat them as consisting, in the general case of 24 points.

The matrix  $D_{\alpha\beta}(\frac{n}{11})$  for a general vector  $\vec{r}(n)$  we mark  $d_{\alpha\beta}(n)$ 

$$m_{1}d_{\alpha\beta}(n) \equiv \phi_{\alpha\beta}(_{11}^{n}) = -\begin{bmatrix} a_{n} & f_{n} & e_{n} \\ f_{n} & b_{n} & d_{n} \\ e_{n} & d_{n} & g_{n} \end{bmatrix} - \begin{bmatrix} 0 & f_{n}^{a} & e_{n}^{a} \\ -f_{n}^{a} & 0 & d_{n}^{a} \\ -e_{n}^{a} & -d_{n}^{a} & 0 \end{bmatrix}$$
(25)

The matrix  $D_{\alpha\beta}(\frac{N}{12})$ (symmetric) for a general vector  $\vec{R}(N)$  is marked by  $D_{\alpha\beta}(N)$ 

$$m_{1}D_{\alpha\beta}(N) \equiv \phi_{\alpha\beta}(N) = - \begin{bmatrix} A_{N} & F_{N} & E_{N} \\ F_{N} & B_{N} & D_{N} \\ E_{N} & D_{N} & G_{N} \end{bmatrix}.$$
 (26)

Symbols n and N stay for triples of indices k, l, m and K, L, M, respectively.

### GENERATION OF LATTICE VECTORS AND FORCE MATRICES

We are interested in setting up the families of equally distant points. This can be done by  $\{T | \vec{0}\}$  operations only. There are in this case twelve rotations that may be expressed by the matrices

$$\hat{\mathbf{T}}^{\mu\nu} = (\hat{\mathbf{T}}_{u})^{\mu} (\hat{\mathbf{T}}_{r})^{\nu} \text{ for } \nu = 0, 1, 2, 3, 4, 5$$
(27)

We mark other vectors generated by them as follows:

$$\vec{r}^{\mu\nu}(n) = \hat{T}^{\mu\nu} \vec{r}(n)$$
 (28)

$$\vec{R}^{\mu\nu}(N) = \hat{T}^{\mu\nu} \vec{R}(N)$$
 (29)

We distinguish them from lattice vectors of  $\vec{R}^{\mu\nu}$  (N) points.

$$\vec{r}^{\mu\nu}(N) = \vec{R}^{\mu\nu}(N) - \vec{r}(2,1)$$
 (30)

Similarly,

$$\hat{d}^{\mu\nu}(n) = \hat{T}^{\mu\nu} \hat{d}(n) \hat{T}^{\mu\nu}$$
(31)

$$\hat{\mathbf{D}}^{\mu\nu} = \hat{\mathbf{T}}^{\mu\nu} \hat{\mathbf{D}}(\mathbf{N}) \hat{\mathbf{T}}^{\mu\nu} . \tag{32}$$

### FOURIER TRANSFORM OF THE DYNAMICAL MATRIX

To ensure that every vector comes into calculations only once, we set up the sub-spaces, generating uniquely all vectors of the structure by symmetry operations. These are (see Fig. 2)



Generating sub-spaces

(a) Sub-space s for  $\vec{r}(n)$  vectors:

$$y \ge \sqrt{3} x \ge 0$$
;  $z \ge 0$ , i.e.  $21 \ge k$ ;  $1 \le 0$ ;  $m \ge 0$ . (33)

(b) Sub-space S for  $\vec{R}(N)$  vectors:

$$y \ge \frac{x}{\sqrt{3}} \ge 0; z \ge 0, i.e. 2L \ge K; L+K \le -1; M \ge 0.$$
 (34)

Points of the sub-spaces do not repeat themselves under the  $\{\hat{T} \mid \vec{0}\}$  operations, with the exception perhaps of the points situated on the limitations of sub-

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spaces (this is discussed later.). The shape of the sub-space s is given by the "inversion" properties of the sub-lattice 1 that has been discussed earlier. Using once more these properties and Eqs. (22) and (24), the Fourier transform of the dynamical matrix is given as follows:

$$D_{\alpha\beta}(\mathbf{q} \mid \mathbf{11}) \equiv d_{\alpha\beta}(\mathbf{q}) = 2 \sum_{\substack{n \in s \\ \mu, \nu}} [\rho_n d_{\alpha\beta}^{s,\mu\nu}(n) \cos(2\pi \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}^{\mu\nu}(n))] - 2i \sum_{\substack{n \in s \\ \mu, \nu}} [\rho_n d_{\alpha\beta}^{a,\mu\nu}(n) \sin(2\pi \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}^{\mu\nu}(n))]$$
(35)

$$D_{\alpha\beta}(q|12) \equiv D_{\alpha\beta}(q) = \sum_{\substack{N \in S \\ \mu, \nu}} \left[ \rho_N D_{\alpha\beta}^{\mu\nu}(N) \exp\left(-2\pi \, i \vec{q} \cdot \vec{r}^{\mu\nu}(N)\right) \right]$$
(36)

$$D_{\alpha\beta}(q|11) = D^*_{\beta\alpha}(q|11) = D^*_{\alpha\beta}(q|22)$$
(37)

$$D_{\alpha\beta}(q|12) = D_{\beta\alpha}(q|12) = D_{\alpha\beta}^{*}(q|21)$$
. (38)

Matrices  $d_{\alpha\beta}(n)$  are written explicitly below. Matrices  $D_{\alpha\beta}(N)$  are not presented explicitly, but their form is exactly the same as the symmetric part of  $d_{\alpha\beta}(n)$ , written in capital letters (see Eqs. 25 and 26).

$$m_{1}d_{\alpha\beta}^{00}(n) = -\begin{bmatrix} a_{n} & f_{n} & e_{n} \\ f_{n} & b_{n} & d_{n} \\ e_{n} & d_{n} & g_{n} \end{bmatrix} - \begin{bmatrix} 0 & f_{n}^{a} & e_{n}^{a} \\ -f_{n}^{a} & 0 & d_{n}^{a} \\ -e_{n}^{a} & -d_{n}^{a} & 0 \end{bmatrix}$$

$$m_{1}d_{\alpha\beta}^{10}(n) = -\begin{bmatrix} a_{n} & -f_{n} & e_{n} \\ -f_{n} & b_{n} & -d_{n} \\ e_{n} & -d_{n} & g_{n} \end{bmatrix} - \begin{bmatrix} 0 & -f_{n}^{a} & e_{n}^{a} \\ f_{n}^{a} & 0 & -d_{n}^{a} \\ -e_{n}^{a} & d_{n}^{a} & 0 \end{bmatrix}$$

$$m_{1}d_{\alpha\beta}^{03}(n) = -\begin{bmatrix} a_{n} & f_{n} & -e_{n} \\ f_{n} & b_{n} & -d_{n} \\ -e_{n} & -d_{n} & g_{n} \end{bmatrix} - \begin{bmatrix} 0 & f_{n}^{a} & -e_{n}^{a} \\ -f_{n}^{a} & 0 & -d_{n}^{a} \\ -f_{n}^{a} & 0 & -d_{n}^{a} \\ e_{n}^{a} & d_{n}^{a} & 0 \end{bmatrix}$$

$$m_{1}d_{\alpha\beta}^{13}(n) = -\begin{bmatrix} a_{n} & -f_{n} & -e_{n} \\ -f_{n} & b_{n} & d_{n} \\ -e_{n} & d_{n} & g_{n} \end{bmatrix} - \begin{bmatrix} 0 & -f_{n}^{a} & -e_{n}^{a} \\ -f_{n}^{a} & 0 & -d_{n}^{a} \\ e_{n}^{a} & -d_{n}^{a} & 0 \end{bmatrix}$$
(39)

$$\begin{split} \mathbf{m}_{1} \mathbf{d}_{\alpha\beta}^{01}(\mathbf{n}) &= - \begin{bmatrix} \frac{1}{4} \mathbf{a}_{n} + \frac{\sqrt{3}}{2} \mathbf{f}_{n} + \frac{3}{4} \mathbf{b}_{n} & -\frac{\sqrt{3}}{4} \mathbf{a}_{n} - \frac{1}{2} \mathbf{f}_{n} + \frac{\sqrt{3}}{4} \mathbf{b}_{n} & \frac{1}{2} \mathbf{e}_{n} + \frac{\sqrt{3}}{2} \mathbf{d}_{n} \\ -\frac{\sqrt{3}}{4} \mathbf{a}_{n} - \frac{1}{2} \mathbf{f}_{n} + \frac{\sqrt{3}}{4} \mathbf{b}_{n} & \frac{3}{4} \mathbf{a}_{n} - \frac{\sqrt{3}}{2} \mathbf{f}_{n} + \frac{1}{4} \mathbf{b}_{n} & -\frac{\sqrt{3}}{2} \mathbf{e}_{n} + \frac{1}{2} \mathbf{d}_{n} \\ \frac{1}{2} \mathbf{e}_{n} + \frac{\sqrt{3}}{2} \mathbf{d}_{n} & -\frac{\sqrt{3}}{2} \mathbf{e}_{n} + \frac{1}{2} \mathbf{d}_{n} & \mathbf{g}_{n} \end{bmatrix} \\ & - \begin{bmatrix} 0 & \mathbf{f}_{n}^{4} & \frac{1}{2} \mathbf{e}_{n}^{4} + \frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} + \frac{1}{2} \mathbf{d}_{n}^{4} \\ -\mathbf{f}_{n}^{8} & 0 & -\frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} + \frac{1}{2} \mathbf{d}_{n}^{4} \\ -\frac{1}{2} \mathbf{e}_{n}^{4} - \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} & \frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} - \frac{1}{2} \mathbf{d}_{n}^{4} & 0 \end{bmatrix} \\ \mathbf{m}_{1} \mathbf{d}_{\alpha\beta}^{04}(\mathbf{n}) &= - \begin{bmatrix} \frac{1}{4} \mathbf{a}_{n} + \frac{\sqrt{3}}{2} \mathbf{f}_{n} + \frac{3}{4} \mathbf{b}_{n} & -\frac{\sqrt{3}}{4} \mathbf{a}_{n} - \frac{1}{2} \mathbf{f}_{n} + \frac{\sqrt{3}}{4} \mathbf{b}_{n} & -\frac{1}{2} \mathbf{e}_{n} - \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} \\ -\frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} - \frac{1}{2} \mathbf{d}_{n}^{4} - \frac{1}{2} \mathbf{d}_{n}^{4} - \frac{1}{2} \mathbf{e}_{n}^{4} - \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} \\ -\frac{1}{2} \mathbf{e}_{n}^{6} - \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} & \frac{\sqrt{3}}{2} \mathbf{e}_{n}^{6} - \frac{1}{2} \mathbf{d}_{n}^{6} & 0 \end{bmatrix} \\ \mathbf{m}_{1} \mathbf{d}_{\alpha\beta}^{04}(\mathbf{n}) &= - \begin{bmatrix} \frac{1}{4} \mathbf{a}_{n} + \frac{\sqrt{3}}{2} \mathbf{f}_{n} + \frac{\sqrt{3}}{4} \mathbf{b}_{n} & \frac{\sqrt{3}}{2} \mathbf{e}_{n} - \frac{1}{2} \mathbf{d}_{n} & \frac{\sqrt{3}}{2} \mathbf{e}_{n} - \frac{1}{2} \mathbf{d}_{n}^{3} \\ -\frac{1}{2} \mathbf{e}_{n} - \frac{\sqrt{3}}{2} \mathbf{d}_{n} & \frac{\sqrt{3}}{2} \mathbf{e}_{n} - \frac{1}{2} \mathbf{d}_{n} & \frac{\sqrt{3}}{2} \mathbf{e}_{n} - \frac{1}{2} \mathbf{d}_{n}^{3} \\ \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{3} \\ -\frac{1}{2} \mathbf{e}_{n}^{4} + \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} & -\frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} + \frac{1}{2} \mathbf{d}_{n}^{2} \mathbf{d}_{n}^{4} \mathbf{d}_{n} \\ -\frac{1}{2} \mathbf{e}_{n}^{4} + \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} & -\frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} + \frac{1}{2} \mathbf{d}_{n}^{4} \mathbf{d}_{n} \\ -\frac{1}{2} \mathbf{e}_{n}^{4} + \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} \mathbf{d}_{n} - \frac{\sqrt{3}}{2} \mathbf{e}_{n}^{4} + \frac{1}{2} \mathbf{d}_{n}^{4} \mathbf{d}_{n} \\ -\frac{1}{2} \mathbf{e}_{n}^{4} + \frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} & -\frac{\sqrt{3}}{2} \mathbf{d}_{n}^{4} \mathbf{d}_{n}^{4} \mathbf{d}_{n}^{4} \mathbf{d$$



$$\begin{split} \mathbf{m}_{1}\mathbf{d}_{\alpha\beta}^{05}(\mathbf{n}) &= - \begin{bmatrix} \frac{1}{4}\mathbf{a}_{n} - \frac{\sqrt{3}}{2}\mathbf{f}_{n} + \frac{3}{4}\mathbf{b}_{n} & \frac{\sqrt{3}}{4}\mathbf{a}_{n} - \frac{1}{2}\mathbf{f}_{n} - \frac{\sqrt{3}}{4}\mathbf{b}_{n} & \frac{1}{2}\mathbf{e}_{n} - \frac{\sqrt{3}}{2}\mathbf{d}_{n} \\ \frac{\sqrt{3}}{4}\mathbf{a}_{n} - \frac{1}{2}\mathbf{f}_{n} - \frac{\sqrt{3}}{4}\mathbf{b}_{n} & \frac{3}{4}\mathbf{a}_{n} + \frac{\sqrt{3}}{2}\mathbf{f}_{n} + \frac{1}{4}\mathbf{b}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} \\ \frac{1}{2}\mathbf{e}_{n} - \frac{\sqrt{3}}{2}\mathbf{d}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} & \mathbf{g}_{n} \end{bmatrix} \\ & - \begin{bmatrix} \mathbf{0} & \mathbf{f}_{n}^{\mathbf{a}} & \frac{1}{2}\mathbf{e}_{n}^{\mathbf{a}} - \frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{1}{2}\mathbf{d}_{n} \\ -\mathbf{f}_{n}^{\mathbf{a}} & \mathbf{0} & \frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{1}{2}\mathbf{d}_{n}^{\mathbf{a}} \\ -\frac{1}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{\sqrt{3}}{2}\mathbf{d}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} - \frac{1}{2}\mathbf{d}_{n}^{\mathbf{a}} & \mathbf{0} \end{bmatrix} \\ \mathbf{m}_{1}\mathbf{d}_{\alpha\beta}^{12}(\mathbf{n}) &= - \begin{bmatrix} \frac{1}{4}\mathbf{a}_{n} - \frac{\sqrt{3}}{2}\mathbf{f}_{n} + \frac{3}{4}\mathbf{b}_{n} & -\frac{\sqrt{3}}{4}\mathbf{a}_{n} + \frac{1}{2}\mathbf{f}_{n} + \frac{\sqrt{3}}{4}\mathbf{b}_{n} & -\frac{1}{2}\mathbf{e}_{n} + \frac{\sqrt{3}}{2}\mathbf{d}_{n} \\ -\frac{1}{2}\mathbf{e}_{n} + \frac{\sqrt{3}}{2}\mathbf{d}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{1}{2}\mathbf{f}_{n} + \frac{\sqrt{3}}{4}\mathbf{b}_{n} & -\frac{1}{2}\mathbf{e}_{n} + \frac{\sqrt{3}}{2}\mathbf{d}_{n} \\ -\frac{1}{2}\mathbf{e}_{n} + \frac{\sqrt{3}}{2}\mathbf{d}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} & \mathbf{g}_{n} \end{bmatrix} \\ \mathbf{m}_{1}\mathbf{d}_{\alpha\beta}^{12}(\mathbf{n}) &= - \begin{bmatrix} \mathbf{0} & -\mathbf{f}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} \\ -\frac{1}{2}\mathbf{e}_{n} + \frac{\sqrt{3}}{2}\mathbf{d}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} & \mathbf{g}_{n} \end{bmatrix} \\ \mathbf{m}_{1}\mathbf{d}_{\alpha\beta}^{12}(\mathbf{n}) &= - \begin{bmatrix} \mathbf{0} & -\mathbf{f}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n} - \frac{1}{2}\mathbf{d}_{n} & \frac{\sqrt{3}}{2}\mathbf{e}_{n} + \frac{1}{2}\mathbf{d}_{n} \\ \mathbf{1} \mathbf{e}\mathbf{e}_{n} - \frac{\sqrt{3}}{2}\mathbf{d}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} - \frac{1}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{1}{2}\mathbf{d}_{n}^{\mathbf{a}} \\ \mathbf{0} & \frac{1}{2}\mathbf{e}_{n} - \frac{\sqrt{3}}{2}\mathbf{d}_{n}^{\mathbf{a}} \\ \mathbf{0} & -\mathbf{f}_{n}^{\mathbf{a}} - \frac{\sqrt{3}}{2}\mathbf{e}_{n} - \frac{1}{2}\mathbf{d}_{n}^{\mathbf{a}} \\ \mathbf{0} & -\mathbf{f}_{n}^{\mathbf{a}} - \frac{1}{2}\mathbf{e}_{n}^{\mathbf{a}} + \frac{1}{2}\mathbf{f}_{n} + \frac{1}{2}\mathbf{f}_{n} \\ \mathbf{0} & \frac{1}{2}\mathbf{e}_{n} - \frac{\sqrt{3}}{2}\mathbf{d}_{n}^{\mathbf{a}} & -\frac{\sqrt{3}}{2}\mathbf{e}_{n}^{\mathbf{a}} - \frac{1}{2}\mathbf{d}_{n}^{\mathbf{a}} \\ \mathbf{0} & -\mathbf{f}_{n}^{\mathbf{a}} - \frac{1}{2}\mathbf{e}_{n}^{\mathbf$$



The matrix  $d_{\alpha\beta}(0)$  describes the force of the point at the origin on itself, due to its own displacement from the equilibrium position. Its form is given by the condition of the translational invariance of the system. As it clearly follows from Eq. (2) this force is attractive if elements of  $d_{\alpha\beta}(0)$  are positive. The lattice vectors of structure points are (see Eqs. (28) and (30)):

$$\vec{r}^{00}(n) = \frac{a}{2} [(21-k)\vec{i} - \sqrt{3}k\vec{j}] + cm\vec{k}$$
  

$$\vec{r}^{01}(n) = \frac{a}{2} [(2k-1)\vec{i} + \sqrt{3}l\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{02}(n) = \frac{a}{2} [-(1+k)\vec{i} + \sqrt{3}(k-1)\vec{j}] + cm\vec{k}$$
  

$$\vec{r}^{03}(n) = \frac{a}{2} [(21-k)\vec{i} - \sqrt{3}k\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{04}(n) = \frac{a}{2} [(2k-1)\vec{i} + \sqrt{3}l\vec{j}] + cm\vec{k}$$
  

$$\vec{r}^{05}(n) = \frac{a}{2} [-(1+k)\vec{i} + \sqrt{3}(k-1)\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{10}(n) = \frac{a}{2} [-(21-k)\vec{i} - \sqrt{3}k\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{11}(n) = \frac{a}{2} [-(21-k)\vec{i} - \sqrt{3}k\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{12}(n) = \frac{a}{2} [(1+k)\vec{i} + \sqrt{3}(k-1)\vec{j}] - cm\vec{k}$$
  

$$\vec{r}^{13}(n) = \frac{a}{2} [-(21-k)\vec{i} - \sqrt{3}k\vec{j}] + cm\vec{k}$$
  

$$\vec{r}^{14}(n) = \frac{a}{2} [-(21-k)\vec{i} - \sqrt{3}k\vec{j}] + cm\vec{k}$$
  

$$\vec{r}^{15}(n) = \frac{a}{2} [(1+k)\vec{i} + \sqrt{3}(k-1)\vec{j}] + cm\vec{k}$$

(40)

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$$\vec{r}^{00}(N) = \frac{a}{2} [(2L-K)\vec{1} - \sqrt{3}K\vec{j}] + cM\vec{k}$$
  
 $\vec{r}^{01}(N) = \frac{a}{2} [(2K-L+1)\vec{1} + \sqrt{3}(L+1)\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{02}(N) = \frac{a}{2} [-(L+K+1)\vec{1} + \sqrt{3}(K-L+1)\vec{j}] + cM\vec{k}$   
 $\vec{r}^{03}(N) = \frac{a}{2} [(2L-K)\vec{i} - \sqrt{3}K\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{04}(N) = \frac{a}{2} [(2K-L+1)\vec{i} + \sqrt{3}(L+1)\vec{j}] + cM\vec{k}$   
 $\vec{r}^{05}(N) = \frac{a}{2} [-(L+K+1)\vec{i} + \sqrt{3}(K-L+1)\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{10}(N) = \frac{a}{2} [-(2L-K)\vec{i} - \sqrt{3}K\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{11}(N) = \frac{a}{2} [-(2K-L+1)\vec{i} + \sqrt{3}(L+1)\vec{j}] + cM\vec{k}$   
 $\vec{r}^{12}(N) = \frac{a}{2} [(L+K+1)\vec{i} + \sqrt{3}(K-L+1)\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{13}(N) = \frac{a}{2} [-(2K-L+1)\vec{i} - \sqrt{3}K\vec{j}] + cM\vec{k}$   
 $\vec{r}^{14}(N) = \frac{a}{2} [-(2K-L+1)\vec{i} + \sqrt{3}(L+1)\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{15}(N) = \frac{a}{2} [(L+K+1)\vec{i} + \sqrt{3}(K-L+1)\vec{j}] - c(M+1)\vec{k}$   
 $\vec{r}^{15}(N) = \frac{a}{2} [(L+K+1)\vec{i} + \sqrt{3}(K-L+1)\vec{j}] + cM\vec{k}$ .

Now let us carry out the summation over  $\mu,~\nu$  in formulas (35) and (36). The elements of the Fourier transform of the dynamical matrix are then as follows:

.

$$m_{1} d_{11}(q) = 6 \sum_{N} \rho_{N} (A_{N} + B_{N}) + \sum_{n} \rho_{n} \{12 (a_{n} + b_{n}) - 2 \cos (2\pi \operatorname{cmq}_{2}) [4a_{n} \cos(\pi a (21 - k) q_{x}) \cos (\sqrt{3}\pi a k q_{y}) + (a_{n} + 2\sqrt{3}f_{n} + 3b_{n}) \cos (\pi a (2k - 1)q_{x}) \cos (\sqrt{3}\pi a l q_{y}) + (a_{n} - 2\sqrt{3}f_{n} + 3b_{n}) \cos (\pi a (1 + k) q_{x}) \cos (\sqrt{3}\pi (k - 1)q_{y})]\}$$

$$(42)$$

$$m_{1}d_{22} (q) = 6 \sum_{N} \rho_{N} (A_{N} + B_{N}) + \sum_{n} \rho_{n} \{12 (a_{n} + b_{n}) - 2 \cos (2\pi \operatorname{cmq}_{2}) [4b_{n} \cos (\pi a(21 - k)q_{x}) \cos (\sqrt{3}\pi \operatorname{akq}_{y}) + (3a_{n} - 2\sqrt{3}f_{n} + b_{n}) \cos (\pi a(2k - 1)q_{x}) \cos (\sqrt{3}\pi \operatorname{alq}_{y}) + (3a_{n} + 2\sqrt{3}f_{n} + b_{n}) \cos (\pi a(1 + k)q_{x}) \cos (\sqrt{3}\pi a(k - 1)q_{y})]$$

$$\begin{split} m_1 d_{33}(q) &= 12 \sum_N \rho_N G_N + \sum_n \rho_n \{ 24 g_n - \\ &- 8g_n \cos(2\pi cmq_z) [\cos(\pi a(21-k)q_x) \cos(\sqrt{3}\pi akq_y) \\ &+ \cos(\pi a(2k-1)q_x) \cos(\sqrt{3}\pi alq_y) + \cos(\pi a(1+k)q_x) \cos(\sqrt{3}\pi a(k-1)q_y) ] \} \end{split}$$

$$\begin{split} m_{1}d_{12}(q) &= -2 \sum_{n} \rho_{n} \left[ \left[ \cos(2\pi cmq_{2}) \left\{ \left[ 4f_{n}\sin(\pi a(21-k)q_{x})\sin(\sqrt{3}\pi akq_{y}) + (\sqrt{3}a_{n} + 2f_{n} - \sqrt{3}b_{n})\sin(\pi a(2k-1)q_{x})\sin(\sqrt{3}\pi alq_{y}) + (\sqrt{3}a_{n} - 2f_{n} - \sqrt{3}b_{n})\sin(\pi a(1+k)q_{x})\sin(\sqrt{3}\pi a(k-1)q_{y}) \right] \\ &- 4if_{n}^{a} \left[ \sin(\pi a(21-k)q_{x})\cos(\sqrt{3}\pi akq_{y}) + \sin(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi alq_{y}) + \sin(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi alq_{y}) - \sin(\pi a(1+k)q_{x})\cos(\sqrt{3}\pi a(k-1)q_{y}) \right] \right] \end{split}$$

$$m_{1}d_{13}(q) = 4 \sum_{n} \rho_{n} [ \sin(2\pi \operatorname{cmq}_{z}) \{ [2e_{n}\sin(\pi a(2l-k)q_{x})\cos(\sqrt{3}\pi akq_{y}) \\ -(e_{n} + \sqrt{3}d_{n})\sin(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi alq_{y}) \\ + (e_{n} - \sqrt{3}d_{n})\sin(\pi a(1+k)q_{x})\cos(\sqrt{3}\pi a(k-1)q_{y}) ] \\ + i [2e_{n}^{a}\sin(\pi a(2l-k)q_{x})\sin(\sqrt{3}\pi akq_{y}) \\ + (e_{n}^{a} + \sqrt{3}d_{n}^{a})\sin(\pi a(2k-1)q_{x})\sin(\sqrt{3}\pi alq_{y}) \\ - (e_{n}^{a} - \sqrt{3}d_{n}^{a})\sin(\pi a(1+k)q_{x})\sin(\sqrt{3}\pi a(k-1)q_{y}) ] \} ]$$

$$\begin{split} m_{1}d_{23}(q) &= -4\sum_{n} \rho_{n} [ [\sin(2\pi cmq_{z}) \{ [2d_{n}\cos(\pi a(21-k)q_{x})\sin(\sqrt{3}\pi akq_{y}) \\ &- (\sqrt{3}e_{n} - d_{n})\cos(\pi a(2k-1)q_{x})\sin(\sqrt{3}\pi alq_{y}) \\ &+ (\sqrt{3}e_{n} + d_{n})\cos(\pi a(1+k)q_{x})\sin(\sqrt{3}\pi a(k-1)q_{y}) \\ &- i [2d_{n}^{a}\cos(\pi a(21-k)q_{x})\cos(\sqrt{3}\pi akq_{y}) \\ &+ (\sqrt{3}e_{n}^{a} - d_{n}^{a})\cos(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi alq_{y}) \\ &- (\sqrt{3}e_{n}^{a} + d_{n}^{a})\cos(\pi a(1+k)q_{x})\cos(\sqrt{3}\pi a(k-1)q_{y}) ] \} ] \end{split}$$

.

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$$\begin{split} \mathbf{m_1 D_{11}(q)} &= -\sum_{N} \rho_N \{ e^{\pi i c q_2} \cos \left( 2\pi c (M + \frac{1}{2}) q_2 \right) [4A_N \cos \left( \pi a (2L - K) q_x \right) e^{\sqrt{3}\pi i a K q_y} \\ &+ (A_N + 2\sqrt{3} F_N + 3B_N) \cos \left( \pi a (2K - L + 1) q_x \right) e^{-\sqrt{3}\pi i a (L + 1) q_y} \\ &+ (A_N - 2\sqrt{3} F_N + 3B_N) \cos \left( \pi a (L + K + 1) q_x \right) e^{-\sqrt{3}\pi i a (K - L + 1) q_y} ] \end{split}$$

$$\begin{split} \mathbf{m}_{1} \mathbf{D}_{22}(\mathbf{q}) &= -\sum_{N} \rho_{N} \left\{ e^{\pi i c q_{z}} \cos \left( 2 \, \pi c (\mathbf{M} + \frac{1}{2}) \mathbf{q}_{z} \right) \left[ 4 \mathbf{B}_{N} \cos \left( \pi a (2 \mathbf{L} - \mathbf{K}) \, \mathbf{q}_{x} \right) e^{\sqrt{3} \pi i a (\mathbf{K} \mathbf{q}_{y})} \right. \\ &+ \left( 3 \mathbf{A}_{N} - 2 \sqrt{3} \mathbf{F}_{N} + \mathbf{B}_{N} \right) \cos \left( \pi a (2 \mathbf{K} - \mathbf{L} + 1) \mathbf{q}_{x} \right) e^{-\sqrt{3} \pi i a (\mathbf{L} + 1) \mathbf{q}_{y}} \\ &+ \left( 3 \mathbf{A}_{N} + 2 \sqrt{3} \mathbf{F}_{N} + \mathbf{B}_{N} \right) \cos \left( \pi a (\mathbf{L} + \mathbf{K} + 1) \mathbf{q}_{x} \right) e^{-\sqrt{3} \pi i a (\mathbf{K} - \mathbf{L} + 1) \mathbf{q}_{y}} \end{split}$$

$$\begin{split} \mathbf{m_1 D_{33}(q)} &= -4 \sum_{N} \rho_N \left\{ \mathbf{G_N} \ \mathbf{e}^{\pi \mathbf{i} \mathbf{c} \mathbf{q}_Z} \ \cos\left(2\pi \mathbf{c} (\mathbf{M} + \frac{1}{2}) \mathbf{q}_Z\right) \left[\cos\left(\pi \mathbf{a} (2\mathbf{L} - \mathbf{K}) \mathbf{q}_X\right) \mathbf{e}^{\sqrt{3}\pi \mathbf{i} \mathbf{a} (\mathbf{K} \mathbf{q}_Y)} \right. \\ &\left. + \cos\left(\pi \mathbf{a} (2\mathbf{K} - \mathbf{L} + 1) \mathbf{q}_X\right) \mathbf{e}^{-\sqrt{3}\pi \mathbf{i} \mathbf{a} (\mathbf{L} + 1) \mathbf{q}_Y} + \cos\left(\pi \mathbf{a} (\mathbf{L} + \mathbf{K} + 1) \mathbf{q}_X\right) \mathbf{e}^{-\sqrt{3}\pi \mathbf{i} \mathbf{a} (\mathbf{K} - \mathbf{L} + 1) \mathbf{q}_Y} \right] \end{split}$$

$$\begin{split} m_{1}D_{12}(q) &= \sum_{N} \rho_{N} \left\{ ie^{\pi i c q_{2}} \cos \left( 2\pi c (M + \frac{1}{2}) q_{2} \right) \left[ 4F_{N} \sin \left( \pi a (2L - K) q_{x} \right) e^{\sqrt{3}\pi i a K q_{y}} \right. \\ &- \left( \sqrt{3}A_{N} + 2F_{N} - \sqrt{3}B_{N} \right) \sin \left( \pi a (2K - L + 1) q_{x} \right) e^{-\sqrt{3}\pi i a (L + 1) q_{y}} \\ &- \left( \sqrt{3}A_{N} - 2F_{N} - \sqrt{3}B_{N} \right) \sin \left( \pi a (L + K + 1) q_{x} \right) e^{-\sqrt{3}\pi i a (K - L + 1) q_{y}} ] \end{split}$$
(42)

$$\begin{split} \mathbf{m}_{1}\mathbf{D}_{13}(\mathbf{q}) &= \sum_{N} \rho_{N} \{ 2e^{\pi i c \mathbf{q}_{Z}} \sin \left(2\pi c (\mathbf{M} + \frac{1}{2}) \mathbf{q}_{Z}\right) [ 2\mathbf{E}_{N} \sin \left(\pi a (2\mathbf{L} - \mathbf{K}) \mathbf{q}_{X}\right) e^{\sqrt{3}\pi i a \mathbf{K} \mathbf{q}_{Y}} \\ &- (\mathbf{E}_{N} + \sqrt{3}\mathbf{D}_{N}) \sin \left(\pi a (2\mathbf{K} - \mathbf{L} + 1) \mathbf{q}_{X}\right) e^{-\sqrt{3}\pi i a (\mathbf{L} + 1) \mathbf{q}_{Y}} \\ &+ (\mathbf{E}_{N} - \sqrt{3}\mathbf{D}_{N}) \sin \left(\pi a (\mathbf{L} + \mathbf{K} + 1) \mathbf{q}_{X}\right) e^{-\sqrt{3}\pi i (\mathbf{K} - \mathbf{L} + 1) \mathbf{q}_{Y}} ] \} \end{split}$$

$$\begin{split} \mathbf{m}_{1}\mathbf{D}_{23}(\mathbf{q}) &= \sum_{N} \rho_{N} \{ 2ie^{\pi i c q_{z}} sin \left( 2\pi c \left( M + \frac{1}{2} \right) \mathbf{q}_{z} \right) \left[ 2\mathbf{D}_{N} cos \left( \pi a \left( 2L - K \right) \mathbf{q}_{x} \right) e^{\sqrt{3}\pi i a K \mathbf{q} y} \right. \\ &+ \left( \sqrt{3}\mathbf{E}_{N} - \mathbf{D}_{N} \right) cos \left( \pi a \left( 2K - L + 1 \right) \mathbf{q}_{x} \right) e^{-\sqrt{3}\pi i a \left( L + 1 \right) \mathbf{q}_{y}} \\ &- \left( \sqrt{3}\mathbf{E}_{N} + \mathbf{D}_{N} \right) cos \left( \pi a \left( L + K + 1 \right) \mathbf{q}_{x} e^{-\sqrt{3}\pi i a \left( K - L + 1 \right) \mathbf{q}_{y}} \right] \} \end{split}$$

# LIMITATIONS AND SIMPLIFICATIONS

If the structure point is situated on the boundary of its sub-space, the related term in Eqs. (42) may usually be simplified, due to the fact that an equidistant family of such a point may be obtained by operations of a sub-group of the  $\{\hat{T} \mid \vec{0}\}$  group. The related term in Eqs.(42) has then to be multiplied by the weight factor, the ratio of an order of the sub-group used to the order of full  $\{\hat{T} \mid \vec{0}\}$  group.

At the same time related force matrices must usually be invariant for physical arguments, with respect to some operations of the  $\{\hat{T} \mid \vec{0}\}$  group. A good example is the force matrix of any point on the z = 0 plane; it must be unchanged by the reflection in this plane because the position of these points is the same. Similar arguments significantly simplify the general forms of matrices.

Sub-lattice 1 has been generated from points of sub-spaces s. The following primitive operations and their combinations have been used: 6-fold rotational inversion, x = y = 0 axis and two-fold rotation, x = z = 0 axis and, in a sense discussed earlier, an inversion. Sub-lattice 2 has been generated from sub-space S using two first operations and their combinations, but there was no "inversion" there. Simplifications and weight factors  $\rho_n$ ,  $\rho_N$ are presented in Table I. The weight factors for general points of subspaces are equal to one.

### PHONON DISPERSION RELATIONS

Let us consider now Eq. (6) and its condition of solubility Eq.(10). For the hcp structure it is an eigenproblem with a determinant  $(6 \times 6)$ . We have to solve it with respect to  $\omega$  to obtain the phonon dispersion relations  $\omega(q)$ . It cannot be done explicitly because of the complicated form of Eq.(10) for a general point of the Brillouin zone. It simplifies however for some special directions of the reciprocal zone. The determinant (10) in its full form is presented below. Subscripts under the terms indicate where in the reciprocal space the term discussed is equal to zero (see Eq.(42)).

It is easy to show, by permutation of rows and columns, that for phonons propagating in the  $q_y$ - or  $q_z$ -directions of the reciprocal space, the determinant factorizes into three determinants (2×2), connected with polarization vectors  $V_x$  (1),  $V_x$  (2);  $V_y$  (1),  $V_y$  (2); and  $V_z$  (1),  $V_z$  (2) respectively. For the  $q_x$ -direction it factorizes to (4×4) and (2×2) determinants. The second one is connected with polarization vectors  $V_z$  (1),  $V_z$  (2). In these cases modes are purely transversal or longitudinal (perpendicular or parallel to

### TABLE II

# FORCE MATRIX FOR STRUCTURE POINT POSITIONS

|       |   | Structure point<br>positions         | ρn; PN<br>weight<br>factors | Force matrix   |
|-------|---|--------------------------------------|-----------------------------|--|
| · .   | 1 | x=0; y>0; z>0<br>21=k; 1<0; m>0      | <u>1</u><br>2               | $-\frac{1}{m_1} \begin{bmatrix} a & 0 & 0 \\ 0 & b & d \\ 0 & d & g \end{bmatrix} -\frac{1}{m_1} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d^a \\ 0 & -d^a & 0 \end{bmatrix}$   |
| space | 2 | y=√3x; x > 0; z > 0<br>1=0; k<0; m>0 | <u>1</u><br>2               | $-\frac{1}{m_{1}}\begin{bmatrix}a & -\frac{\sqrt{3}}{2}(a-b) & e\\ -\frac{\sqrt{3}}{2}(a-b) & b & \sqrt{3}e\\ e & \sqrt{3}e & g\end{bmatrix} -\frac{1}{m_{1}}\begin{bmatrix}0 & f^{a} & \sqrt{3}d^{a}\\ -f^{a} & 0 & d^{a}\\ -\sqrt{3}d^{a} & -d^{a} & 0\end{bmatrix}$ |
| dus s | 3 | y>√3x>0; z=0<br>0>21>k; m=0          | <u>1</u><br>2               | $-\frac{1}{m_{1}}\begin{bmatrix}a & f & 0\\ f & b & 0\\ 0 & 0 & g\end{bmatrix} -\frac{1}{m_{1}}\begin{bmatrix}0 & f^{a} & 0\\ -f^{a} & 0 & 0\\ 0 & 0 & 0\end{bmatrix}$   |
|       | 4 | x=0; y>0; z=0<br>21=k; 1<0; m=0      | . <u>1</u><br>4             | $-\frac{1}{m_1} \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & g \end{bmatrix}$   |

LATTICE DYNAMICS OF HCP STRUCTURE

| -        |   | Structure point<br>positions                         | ρη; ρ <sub>Ν</sub><br>weight<br>factors | Force matrix  |
|----------|---|--|---|---|
| pace     | 5 | $y = \sqrt{3}x; x > 0; z = 0$<br>l = 0; k < 0; m = 0 | <u>1</u><br>4                           | $\begin{bmatrix} a & -\frac{\sqrt{3}}{2}(a-b) & 0 \\ -\frac{\sqrt{3}}{2}(a-b) & b & 0 \\ 0 & 0 & g \end{bmatrix} -\frac{1}{m_1} \begin{bmatrix} 0 & f^a & 0 \\ -f^a & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ |
| s-sub-s  | 6 | x = y = 0; z > 0<br>1 = k = 0; m > 0                 | $\frac{1}{12}$                          | $-\frac{1}{m_1} \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & g \end{bmatrix}$  |
| e        | 7 | x = 0; y > 0; z > 0<br>2L=K; K < 0; M≥0              | $\frac{1}{2}$                           | $-\frac{1}{m_{1}}\begin{bmatrix} A & 0 & 0 \\ 0 & B & D \\ 0 & D & G \end{bmatrix}$   |
| S-sub-sp | 8 | y=x/√3; x > 0; z > 0<br>L+K+1=0; K < 0; M ≥ 0        | 12                                      | $-\frac{1}{m_1} \begin{bmatrix} A & \frac{\sqrt{3}}{2} (A - B) & \sqrt{3}D \\ \frac{\sqrt{3}}{2} (A + B) & B & D \\ \sqrt{3}D & D & G \end{bmatrix}$  |

TABLE II (cont.)



The Brillouin zone for a hexagonal lattice

the direction of phonon propagation) and the explicit forms of dispersion relations can be written easily. The Brillouin zone for a hexagonal lattice is shown in Fig. 3.

The phonon dispersion relation for symmetry directions and corresponding elastic constants are given below:

(1)  $q_z$  -direction, z - polarization,  $c_{33}$ .

$$\omega^{2}(q_{z}) = d_{33}(q_{x} = q_{y} = 0) \pm D_{33}(q_{x} = q_{y} = 0)$$

(2)  $q_z$  - direction, x or y - polarization,  $c_{44}$ .

$$\omega^{2}(q_{z}) = d_{11}(q_{x} = q_{y} = 0) \pm |D_{11}(q_{x} = q_{y} = 0)|$$

(3)  $q_y$  - direction, y - polarization,  $c_{11}$ .

$$\omega^{z}(q_{y}) = d_{22}(q_{x} = q_{z} = 0) \pm D_{22}(q_{x} = q_{z} = 0)$$

(4)  $q_y$  - direction, x - polarization,  $c_{66}$ .

$$\omega^{2}(q_{y}) = d_{11}(q_{x} = q_{z} = 0) \pm D_{11}(q_{x} = q_{z} = 0)$$

(5)  $q_y$  - direction, z - polarization,  $c_{44}$ .

$$\omega^{2}(q_{y}) = d_{33}(q_{x} = q_{z} = 0) \pm D_{33}(q_{x} = q_{z} = 0)$$

(6)  $q_x$  - direction, z - polarization,  $c_{44}$ .

$$\omega^{z}(q_{x}) = d_{33}(q_{y} = q_{z} = 0) \pm |D_{33}(q_{y} = q_{z} = 0)|$$

### ELASTIC CONSTANTS

The easiest way to obtain elastic constants expressed as a function of force constants is to put  $|\vec{q}| \rightarrow 0$  in the dispersion relations of (44). Acoustic branches in this region are linear

(44)

$$\omega = 2\pi s \left| \vec{q} \right|, \tag{45}$$

where the velocity of sound s is connected with the elastic constant c and density  $\rho$  as follows:

$$s = \sqrt{\frac{c}{\rho}}.$$
 (46)

In the case under discussion however, it is impossible to obtain all elastic constants in this way. The reason is that one cannot factorize the determinant in Eq. (43) everywhere and therefore, one of the elastic constants  $c_{13}$  is not included in formulas (44). We shall find them all, going through the standard long waves procedure.

Let us consider Eq. (7) for the case of long waves, i.e.  $q \rightarrow 0$ . We expand all quantities in Eq. (7) as power expansions in  $\vec{q}$ , compare equal powers and find out an explicit form of the second-order approximation. One has then [7]

$$\sum_{\beta k'}^{(0)} (\mathbf{k}\mathbf{k'}) \mathbf{W}_{\beta}^{(1)}(\mathbf{k'}) = -\sum_{\beta k'} \sqrt{m_{k}} \mathbf{C}^{(1)}(\mathbf{q} | \mathbf{k}\mathbf{k'}) \mathbf{U}_{\beta}$$
(47)

$$\sum_{\mathbf{k}'} \mathbf{m}_{\mathbf{k}'} \omega^2 \mathbf{U}_{\alpha} = \sum_{\beta \mathbf{k} \mathbf{k}'} \sqrt{\mathbf{m}_{\mathbf{k}}} C_{\alpha\beta}^{(1)} (\mathbf{q} | \mathbf{k} \mathbf{k}') W_{\beta}^{(1)} (\mathbf{k}') + \sum_{\beta \mathbf{k} \mathbf{k}'} \sqrt{\mathbf{m}_{\mathbf{k}}} m_{\mathbf{k}'} C_{\alpha\beta}^{(2)} (\mathbf{q} | \mathbf{k} \mathbf{k}') \mathbf{U}_{\beta}, \quad (48)$$

where  $U_{\alpha}$  is some translation of the crystal as a whole. After elimination of  $W_{\beta}(k')$  the result has the form:

$$\rho \,\omega^2 \,\mathrm{U}_{\alpha} = 4 \,\pi^2 \, \sum_{\beta} \mathrm{D'}_{\alpha\beta}(\mathbf{q}) \,\mathrm{U}_{\beta} \,. \tag{49}$$

By comparison with the elasticity theory, elements of the matrix  $D^{I}_{\alpha\beta}(q)$  are equivalent to elastic constants that may be written as follows:

| D'11              |   | c <sub>11</sub>   | c <sub>65</sub>   | c <sub>55</sub>        | c <sub>65</sub>                                    | c <sub>51</sub>                                    | c <sub>16</sub>                | ſ |                                |      |
|-------------------|---|-------------------|-------------------|------------------------|--|--|--------------------------------|---|--------------------------------|------|
| $D_{22}^{\prime}$ |   | с <sub>66</sub>   | c <sub>22</sub>   | c <sub>44</sub>        | c <sub>24</sub>                                    | $c_{46}$   | с <sub>62</sub>                |   | $q_y^2$                        |      |
| D'_33             | = | $\mathbf{c}_{55}$ | c <sub>44</sub>   | c <sub>33</sub>        | c <sub>43</sub>                                    | c <sub>35</sub>                                    | c <sub>54</sub>                |   | $q_z^2$                        | (50) |
| $D_{23}^{\prime}$ |   | c <sub>65</sub>   | $\mathbf{c}_{24}$ | c <sub>43</sub>        | $\frac{1}{2}$ (c <sub>23</sub> + c <sub>44</sub> ) | $\frac{1}{2}(c_{45} + c_{36})$                     | $\frac{1}{2}(c_{64} + c_{25})$ |   | $2q_yq_z$                      |      |
| D'_{31            |   | $\mathbf{c}_{51}$ | $c_{46}$          | <b>c</b> <sub>35</sub> | $\frac{1}{2}(c_{45} + c_{36})$                     | $\frac{1}{2}(c_{31} + c_{55})$                     | $\frac{1}{2}(c_{56} + c_{16})$ | ĺ | $2q_zq_x$                      |      |
| $D_{12}$          |   | c <sub>16</sub>   | $c_{62}$          | c <sub>54</sub>        | $\frac{1}{2}$ (c <sub>64</sub> + c <sub>25</sub> ) | $\frac{1}{2}$ (c <sub>56</sub> + c <sub>14</sub> ) | $\frac{1}{2}(c_{12} + c_{66})$ |   | 2q <sub>x</sub> q <sub>y</sub> |      |

These general formulas will now be specialized. For the hcp structure we have (see Eq.(8))

$$C_{\alpha\beta}(q|11) = C_{\alpha\beta}^{*}(q|22) = d_{\alpha\beta}(q)$$

$$C_{\alpha\beta}(q|12) = C_{\alpha\beta}^{*}(q|21) = D_{\alpha\beta}(q) e^{\frac{2}{3}\sqrt{3\pi i a q y^{-\pi i c q z}}}$$
(51)

$$\begin{pmatrix} 0 \\ C_{\alpha\beta}(11) = \frac{6}{m_1} \sum_{N} \rho_N \begin{bmatrix} A_N + B_N & 0 & 0 \\ 0 & A_N + B_N & 0 \\ 0 & 0 & 2G_N \end{bmatrix} = - \begin{pmatrix} 0 \\ C_{\alpha\beta}(12) \end{bmatrix}$$

$$\begin{pmatrix} 1 \\ C_{\alpha\beta}(q | 11) = 0 \\ C_{\alpha\beta}(q | 12) = -\sqrt{3}\pi i \frac{a}{m_1} \sum_{N} \rho_N \left[ (A_N - B_N)(3K + 2) - 2\sqrt{3} F_N(2L - K) \right] \begin{bmatrix} q_y & q_x & 0 \\ q_x - q_y & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$(52)$$

Using these properties and Eqs. (47) and (48) one has:

$$\sum_{\beta}^{(0)} C_{\alpha\beta}^{(11)} (\overset{(1)}{W}_{\beta}^{(1)} - \overset{(1)}{W}_{\beta}^{(2)} ) = -\sum_{\beta} \sqrt{m_{1}} C_{\alpha\beta}^{(1)} (q | 12) U_{\beta}$$

$$(53)$$

$$2m_{1} \omega^{2} U_{\alpha} = -\sqrt{m_{1}} \sum_{\beta}^{(1)} C_{\alpha\beta}^{(1)} (\overset{(1)}{W}_{\beta}^{(1)} - \overset{(1)}{W}_{\beta}^{(2)} ) + 2m_{1} \sum_{\beta}^{(2)} (C_{\alpha\beta}^{(2)} (q | 11) + \overset{(2)}{C}_{\alpha\beta}^{(2)} (q | 12) ) U_{\beta}$$

Now  $W_{\alpha}^{(1)} = W_{\alpha}^{(1)}(2)$  may be eliminated from the second Eq.(53).

$$\frac{\rho}{4\pi^2}\omega^2 U_{\alpha} = \frac{m_1}{\sqrt{3\pi^2 a^2 c}} \sum_{\beta} \left[ \frac{m_1}{12\sum_{N} \rho_N (A_N + B_N)} \sum_{\delta} C_{\alpha\delta}^{(1)}(q|12) C_{\delta\beta}^{(1)}(q|12) + C_{\alpha\beta}^{(2)}(q|11) + C_{\alpha\beta}^{(2)}(q|12)) \right] U_{\beta}$$
(54)

The comparison of this equation with Eqs.(49) and (50) enables us to write the elastic constants expressed by atomic force constants  $\phi_{\alpha\beta}({}^{i}_{kk'})$ . They are as follows:

$$C_{11} = \frac{1}{2\sqrt{3}c} \{ 2 \sum_{n} \rho_{n} [a_{n}(181^{2} + 9k^{2} - 18k1) + b_{n}(61^{2} + 15k^{2} - 6k1) + \sqrt{3}f_{n}(6k^{2} - 12k1)] + \sum_{N} \rho_{N} [A_{N}(18L^{2} + 9K^{2} - 18KL + 6K + 2) + B_{N}(6L^{2} + 15K^{2} - 6KL + 18K + 6)] + \sqrt{3}F_{N} (6K^{2} - 12KL - 8L + 4K)] - P \}$$

$$(55)$$

$$\begin{split} \mathbf{C}_{66} &= \frac{1}{2\sqrt{3}c} \left\{ 2\sum_{n} \rho_{n} \left[ \mathbf{a}_{n} (6l^{2} + 15k^{2} - 6kl) + \mathbf{b}_{n} \left( 18l^{2} + 9k^{2} - 18kl \right) - \sqrt{3} f_{n} \left( 6k^{2} - 12kl \right) \right] \\ &+ \sum_{N} \rho_{N} \left[ \mathbf{A}_{N} \left( 6L^{2} + 15K^{2} - 6KL + 18K + 6 \right) + \mathbf{B}_{N} \left( 18L^{2} + 9K^{2} - 18KL + 6K + 2 \right) \right] \\ &- \sqrt{3} F_{N} \left( 6K^{2} - 12KL - 8L + 4K \right) - \mathbf{P} \right\} \end{split}$$

It is worthwhile to notice that elastic constants are given by the symmetrical part of the dynamical matrix. The invariance of the potential  $\phi$  with respect to rotation of the crystal as a whole gives the following relation between force constants:

$$\frac{c^{2}}{a^{2}} \left\{ 2 \sum_{n} \rho_{n} \left[ (a_{n} + b_{n})m^{2} \right] + \sum_{N} \rho_{N} \left[ (A_{N} + B_{N}) (M + \frac{1}{2})^{2} \right] \right\}$$
$$= 2 \sum_{n} \rho_{n} g_{n} (k^{2} + 1^{2} - k1) + \sum_{N} \rho_{N} \left[ G_{N} (K^{2} + L^{2} - KL + K + \frac{1}{3}) \right] .$$
(56)

### OTHER INFORMATION CONCERNING HCP STRUCTURE DYNAMICS

### 1. The optical frequencies at q = 0 are as follows:

$$\omega = \left(\frac{12\sum_{N} \rho_{N} \left(A_{N} + B_{N}\right)}{m_{1}}\right)^{\frac{1}{2}}, \omega = \left(\frac{24\sum_{N} \rho_{N} G_{N}}{m_{1}}\right)^{\frac{1}{2}}.$$
(57)

2. The trace of Fourier transform of the dynamical matrix gives the sum of squared frequencies

$$m_{1}\Sigma \omega_{1}^{2} = 48\sum_{n} \rho_{n}(a_{n}+b_{n}+g_{n}) + 24\sum_{N} \rho_{N} (A_{N}+B_{N}+G_{N})$$

$$-16\sum_{n} \{\rho_{n}(a_{n}+b_{n}+g_{n})\cos(2\pi \operatorname{cmq}_{z})[\cos(\pi a(21-k)q_{x})\cos(\sqrt{3}\pi akq_{y}) + \cos(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi a(k-1)q_{y})]\}$$

$$+\cos(\pi a(2k-1)q_{x})\cos(\sqrt{3}\pi aq_{y}) + \cos(\pi a(1+k)q_{x})\cos(\sqrt{3}\pi a(k-1)q_{y})]\}$$
(58)

3. The propagation of phonons along the c-direction shows an interesting feature. The dispersion relations for this direction are of the form

$$m_{1}\omega^{2} = \sum_{m \ge 0} x_{m} [1 - \cos(2\pi cmq_{z})] + \sum_{M \ge 0} \cdot X_{M} \{1 \pm \cos[2\pi c(M + \frac{1}{2})q_{z}]\}$$
(59)

where for longitudinal modes

$$x_{m} = 24 \sum_{kl} g_{klm} \rho_{n}; \qquad X_{M} = 12 \sum_{KL} G_{KLM} \rho_{N}$$
(60)

and for transversal modes

$$x_{m} = 12 \sum_{kl} (a_{klm} + b_{klm}) \rho_{n}; \qquad X_{M} = 6 \sum_{KL} (A_{KLM} + B_{KLM}) \rho_{N}$$
 (61)

This relation may be substituted by its acoustic branch taken in a region twice as wide as the Brillouin zone –  $1/c\leqslant q_z\leqslant 1/c$ 





A qualitative picture of the phonon dispersion curve for  $q_z$ -direction drawn in the Brillouin zone (B. Z.) and the Jones zone (J. Z.)

One has (see Fig. 4)

$$m_1 \omega^2 = \sum_{s} y_s [1 - \cos(\pi c \, s \, q_z)],$$
 (62)

where

 $y_s = x_s$  for  $s \ge 0$  and even  $y_s = X_{s-1}$  for  $s \ge 0$  and odd,

This is identical with the phonon dispersion relation for a monatomic linear chain with many-neighbour interactions [9]. We see that atomic planes perpendicular to the c-direction vibrate as a whole, and because all atoms are of equal mass, their vibrations may be described by the dispersion relations of an acoustic type. In this approach atomic planes situated at  $0, \pm \frac{1}{2}, +c, \pm \frac{3}{2}, \ldots$  along the c-axis are treated as identical atoms of a linear chain. The increase of a q<sub>z</sub> periodicity range corresponds to a substitution of the Jones zone for a Brillouin zone for hcp structure [10].

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# NOTE ON DISPERSION CURVE CALCULATIONS IN ZINC

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#### (Presented by B. Buras)

#### Abstract — Résumé — Аннотация — Resumen

NOTE ON DISPERSION CURVE CALCULATIONS IN ZINC. An attempt has been made to describe an irregular shape of the experimental phonon dispersion curve in  $[01\overline{1}0]$  direction for zinc, using harmonic approximation of the Born-von Kármán theory.

The general dispersion relations for hexagonal close-packed structures given as functions of atomic force constants of an unlimited number of neighbours were employed. By means of them, the least squares fitting of theoretical curves to experimental points, considering the neighbours situated up to the distance three times lattice constant a, has been performed. In spite of that, the calculated curves do not follow experimental points satisfactorily. It allows one to suppose that the observed irregularity is to be explained by anharmonic or electron-phonon interaction effects rather than by harmonic theory.

OBSERVATIONS SUR LES CALCULS DE COURBES DE DISPERSION DANS LE ZINC. On s'est ettorcé de décrire une forme irrégulière de la courbe de dispersion expérimentale des phonons dans la direction [0110] pour le zinc, en utilisant l'approximation harmonique de la théorie de Born et von Kármán.

On a utilisé les relations générales de la dispersion pour les structures hexagonales compactes, exprimées en fonction des constantes des forces atomiques s'exerçant entre un nombre illimité d'atomes voisins. Au moyen de ces relations, l'auteur a pu adapter, par la méthode des moindres carrés, les courbes théoriques aux points obtenus expérimentalement en considérant les atomes voisins situés jusqu'à une distance égale à 3 a, a étant la constante du réseau. Toutefois, les courbes calculées ne suivent pas de manière satisfaisante le tracé des points expérimentaux. Ceci donne à penser que l'irrégularité observée doit s'expliquer par des effets anharmoniques ou par des interactions électrons-phonons, plutôt que par la théorie des harmoniques.

ОТНОСИТЕЛЬНО РАСЧЕТОВ ДИСПЕРСИОННЫХ КРИВЫХ В ЦИНКЕ. Была сделана попытка описать с помощью теории гармонического приближения Борна фон Кармана необычную форму экспериментальной кривой фононной дисперсии в направлении [0110] для цинка.

Были использованы общие дисперсионные соотношения для гексагональной структуры с плотной упаковкой, представляющие функции констант атомных сил неограниченного количества соседних атомов.

С их помощью было проделано выравнивание методом наименьших квадратов теоретических кривых по экспериментальным точкам с учетом соседних атомов, расположенных на расстоянии трехкратной константы решетки а. Несмотря на это, рассчитанные кривые не совпали достаточно хорошо с экспериментальными точками. Это дает основание предполагать, что наблюдавшаяся необычность формы должна быть объяснена эффектами негармоничных или электрон-фононных взаимодействий, а не теорией гармоний.

NOTA SOBRE EL CALCULO DE CURVAS DE DISPERSION EN EL CINC. El autor procura explicar la forma irregular de la curva experimental de dispersión fonónica en la dirección [0110] del cinc, aplicando la aproximación armónica de la teoría de Born-von Kármán.

Utiliza las relaciones generales de dispersión para una estructura hexagonal compacta, expresada en función de las constantes de fuerza para un número ilimitado de átomos vecinos.

Basándose en dichas relaciones, ajusta por el método de los cuadrados mínimos las curvas teóricas a los puntos experimentales, tomando en consideración los átomos vecinos situados hasta una distancia igual al triple de la constante reticular a. A pesar de ello, las curvas calculadas no se ajustan satisfactoriamente a los puntos experimentales. Ello permite suponer que la explicación de la irregularidad observada radica en los efectos anarmónicos o en los de las interacciones electrón-fonón, y no en la teoría armónica.

The acoustical branch polarized in the c-direction of the dispersion curve for zinc in the  $[01\overline{1}0]$  direction, measured earlier in this Laboratory [1], has an unusual depression for  $q \approx 0.11$  Å<sup>-1</sup> (see Fig.1 - experimental points are marked as circles).

The intention of this work was to check whether this dispersion curve can be described by the Born-von Kármán theory. The dispersion relations for phonons in the hexagonal close-packed structure, derived by CZACHOR [2] as functions of the force constants of an unlimited number of neighbours, were used. For the branch and direction under consideration, those relations may be transformed into the following form:

$$\mathbf{m}\omega^{2} = \mathbf{B} + \sum_{r=1}^{\infty} \alpha_{r} (1 - C_{r}) \pm \left|\beta_{0} + \sum_{r=1}^{\infty} (\beta_{r}C_{r} + i\gamma_{r}S_{r})\right|,$$

where

 $\pm \text{ gives optical and acoustical branches, respectively,}$ m is the mass of an atom,a is the lattice constant, $<math display="block">C_{r} = \cos (r \sqrt{3} \pi a q_{y}),$  $S_{r} = \sin(r \sqrt{3} \pi a q_{y}),$  $B = \sum_{r=0}^{\infty} \beta_{r}$ 

 $\alpha_{r},\ \beta_{r},\ \gamma_{r}$  are force constants which are subject to the additional conditions:

$$\sum_{r=1}^{\infty} \gamma_r \cdot r = -\frac{2}{3} B,$$

$$\sum_{r=1}^{\infty} (\alpha_r + \beta_r) r^2 = \frac{2}{\sqrt{3}} c C_{44} + \frac{4}{9} B,$$

where  $C_{44}$  is the elastic constant and c is the lattice constant.

The frequency  $\omega_0$  of the optical phonon at the centre of the Brillouin zone obtained from measurements in the [0001] direction, gives the value of the constant B, since

$$m\omega_0^2 = 2 B.$$

Thus dispersion relations may be expressed in terms of  $\alpha_2, \alpha_3, \ldots$ ,  $\beta_1, \beta_2, \beta_3, \ldots, \gamma_2, \gamma_3, \ldots$  as independent parameters, while  $\alpha_1, \beta_0$  and  $\gamma_1$ , may be evaluated using the above-mentioned conditions.

Force constants  $\alpha_r$ ,  $\beta_r$ ,  $\gamma_r$  are linear combinations of atomic force constants  $\Phi_{33}(\frac{1}{kk})$ , namely  $\alpha_r$  for atoms of the same sub-lattice (k = k'= 1) and



Dispersion relations for phonons in zinc for the [0110] direction, polarization parallel to the c-direction.



The projection of the hexagonal close-packed structure on the basal plane

 $\beta_r$ ,  $\gamma_r$  for atoms of different sub-lattices (k = 1, k' = 2). It is interesting to note, that every element of those combinations is the sum of force constants of all atoms situated along the same line perpendicular to the basal plane.

Figure 2 shows the projections of such lines on the basal plane. Lines used in calculations in a model with three independent parameters are indicated by the number 3; in a model with four parameters, by numbers 3 and 4 and in a model with seven parameters, by numbers 3, 4 and 7.

The calculations were performed using the electronic computer GIER. The least squares procedure was used to fit theoretical curves to experimental points. The resultant values of force constants are shown in Table I, and the corresponding dispersion curves in Fig.1: the dotted line is for the 3-parameter model, the dashed line for the 4-parameter model, and the solid line for the 7-parameter model.

As can be seen, the calculated curves do not follow satisfactorily the experimental points. The use of a model with a higher number of independent parameters seems to be doubtful for two reasons:

(1) The number of independent parameters would be too high compared to the number of experimental points and

#### TABLE I

| Force constants | Model    |                 |           |
|-----------------|----------|-----------------|-----------|
|                 | 3        | 4               | 7         |
| α1              | - 8,728  | - 8.315         | - 8.156   |
| $\alpha_2$      | 3, 530   | 3, 183          | 3,183     |
| α3              |          |                 | - 0.00045 |
| β <sub>0</sub>  | 16.59    | 15.73           | 15,89     |
| β <sub>1</sub>  | 14.68    | 15 <b>. 5</b> 6 | 15.40     |
| β <sub>2</sub>  | 4,512    | 4.544           | 4.544     |
| ßs              |          |                 | 0.00041   |
| γ1              | -14.68   | -22.91          | -23, 77   |
| γ2              | - 4.512* | - 0.4895        | - 1.096   |
| γ3              |          |                 | 0,6928    |

# FORCE CONSTANTS (10<sup>3</sup>dyn/cm)

\* In this model  $\gamma_2 = -\beta_2$ .

(2) The slight improvement of fitting by changing from model 4 to model
 7 does not allow expectation of really better results for a higher number of parameters.

Therefore one should probably look for an explanation of the observed irregularities of the dispersion curve in anharmonic effects or electron-phonon interaction.

#### ACKNOWLEDGEMENTS

I should like to thank Professor B. Buras and Mr. A. Czachor for their stimulating discussion and advice.

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#### DISCUSSION

G. CAGLIOTI: I should like to mention that anomalous changes in the slope of the [01T0] TA perpendicular branch of zinc, though much less pronounced than the depression at  $q_0 = 0.11 A^{-1}$  discussed in Dr. Holas' paper, were also found at the Ispra Laboratory<sup>\*</sup>. In the latter study, however, the data had not been obtained in sufficiently small increments of  $q/q_{max}$  and at conveniently low energies of the impinging neutrons for us to be able to discuss the details of these anomalies. Further work in this direction is planned for the near future.

B. BURAS: Figure 2 of Mr. Holas' paper shows that the depression is quite pronounced. The measurements were made twice with two zinc singlecrystals. They were then repeated after we learned about Dr. Caglioti's work. We therefore believe that the depression really exists. I am very glad, however, to hear that Dr. Caglioti is going to repeat his measurement. It is always good to check against the possibility of the results depending on geographical altitude.

\* See BORGONOVI, G., CAGLIOTI, G. and ANTAL, J.J., Phys. Rev. 132 (1963) 683.

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# PHONONS IN ALUMINIUM AT 80°K

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#### Abstract — Résumé — Аннотация — Resumen

PHONONS IN ALUMINIUM AT  $80^{\circ}$ K. The dispersion relations for aluminium have been determined fairly completely at  $80^{\circ}$ K by measurements with a new three-axis crystal spectrometer at the  $30^{\circ}$ MW research reactor R2 at Studsvik. Complete dispersion curves have been obtained for the three symmetry directions, together with interpolation points on the zone boundaries and elsewhere. The results are presented as dispersion curves and as contour maps of dispersion surfaces.

The series of measurements was the first undertaken with the spectrometer, and to establish a sound experimental routine, considerable attention was devoted to details such as resolution, reproducibility and the avoidance of disturbing effects. A focusing technique was used throughout to optimize resolution. The results consequently were of a rather high degree of accuracy and were utilized to search for Kohn anomalies, but no clear examples were found. Such effects are evidently small in aluminium, but there are indications that a moderate improvement of experimental technique may render them discernible.

Phonon widths at 80°K could often be determined from the widths of observed resonances via a calculated resolution width. In another series of measurements at  $300^{\circ}K$  – not yet completed – widths could always be determined. Examples are given of broadenings and energy shifts in passing from 80 to  $300^{\circ}K$ . A noteworthy effect was found at  $\vec{q} = (0.8, 0.0)$ : the phonon width there increased in an anomalous fashion in passing from 80 to  $300^{\circ}K$ .

Another observation is that points for small  $\vec{a}$  on transverse branches tend to lie significantly above the lines through the origin having slopes corresponding to the velocity of 10-Mc/s sound waves.

PHONONS DANS L'ALUMINIUM A 80°K. Les auteurs ont déterminé de manière assez complète les relations de dispersion pour l'aluminium à 80°K par des mesures effectuées au moyen du spectromètre à cristal triaxial récemment installé près du réacteur de recherche R2, de 30 MW, situé à Studsvik. Ils ont établi des courbes de dispersion complètes pour les trois directions de symétrie, ainsi que des points d'interpolation situés tant aux frontières de zone qu'ailleurs. Les résultats obtenus sont présentés sous forme de courbes de dispersion et de lignes de niveau des surfaces de dispersion.

Cette série de mesures est la première que l'on ait effectuée avec le spectromètre, et pour fixer de manière rationnelle les conditions des expériences futures, les auteurs ont apporté une grande attention à certains aspects particuliers tels que la résolution, la reproductibilité et l'élimination des effets parasites. Pour optimiser la résolution, ils ont utilisé un système de focalisation pendant toute la durée des mesures. Ils ont ainsi obtenu des résultats d'une assez grande précision, dont ils se sont servis pour la recherche d'anomalies de Kohn, sans cependant trouver d'exemples bien nets. Bien entendu, des effets de ce genre sont faibles dans l'aluminium mais, d'après certaines indications, une légère amélioration de la technique expérimentale peut les rendre perceptibles.

A partir des largeurs des résonances observées, il a souvent été possible de déterminer les largeurs des phonons à 80°K par l'intermédiaire de la largeur de résolution calculée. Au cours d'une autre série de mesures à 300°K – qui n'est pas encore achevée – il a toujours été possible de déterminer les largeurs. Les auteurs donnent des exemples d'élargissements et de déplacements d'énergie observés lorsque la température passe de 80°K à 300°K. Un effet digne d'attention a été relevé pour  $\vec{q} = (0, 8, 0, 0)$ : dans ce cas, la largeur des phonons a augmenté de façon anormale lorsque la température a passé de 80 à 300°K.

D'autre part, les auteurs ont observé que des points pour  $\hat{q}$  petit sur les branches transversales tendent à se trouver sensiblement au-dessus des lignes passant par l'origine et ayant des pentes qui correspondent à la vitesse des ondes sonores de 10 Mc/s.

ФОНОНЫ В АЛЮМИНИИ ПРИ 80°К. Довольно подробно были определены дисперсионные соотношения для алюминия при 80°К путем измерений с помощью нового трехосевого кристаллического спектрометра на исследовательском реакторе R2 мощностью 30 мгвт в Студсвике. Получены полные кривые дисперсии для трех направлений симметрии вместе с интерполяционными точками на границах зон и в других местах. Результаты представлены в виде кривых дисперсии и контурных диаграмм дисперсионных поверхностей.

Эта серия измерений была впервые произведена с помощью спектрометра. В целях разработки надежной программы экспериментов значительное внимание уделялось таким деталям, как разрешающая способность, воспроизводимость и избежание возмущающих эффектов. Для оптимизации разрешающей способности с самого начала и до конца использовался метод фокусировки. Поэтому результаты имеют довольно высокую степень точности.

Это было использовано для нахождения аномалий Кона, но очевидных примеров обнаружено не было. В алюминии такие эффекты являются, безусловно, небольшими, но есть основания полагать, что небольшое усовершенствование экспериментального метода может сделать их различимыми.

Фононную ширину при 80°К часто можно определить по ширине наблюдаемых резонансов посредством высчитанной ширины разрешающей способности. Во время другой серии измерений, которые еще не завершены, при 300°К ширину всегда можно было определить. Приводятся примеры уширений и смещений вследствие энергии при переходе от 80°К к 300°К.

Заслуживающий внимания эффект был обнаружен при q́' =(0,8;0;0): фононная ширина увеличилась необычным образом в промежутке от 80 до 300°К.

Замечено также, что точки для небольших значений q́' на поперечных ветвях чаще всего лежат значительно выше линий, проходящих через начало координат и имеющих склоны, соответствующие скорости звуковых волн с частотой колебания 10 мгц.

ESTUDIO DE LOS FONONES EN EL ALUMINIO A 80°K. Los autores han determinado de una manera bastante completa las relaciones de dispersión en el aluminio a 80°K, mediante mediciones realizadas con un nuevo espectrómetro triaxial de cristal en el reactor de investigación R2 de 30 MW, de Studsvik. Han obtenido curvas de dispersión completas para las tres direcciones de simetría, así como puntos de interpolación en las zonas limítrofes. Los resultados se presentan como curvas de dispersión y como curvas de nivel de las superficies de dispersión.

Como esta serie de mediciones fue la primera llevada a cabo con el espectrómetro, se prestó considerable atención a detalles tales como el poder de resolución, la posibilidad de repetición y la eliminación de efectos perturbadores, a fin de establecer un procedimiento corriente de experimentación sobre una base firme. En todo el proceso se ha utilizado una técnica de colimación con el propósito de conseguir una resolución óptima. Esta técnica se aplicó para detectar anomalfas de Kohn, pero no pudieron observarse casos netamente definidos. Esos efectos son evidentemente débiles en el aluminio, pero hay indicios de que, mejorando ligeramente la técnica experimental, sería posible distinguirlos.

Con frecuencia ha sido posible determinar las amplitudes fonônicas a una temperatura de 80°K partiendo de la amplitud de las resonancias observadas y de una amplitud de resolución calculada. En otra serie de mediciones -todavía sin terminar- han podido determinarse siempre las amplitudes a una temperatura de 300°K. Los autores exponen ejemplos de ensanchamientos y de desplazamientos de la energía al pasar de 80°K a 300°K.

Un efecto digno de mención se observó para  $\vec{q}^* = (0, 8, 0, 0)$ : en este punto, la amplitud fonónica aumentó de manera anómala al pasar de 80 a 300°K.

Asimismo, se ha observado que los puntos de  $\vec{q}$  pequeño en ramas transversales tienden a situarse sensiblemente por encima de las líneas que pasan por el origen con pendientes correspondientes a la velocidad de ondas acústicas de 10 Mc/s.

### 1. INTRODUCTION

When our new three-axis spectrometer began to operate, it was decided to do the first measurements on aluminium because it is a good experimental substance. It was available in large single crystals of a simple structure, with low absorption and incoherent cross-sections (the coherent crosssection is also unfortunately rather low), and was previously the object of neutron measurements [1-4]. But perhaps the main reason for our choice was that D. Saunderson of Harwell lent us an unusually good single crystal. The measurements were more extensive than originally intended because our apparatus and technique improved considerably during the course of measurements, so that we were able to examine phonon resonances in some detail, while at the same time adverse experience made us aware of several disturbing effects which had to be guarded against.

Preoccupation with experimental method during the measurements on aluminium is reflected in this presentation of our results. While the data and comments on them are naturally the principal interest, rather more space than usual has been devoted to experimental technique, because this is of particular importance in the development of phonon spectrometry towards more refined measurements, which is our general aim.

### 2. APPARATUS AND METHOD

The spectrometer is at the 30-MW research reactor R2 at Studsvik. The beam from the reactor passes through a quartz filter, cooled to  $80^{\circ}$  K, before striking the monochromator, usually Cu(220). The shielding around this beam is 20-30 cm of iron surrounded by about 30 cm of water or polythene. The BF<sub>3</sub> detector and the analyser crystal are completely surrounded by 10 cm of paraffin wax lined with boron carbide and cadmium. This shielding, together with the filter, results in a background of about 20 counts per hour, disregarding thermal neutrons scattered in the sample.

Spectrometer movements are in multiples of a  $0.01^{\circ}$ -step and follow a programme tape. Counting periods are determined by a monitor in the beam incident on the sample. The normal mode of operation is constant- $\kappa$  (Brockhouse's "constant- $\vec{Q}$ ").

For the measurements described here the sample was mounted in a cryostat and cooled to liquid nitrogen temperature, here given as 80°K. A complete series of measurements at 300°K has also been made, and examples are shown in Fig.4

The attainment of good resolution involves a reduction of momentum resolution as much as available intensity will allow, and the application of a focusing technique. The spectrometer design takes account of these requirements in that a wide range of angles is accessible in each angular motion; collimators and crystals are easily exchangeable and several monochromator and analyser crystals are available.

#### 2.1. Focusing

A focusing technique for improving resolution was devised some years ago and has been applied in all measurements with the present spectrometer. The idea may be explained very briefly as follows.

First a few words on our notation. Neutron variables are  $\vec{k}_1$ ,  $\vec{k}_2$ ,  $\vec{k}$ ,  $\epsilon$ .  $\vec{k}_1$  is the momentum of a neutron before scattering,  $\vec{k}_2$  the momentum after scattering;  $\vec{k} = \vec{k}_1 - \vec{k}_2$ ,  $\epsilon = (k_1^2 - k_2^2)/2$ . The units are such that  $\hbar = 1$  and the neutron mass is also 1. Phonon variables are  $\omega$  and  $\vec{Q}$  (reduced:  $\vec{q}$ ), and the condition for a one-phonon scattering resonance is  $(\vec{k}, \epsilon) = (\vec{Q}, \omega)$ . A dispersion surface may be transferred to  $(\vec{k}, \epsilon)$  space, where it becomes a surface of one-phonon resonances. The course of a measurement is illustrated in Fig. 1. The spectrometer, at any setting, looks at a region around a point



Fig.1

The correspondence between a recorded one-phonon resonance (right) and the spectrometer's traversing of a dispersion surface (left) Widths of distributions are indicated by half-maximum contours, shown in section.

 $(\vec{k}, \epsilon)$ . The intensity distribution around this point may be visualized by its half-maximum contour, which is to a good approximation an ellipsoid. If momentum and energy have relative scales of the order usual in diagrams of dispersion curves, this ellipsoid is quite thin in the energy direction. Consequently, if it is possible to tilt this disk so that it is locally parallel to the dispersion surface under investigation, the observed resonance will be narrower and higher than it would otherwise have been. A focusing condition has then been achieved.

A further advantage of focusing is that it minimizes a source of error associated with the circumstance that the real mean of the region seen by the spectrometer does not always coincide with the nominal mean (that corresponding to the spectrometer settings) on account of instrumental uncertainties.

In practice, focusing is seldom exact, but even approximate focusing is valuable. A full account of how focusing is achieved is quite long. Here it is sufficient to say that this is done by an appropriate choice of  $\vec{Q}$  (given  $\vec{q}$ ), the analyser crystal and its setting, the monochromator and the beam path (from four alternatives).

#### 3. RESOLUTION AND PHONON WIDTHS

Energy resolution may be calculated with respect to a plane parallel to the dispersion surface at the relevant point, (Vertical components of momentum are of no consequence.) There are four contributions, each an energy deviation from this plane. They are associated with: the mosaic width of the monochromator, the width of the entrance collimator (between the monochromator and the sample, i.e. the dominating collimator on the monochromator side in our arrangement), the mosaic width of the analyser and the width of the exit collimator (between the sample and the analyser). The contributions are mutually independent and can be combined by adding squares and taking the root in accordance with a well-known result on the second moments of folded distributions. In practice we designate the width of a distribution by the full width at half-maximum height, but since all distributions are bell-shaped and have no large contribution from the wings, the ratio of this practical parameter to the standard deviation may safely be assumed to be the same for all the distributions concerned (compare, for instance, a triangular distribution and a Gaussian).

The phonon widths reported here are determined by the same simple procedure: the square of the calculated resolution width is subtracted from the square of the width of the observed resonance and the square root then taken. This assumes the phonon energy distribution to be such that the contribution to the second moment from the wings is not large, but in any case the wings are inevitably curtailed in the somewhat arbitrary process of deciding what is background and what is peak in the observed resonance. A phonon width is referred to as  $\Delta \omega$ . This may not be a true phonon width in the sense of an energy uncertainty (thickness of the dispersion surface); it may be due to unresolved structure of the dispersion surface. The errors quoted for phonon widths are wholly due to the estimated effect of counting statistics on observed resonances.

#### 4. DISTURBANCES

There are other processes than the one-phonon scattering under investigation that lead to peaks (or occasionally valleys) in the detector counting rate. Where such peaks are expected and separable from the effect under observation they are tolerable, but an unexpected small effect may remain undetected and lead to a displacement of the observed peak and an alteration of its width. We have observed several instances of disturbing effects and are introducing devices to eliminate them. In the measurements we report here we have made every effort to detect and avoid disturbances and are confident that the results are not marred by them except perhaps in some overlooked isolated cases. The following is a list of disturbances and remedial measures.

#### 4.1. The analyser second-order effect

The crystals ordinarily used as monochromators and analysers reflect neutrons of momentum  $2\vec{k}$ ,  $3\vec{k}$ , ... as well as  $\vec{k}$ . Consequently the spectrometer "looks at" several points of  $(\vec{k}, \epsilon)$  space simultaneously (any combination  $m\vec{k}_1$ ,  $n\vec{k}_2$  gives a point), and any of these points can give rise to an inelastic scattering resonance. With aluminium the only case of importance is the combination  $\vec{k}_1$ ,  $2\vec{k}_2$  and low-energy one-phonon scattering.

A radical remedy is to use an analyser without a second-order reflection, e.g. Ge(111). The difficulty is to obtain a large enough crystal with sufficiently large mosaic width. A Ge (111) analyser should be suitable for measurements on high-energy phonons, where this second-order disturbance is particularly troublesome.

The scattering plane is usually a plane of high symmetry, and a simple diagram (or a computer programme) is then sufficient to see whether the effect is likely to occur. If it is, the experimental conditions may be adjusted to avoid it. The effect is very likely to occur if  $\vec{k}_1 - 2\vec{k}_2$  lies somewhere near a reciprocal lattice point and  $(k_1^2 - 4k_2^2)/2$  is small.

A partial remedy is to rotate the sample a few degrees around the  $\vec{\kappa}$ -direction so that the scattering plane no longer contains many lattice points

(cf. previous paragraph). We have done this for measurements on longitudinal phonons ( $\vec{q}$  parallel to  $\vec{Q}$ ), and now have an arrangement which allows this to be done for all measurements.

If the effect is suspected to have occurred, the measurement may be checked by repeating it with an analyser set to  $2\vec{k}_2$ . In this case it is preferable to change the analyser to one with a lattice spacing about half that of the crystal originally used (so that momentum resolution for  $2\vec{k}_2$  is about the same in both cases). Good resolution (good momentum resolution and focusing) reduces the incidence of this disturbance, and makes it easier to discover it when it does occur. This applies generally to all disturbances, of course. The incidence of the effect is also less at low sample temperatures, because energy-gain processes are then of minor importance.

#### 4.2. Bragg scattering in the sample

Each reciprocal lattice point  $\vec{G}$  has an associated "Bragg plane", which is the perpendicular bisector of  $\vec{G}$ . A neutron of momentum k undergoes Bragg reflection if  $\vec{k}$  lies on such a plane. Figure 2 shows the traces of



Fig. 2

The traces of Bragg planes in a principal plane of the reciprocal lattice for a fcc crystal Each plane is the perpendicular bisector of a reciprocal lattice vector.

such Bragg planes in a principal plane of the reciprocal lattice for a facecentred cubic (fcc) crystal. It will be seen that Bragg reflection of either  $\vec{k}_1$  or  $\vec{k}_2$  is difficult to avoid entirely, particularly for the longer  $\vec{k}_1$ .

One might expect such reflection to attenuate the incident or scattered beam and thus distort the observed peak. This effect is negligible in our sample, because its mosaic width is so small (secondary extinction so large), but a poor quality crystal may well exhibit this attenuation effect. The neighbourhood of such points as the nodes in Fig. 2 may be expected to be particularly unfavourable. These are avoided if the sample is tilted around  $\vec{k}$ .

Incident neutrons may be Bragg-scattered into the analyser, and some of them there scattered into the detector. This is avoided by tilting the crystal around  $\vec{k}$ . A monitor behind the analyser crystal discloses the effect.

An effect analogous to that just mentioned may be expected to arise from "non-Bragg" scattering in the monochromator, and subsequent Bragg scattering in the sample and analyser. The remedy is to tilt the sample.

#### 4.3. Bragg scattering from extraneous material near the sample

A few cubic millimetres of polycrystalline material in the sample holder or cryostat can produce a disturbance if  $k_1$  is roughly equal to  $2k_2$ . The remedy lies in design of the sample holder etc. and in avoiding the conjunction  $k_1 = 2k_2$  (which responds to any incoherent elastic scattering also, of course). A monitor, after the analyser crystal, discloses the effect. Small inclusions in the sample crystal give rise to a similar effect, which again points to the need of high quality sample crystals.

### 5. RESULTS

Dispersion curves for the [111], [200] and [220] directions are shown in Figs. 3-5. Below the curves are values for the energy widths of phonons, values being determined as described in section 3 and widths in the sense explained there. Results for  $300^{\circ}$ K are included in the figure for the [200] direction. It should perhaps be mentioned that all these measurements were by energy loss for the neutrons.

The lines through the origin in each figure have slopes corresponding to the appropriate velocity of sound in the direction concerned, from measurements at 10 Mhz [5].

Figures 6-8 are derived from the dispersion curves, together with some further measurements which are indicated by +. They show energy contours on the inner surfaces of an elemental tetrahedron in reciprocal space. This tetrahedron is indicated in the small insets accompanying each figure. It is more convenient to use this figure instead of the usual segment of the first Brillouin zone with its more complicated boundary and more complicated symmetry conditions at the boundary.

#### 6. ERRORS

The probable error in the assignment of a mean position to an observed resonance was estimated in each case with regard to counting statistics and the shape of the resonance. Its magnitude is between 0.01 and 0.03 ( $\times 10^{13}$  rad/s), the higher value occurring near the maxima of dispersion curves. Another error arises from uncertainty in the calibration of the instrument: we believe this error is negligible for longitudinal branches and where the slope of dispersion curves is small; elsewhere it may be up to  $0.03 \times 10^{13}$  rad/s. Yet another error arises from the curvature of dispersion surfaces, since the spectrometer records an average for a certain region. Momentum resolution was typically about 0.07 in q' in all directions, and it can be shown that the error due to curvature of the surface is then negligible except at small q', where a small correction has been made.





Dispersion curves for phonons in the [111] direction in Al at 80°K Below: phonon widths for the respective branches.



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Dispersion curves for phonons in the [200] direction in Al. The main curves are for 80°K, the dashed curves for 300°K. Below: phonon widths for the respective branches:  $\frac{1}{2}$  80°K,  $\frac{1}{2}$  300°K,







A contour map of phonon frequency for the L branch on the unfolded inner surface of the elemental tetrahedron shown in the inset

Contours at intervals of  $0.5 \times 10^{13}$  rad/s. + indicates the site of a measurement off the symmetry directions.  $\Theta$ ,  $\Phi$  and  $\Theta$  indicate polarization.

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A contour map of phonon frequency for the T<sub>i</sub> branch on the unfolded inner surface of the elemental tetrahedron shown in the inset
 Contours at intervals of 0, 5 × 10<sup>13</sup> rad/s. + indicates the site of a measurement off the symmetry directions. Θ, Φ and ⊙ indicate polarization.

Resolution widths varied between 0.03 and 0.2 ( $\times 10^{13} \text{ rad/s}$ ); they appear indirectly in the information on phonon widths. Of course it will be seen that resolution was particularly good for transverse branches and poorer near the maxima of dispersion curves.

7. COMMENTS

A rather large number of measurements was made in the [220] direction because this happened to be the first direction investigated, and we did new measurements as experimental improvements were made. It also seemed that there was a variation of real or apparent phonon width with q' which might be associated with Kohn anomalies, so we made more detailed measurements. Subsequently we found that the blurred situation near q' = 0.96 is due to a singularity in the dispersion surfaces at the crossing point of two branches, and no connection was established between phonon widths and the Fermi surface. However, the width of the T<sub>1</sub> branch between q' = 1.2 and



Fig. 8

A contour map of phonon frequency for the  $T_2$  branch on the unfolded inner surface of the elemental tetrahedron shown in the inset

Contours at intervals of  $0.5 \times 10^{13}$  rad/s. + indicates the site of a measurement off the symmetry directions.  $\Theta$ ,  $\Phi$  and  $\odot$  indicate polarization.

q' = 1.35 is notably small, and there seems to be a suggestion of a knee at about q' = 0.4 on the L-branch, and perhaps at q' = 0.7. When the behaviour of widths on other branches is also considered, it appears that the search for Kohn anomalies may still be rewarding.

The sound velocities from ultrasonic measurements fit well to the lower parts of our longitudinal dispersion curves, but for the transverse branches they lie below the dispersion curves. Although the discrepancy is small, it appears to be definite, cf. in particular the [220]  $T_1$  branch when the sound velocity line is produced to larger q'.

The maps of phonon energies are generally similar to those of WALKER [6], though considerably different in detail. Our higher frequency values are consistently a good deal higher than Walker's; the frequency of the maximum for the [200] L branch is some 12% higher and plateau-like formations in our maps are not present in his. The  $\omega$ -distribution should therefore be significantly different from that of Walker, and it may be that the discrepancy between the corresponding specific heat curve and the measured specific heat will disappear. It is intended to carry out an interpolation of  $\omega$  for the complete volume of the elemental tetrahedron, which will enable the  $\omega$ -distribution to be constructed almost directly from measurements.

The dispersion curve for the [200] direction at 300°K exhibits a noteworthy effect: around q' = 0.8,  $\omega$  is depressed relative to the 80°K values more than it is elsewhere, and the phonon width increases in a pronounced fashion. We have thoroughly checked this effect and there is no doubt that it is real.

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### DLSCUSSION

P. EGELSTAFF: It seems to me that your data are comparable with those of Yarnell and Warren. If I remember correctly, they, too, noted the difference between the neutron data and the ultrasonic data. Perhaps Mr. Warren could confirm this.

J. WARREN: This is true, and Yarnell also saw slopes which were above those predicted by the elastic constants. However, we found that our resolution in wave vector produced a wave-vector-dependent correction which essentially eliminated the discrepancy observed between our results and those of the elastic constants.

P. EGELSTAFF: Don't you think that the possibility of the Kohn effect contributing to the large width mentioned in the last paragraph of your paper should be investigated theoretically before you draw any conclusions?

R. STEDMAN: As I indicated in my oral presentation, I am hesitant about putting forward any suggestion. However, there is nothing in the Kohn anomalies, as they are accounted for at present, that would lead one to expect a temperature-dependent effect like the one we observed.

S. SINHA: In measuring the phonon width by subtracting the second moment of your resolution function from that of your observed distribution, you may run into a difficulty in interpreting the second moment of your natural line-width. For a Lorentzian shape this second moment diverges. In any case, I think it is a complicated, and perhaps temperature-dependent, function of your phonon lifetime. The question is then, what is it that you are measuring?

R. STEDMAN: In our width analysis we assume that all distributions are bell-shaped and that there are small contributions to the second moment from the wings. The ratio of the width at half-maximum height to the standard deviation varies little for such distributions. A Lorentzian distribution does not fit into this scheme because the wings are not negligible. Moreover, a more rigorous analysis which would cover this distribution as well is made difficult by the experimental circumstance that the wings of the observed resonance are in any case cut off somewhat arbitrarily when the background is subtracted.

P.K. IYENGAR: Dr. Stedman has given a fine description of the distortions that may be introduced in the so-called phonon resonance when one uses a crystal spectrometer method. But, so far, this type of description does not appear to have been done with chopper time-of-flight methods, and I wonder whether the pitfalls in locating the point in q-space would occur with the latter technique. I think it would be worth investigating to see if the method introduces some errors in the placing of the phonons at the proper q-values. This is probably also relevant to the work Sinha presented, in which he does not see the type of forbidden reflection or diffused scattering which Caglioti reported in his paper.

As regards our own paper on magnesium<sup>\*</sup>, I think the point Mr.Roy was trying to make was that, by using a four-neighbour T-F (tensor-force) model, you get simultaneous agreement on the longitudinal-optical and the longitudinal-acoustical modes as well as on the slope of the dispersion curve in the acoustical region. This is why we feel that the T-F model is more appropriate. The limitations of our experiment in respect of small values of q is secondary.

<sup>\*</sup> IYENGAR, P.K., VENKATARAMAN, G., VIJAYARAGHAVAN, P.R. and ROY, A.P., "Lattice dynamics of magnesium", these Proceedings I.

# THEORETICAL INVESTIGATIONS OF THE INFLUENCE OF ANHARMONICITY AND IMPURITIES ON NEUTRON SCATTERING BY CRYSTALS AND ON THE MOSSBAUER EFFECT

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#### Abstract — Résumé — Аннотация — Resumen

THEORETICAL INVESTIGATIONS OF THE INFLUENCE OF ANHARMONICITY AND IMPURITIES ON NEUTRON SCATTERING BY CRYSTALS AND ON THE MÖSSBAUER EFFECT. Some aspects will be given concerning the effect of diluted substitutional impurities and concerning the combined effect of impurities and anharmonicity on the Mössbauer effect and on neutron scattering by crystals. Published papers by various investigators and some unpublished work by the author, partly in collaboration with Lax, are considered.

ÉTUDE THÉORIQUE DE L'INFLUENCE DE L'ANHARMONICITÉ ET DES IMPURETÉS SUR LA DIFFUSION DES NEUTRONS DANS LES CRISTAUX ET SUR L'EFFET MÖSSBAUER. L'auteur s'intéresse à l'influence des impuretés de substitution diluées et à l'influence combinée des impuretés et de l'anharmonicité sur l'effet Mössbauer et sur la diffusion des neutrons dans les cristaux. Il passe en revue des mémoires publiés par divers chercheurs, ainsi que des travaux inédits qu'il a faits lui-même, dont plusieurs en collaboration avec Lax.

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ВЛИЯНИЯ НЕГАРМОНИЧНОСТИ И ПРИМЕСЕЙ НА РАССЕЯНИЕ НЕИТРОНОВ НА КРИСТАЛЛАХ И НА ЭФФЕКТ МЕССБАУЭРА. Излагаются некоторые аспекты влияния разбавленных замещающих примесей и общего влияния примесей и негармоничности на эффект Мессбауэра и на рассеяние нейтронов на кристаллах. Рассматриваются опубликованные работы ряда исследователей и некоторые неопубликованные работы автора, выполненные частично совместно с Лаксом.

ESTUDIO TEÓRICO DE LA INFLUENCIA DE LA ANARMONICIDAD Y DE LAS IMPUREZAS EN LA DIS-PERSIÓN NEUTRÓNICA POR CRISTALES Y EN EL EFECTO MOSSBAUER. Se exponen algunas cuestiones relativas al efecto de las impurezas de sustitución diluidas, así como a la influencia combinada de las impurezas y de la anarmonicidad sobre efecto Mossbauer y la dispersión neutrónica por cristales. Se examinan memorias publicadas por varios investigadores y algunos trabajos inéditos del autor, realizados en parte en colaboración con Lax.

The problem of the influence of anharmonicity on the Mössbauer effect, when the nucleus emitting or absorbing Mössbauer gamma-rays belongs to an impurity atom in a crystal, has been treated in a recent paper by KRIVOGLAZ [1]. Not being aware of this publication, LAX and WALLER [2] have recently given a treatment of the same problem from somewhat different and perhaps more general aspects. It is the purpose of this paper to apply a similar treatment to some simple cases of neutron scattering by crystals containing impurities. The results in [2] can be obtained as a special case of the present paper. As we did in [2], I want to give some clarification of the so-called "Bessel function enhancement" noted by KAUFMAN and LIPKIN [3] and considered by ELLIOTT and MARADUDIN [4]

#### I. WALLER

and others. This effect has been claimed to give an enhancement of the ordinary temperature factor for the Mössbauer effect and to act similarly in neutron scattering and would appear when the impurity causes a frequency mode above the bands of the host lattice or between such bands. Such modes are localized to the environment of the impurity and are therefore called localized modes. They were first investigated by LIFSHITZ [5] and later by other authors [6-8]. It was emphasized in [1] and [7] and in particular in [2] for the Mössbauer effect that in practice, because of the usually larger frequency width of a localized mode, this enhancement does not appear in ordinary Mössbauer experiments because of the high energy resolution of the detector absorber. In this paper a corresponding problem for neutron scattering is considered first.

Making a slight generalization of the well-known Van Hove formula for the differential cross-section reaction for neutrons, we obtain in the harmonic approximation for a lattice containing impurities

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d} v \mathrm{d} \Omega} = \frac{\mathrm{k}}{\mathrm{k}_0} \mathrm{S}\left(\vec{\kappa}, \mathrm{v}\right),\tag{1}$$

where

$$S(\vec{k}, v) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-ivt} \sum_{RR'} (b_R b_{R'} + \delta_{RR'} C_R^2) \exp \left[2 W_{RR'}(t)\right] \exp\left[i\vec{k}(\vec{R} - \vec{R}')\right] (2)$$

Here

$$\mathbf{v} = \frac{\hbar}{2\mathrm{m}} (\mathbf{k}_0^2 - \mathbf{k}^2); \qquad \vec{\kappa} = \vec{\mathbf{k}}_0 - \vec{\mathbf{k}}, \qquad (3)$$

 $\vec{k}_0$  and  $\vec{k}$  being the wave vectors of the neutron before and after scattering respectively and fix and fix therefore the energy and the momentum transferred to the lattice; m is the neutron mass.

$$\mathbf{b}_{\mathbf{R}} = \langle \mathbf{a}_{\mathbf{R}} \rangle e^{-\mathbf{W}}; \qquad \mathbf{C}_{\mathbf{R}}^2 = \langle \mathbf{a}_{\mathbf{R}}^2 \rangle e^{-2\mathbf{W}} - \mathbf{b}_{\mathbf{R}}^2$$
(4)

are the coherent and squared incoherent scattering lengths including the temperature factors. The positions of the nuclei are denoted by  $\vec{R}$  and we use this (for shortness written as R) to denote the nuclear mean positions at the temperature of the lattice. The displacement at the time t of the nucleus R is written as  $\vec{u}_R$  (t) and we have

$$W_{RR'}(t) = \frac{1}{2} \left\langle [\vec{\kappa} \cdot \vec{u}_{R}(0)] \ [\vec{\kappa} \cdot \vec{u}_{R}(t)] \right\rangle$$
(5)

where  $\langle \dots \rangle$  signifies a statistical mean value for the equilibrium state at the temperature T.

We have expressed the displacements in normal modes, numbered by S, in the following way ( $\omega_s$  being the frequency of the modes)

$$\int_{J} u_{Rx}(t) = \sum_{s} \left( \frac{\hbar}{2M_{R}\omega_{s}} \right)^{\frac{1}{2}} e_{Rx}^{s} [a_{s}^{*}(t) + a_{s}(t)], \qquad (6)$$

 $e_{Rx}^s$  being real. Then if  $M_R$  is the mass of the nucleus R

$$W_{RR'}(t) = \sum_{s=\pm 1} \sum_{xx'} \frac{\hbar}{4\omega_s} \kappa_x \kappa_{x'} (\mathbf{M}_R \mathbf{M}_{R'})^{-\frac{1}{2}} \mathbf{e}_{Rx}^s \mathbf{e}_{R'x'}^s \mathbf{N}_{\zeta}(\omega_s, t), \quad (7)$$

where terms which vanish in the harmonic approximation have been neglected and where

$$\begin{split} \mathbf{N}_{\zeta}\left(\boldsymbol{\omega}_{s}, t\right) = & \left\langle \mathbf{a}_{s}(0)\mathbf{a}_{s}^{*}(t) \right\rangle \quad \text{for } \zeta = +1 \\ \mathbf{N}_{\zeta}\left(\boldsymbol{\omega}_{s}, t\right) = & \left\langle \mathbf{a}_{s}^{*}\left(0\right)\mathbf{a}_{s}\left(t\right) \right\rangle \quad \text{for } \zeta = -1 \end{split}$$

In the harmonic approximation

$$N_{\zeta}(\omega_{s}, t) = \frac{1}{2} \left( \coth \frac{\hbar \omega_{s}}{2kT} + \zeta \right) \exp (i\zeta \omega_{s} t) = n_{\zeta}(\omega_{s}, t) \exp(i\zeta \omega_{s} t).$$
(8)

If anharmonic or other damping effects are present we have under very general conditions for large enough t, as emphasized in [2],

$$N_{r}(\omega_{s}, t) = n_{r}(\omega_{s}) \exp \left[i\zeta\omega_{s}t - \gamma_{s}(t)\right]$$
(9)

where  $\gamma_s$  is a damping constant. There is also a frequency shift which we suppose is included in  $\omega_s$ .

We consider for the sake of brevity the simple case that there is a single impurity at the position  $\mathbf{R} = 0$ , which gives rise to a localized mode above the continuum of states which then has the same extension in the perturbed lattice as in the host lattice. We assume further that the lattice has cubic symmetry with respect to the impurity site.

To clarify some essential points, we assume further that the impurity has such a large and dominating incoherent scattering length  $C_0$  that only that term in Eq. (2) which is proportional to  $C_0^{\circ}$  need be considered. Such a situation may, for example, be approximated if the impurity is hydrogen Then

$$S(\vec{\kappa}, v) = C_0^2 \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{-ivt} \ e^{2W(t)} , \qquad (9')$$

where

$$W(t) = \kappa^2 \sum_{\zeta=\pm 1} \sum_{s} \frac{\hbar}{4M_0 \omega_s} (e_0^s)^2 n_{\zeta}(\omega_s) \exp[i\zeta \omega_s t - \gamma_s(t)].$$
(10)

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We separate W(t) in two parts

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$$W(t) = W_{C}(t) + W_{L}(t),$$
 (11)

where  $W_C(t)$  comes from that part of the sum in Eq. (10) which refers to modes of the continuous bands and  $W_L(t)$  is the contribution of the localized mode to this sum. We can write

$$2W_{L}(t) = \rho_{L} \sum_{\zeta=\pm 1} n_{\zeta}(\omega_{L}) \exp [i\zeta \omega_{L}t - \gamma_{L}(t)], \qquad (12)$$

where

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$$\rho_{\rm L} = \frac{\hbar \kappa^2}{6 \, {\rm M}_0 \omega_0} \, {\rm e}_{0{\rm L}}^2 \, , \qquad (13)$$

 $\omega_L$  being the mean frequency and  $\gamma_L$  the half-width of the localized mode. We introduce the mean quantum number  $\overline{n}_L$  for the localized mode and expand thus

$$\exp\left[2 W_{C}(t)\right] = 1 + 2 W_{C}(t) + \frac{1}{2} \left[2 W_{C}(t)\right]^{2} + \dots \qquad (14)$$

$$\exp\left[2W_{L}(t)\right] = \sum_{r,s=0}^{\infty} \rho_{L}^{r+s} \exp\left[-(r+s)\gamma_{L}(t)\right] \frac{(\overline{n}_{L}+1)^{r} \overline{n}_{L}^{s}}{r! s!} \exp\left[i(r-s)\omega_{L}t\right].(15)$$

We see that all terms in these expansions give rise to continuous bands except those modes which come from the first term in Eq. (14) multiplied by Eq. (15). When substituted in Eq. (9') these terms give the following contribution

$$S_{L}(\vec{\kappa}, v) = \frac{1}{2\pi} C_{0}^{2} \sum_{r,s} \frac{2(r+s)\gamma_{L}}{[v - (r-s)\omega_{L}]^{2} + (\gamma + s)^{2}\gamma_{L}^{2}}.$$
 (16)

To a term r, s in this sum corresponds a scattering process where the lattice has taken up an energy  $(r-s)\omega_L$ , i.e. a process in which r local phonons have been created and s such phonons destroyed. The term for which r = s = 0should properly be written as  $2\pi\delta(v)$  and describes elastic scattering. The terms r = 0, s = 1 and r = 1, s = 0 give scattering processes where the neutron has lost or gained the energy amount  $\omega_L$  respectively. These scattering peaks both have the same width as the localized mode. The terms  $r = s \ge 1$ give bumps of the widths  $2r\gamma_L$  in the vicinity of the elastic line. The integrated intensity of all these bumps is

$$C_0^2 \sum_{r} \rho_L^{2r} \frac{(\overline{n}+1)^r \overline{n}^r}{(r!)^2} \equiv C_0^2 I_0(Z), \qquad (17)$$

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where

$$L = 2 \rho_L (\bar{n}_L + 1)^{\frac{1}{2}} \bar{n}_L^{\frac{1}{2}}.$$
 (18)

The factor containing the Bessel function

$$I_0(Z) = \sum_{s=0}^{\infty} \frac{(Z/2)^{2s}}{(s!)^2}$$
(19)

is the "Bessel function enhancement" in this case.

We represent the energy resolution attained in the measurement by the function

$$f(v) = \frac{\Gamma}{(v - v_0)^2 + \Gamma^2}$$
(20)

which means that the measured differential cross-section for the scattering processes just considered is

$$\int_{-\infty}^{+\infty} f(v) \frac{k}{k_0} S(\vec{k}, v) dv$$

i.e.

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\mathbf{v}\mathrm{d}\Omega} = \frac{\mathbf{k}}{\mathbf{k}_0} \frac{1}{\pi} C_0^2 \sum_{\mathbf{r},\mathbf{s}} \frac{\Gamma + (\mathbf{r} + \mathbf{s})\gamma_L}{[\mathbf{v}_0 - (\mathbf{r} - \mathbf{s})\omega_L]^2 + [\Gamma + (\mathbf{r} + \mathbf{s})\gamma_L]^2}.$$
 (21)

This result can be applied to the Mössbauer effect for an impurity atom. We have in this case a nucleus which emits gamma rays and, because of its recoil, exchanges energy with the lattice. It can be easily understood that Eq. (21) gives the intensity of the emitted gamma rays resulting from the interactions with the localized mode provided we make the following interpretations.

On the left of Eq. (21) we have the intensity emitted per unit frequency range and unit solid angle. On the right  $C_0^2$  is the total intensity emitted per unit solid angle from a <u>fixed</u> nucleus. Its intensity distribution is a Lorentz distribution of the form of Eq. (20), 2  $\Gamma$  being the mean lifetime of the nucleus in its excited state. Further  $v_0$  is the difference in energy between the emitted gamma ray and the centre of the gamma-ray line.

It is easy to get a qualitative understanding of the bumps surrounding the elastic peak and also the corresponding phenomena, e.g. the one-phonon peak, by considering the possible single-phonon emission and absorption and the corresponding widths.

It is also easy to include the damping of the phonons in those formulae for the scattering of neutrons by a crystal containing isolated impurities, which was published some time ago [9]. One of these formulae has later been derived in a preprint by ELLIOTT and MARADUDIN [4] and they have made an interesting discussion of this formula.

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### DISCUSSION

K.P. SINHA: You have discussed the case of an impurity atom of mass different from that of the host atoms. If, however, we introduce ionized defects without altering the mass, we may also expect additional lattice modes and the electronic states around the defects will probably also be modified. For polar systems we may expect strong interactions between the localized lattice modes and electronic states. How will this affect the Mössbauer spectra of such systems?

I. WALLER: I think the situation you are referring to is included in the formalism I have given.

A. SJÖLANDER: You referred to Ambegaokar and Maradudin in order to justify cutting the cumulant expansion. If I remember correctly, they only consider a regular lattice, where the frequency distribution extends over a large region. I think the situation is quite different if you are looking at a sharp, localized mode. Could you comment on this?

I. WALLER: It is true that Ambegaokar and Maradudin have treated only regular crystals. It seems to me, however, that there is also qualitative validity for a crystal with a localized mode, because the mechanisms for the appearance of an energy shift and its associated width are essentially the same. Other interaction terms may become important if the frequency of the localized mode is very high.

F.L. SHAPIRO: In some molecular crystals there exist very narrow peaks in the frequency spectra attributed to torsional oscillations of such groups as  $NH_4$ . Are your considerations regarding the widening of the elastic and one-phonon peaks for localized modes applicable to the case of torsional oscillations?

I. WALLER: This is an interesting question. I think that considerations similar to those I have given will apply to the case you mention.

# THEORY OF NEUTRON SCATTERING BY LATTICE VIBRATIONS IN IMPERFECT CRYSTALS

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#### Abstract — Résumé — Аннотация — Resumen

THEORY OF NEUTRON SCATTERING BY LATTICE VIBRATIONS IN IMPERFECT CRYSTALS. Theoretical formulae are derived for the one-phonon inelastic scattering cross-section of neutrons by crystals containing a small finite concentration of impurities, on the assumption that the defect atoms have only a different mass from the atoms of the host crystal and that the force constants are unchanged. For defects of mass much lighter than the host, localized modes appear at frequencies well above the frequency band in the perfect lattice. The coherent cross-section in this case shows that it should be possible to determine experimentally the spatial extent of the localized modes and to relate it to the frequency spectrum of the perfect lattice. The wave-like modes of the perfect lattice give, in principle, a coherent inelastic differential cross-section at discrete frequencies which satisfy energy and wave vector conservation as determined by the frequency spectrum. In the presence of impurities these lines are shifted and broadened by the scattering of the lattice wave from the disordered array. The shift and broadening are calculated as the real and imaginary part of the self energy of the phonons to first order in the concentration c of impurities. For some defects resonance modes occur within the frequency band and these are particularly well defined for impurity masses much greater than those of the host, The frequency shift shows a change in sign in passing from frequencies on either side of the resonance, and the width shows a maximum there. These effects should be observable and provide direct evidence of the resonance character of these modes. The incoherent scattering cross-sections reflect the change in the vibrational amplitudes of the atoms of the imperfect crystal, and under most circumstances lead to small effects at low concentrations.

THÉORIE DE LA DIFFUSION DES NEUTRONS PAR LES VIBRATIONS DU RÉSEAU DANS LES CRISTAUX PRÉSENTANT DES IMPERFECTIONS, Les auteurs établissent des formules théoriques de la section efficace de diffusion inélastique des neutrons, à un phonon, dans des cristaux contenant des impuretés à faible concentration, en prenant comme hypothèse que les atomes d'impuretés ne différent des atomes du cristal hôte que par la masse et que les constantes de forces restent les mêmes. Pour les impuretés ayant une masse beaucoup plus faible que celle du cristal hôte, des modes localisés apparaissent à des fréquences bien supérieures à la bande de fréquences dans le réseau parfait. D'après la section efficace de diffusion cohérente dans ce cas, il doit être possible de déterminer expérimentalement l'étendue spatiale des modes localisés et de la rapporter au spectre des fréquences du réseau parfait. Les modes à caractère ondulatoire du réseau parfait donnent théoriquement une section efficace différentielle de diffusion inélastique cohérente, déterminée par le spectre de fréquences, pour des fréquences discrètes qui sont conformes au principe de la conservation de l'énergie et du vecteur d'ondes. En présence d'impuretés, ces raies sont déplacées et élargies par la diffusion de l'onde du réseau due à la structure désordonnée. Le déplacement et l'élargissement sont calculés en tant que partie réelle et imaginaire de l'énergie propre des phonons jusqu'au premier ordre de la concentration c des impuretés. Pour certaines impuretés, des modes de résonance apparaissent dans la bande des fréquences, et ces modes sont particulièrement bien définis pour des masses très supérieures à celles du cristal hôte. Le déplacement de fréquence change de signe lorsque les fréquences passent de l'un à l'autre côté de la résonance, et la largeur présente un maximum à cet endroit. Ces effets devraient être observables et donner une preuve directe du caractère de résonance de ces modes. Les sections efficaces de diffusion incohérente mettent en évidence la modification des amplitudes des vibrations des atomes du cristal imparfait, et dans la plupart des cas les effets observés sont peu importants à faibles concentrations.

ТЕОРИЯ РАССЕЯНИЯ НЕЙТРОНОВ ПРИ КОЛЕБАНИЯХ РЕШЕТКИ В НЕСОВЕРШЕН-НЫХ КРИСТАЛЛАХ. Выводятся теоретические формулы для сечения однофононного неупругого рассеяния нейтронов с помощью кристаллов, содержащих небольшую ограниченную концентрацию примесей, исходя из предположения, что атомы примесей отличаются от атомов ядра кристалла только по массе и что константы силы являются неизменными. Для дефектов массы, которая намного меньше массы ядра кристалла, локализованные колебания появляются при частотах, которые намного превышают полосу частот в совершенной решетке. Сечение когерентного рассеяния в этом случае показывает, что можно определять экспериментальным путем пространственную величину локализованных колебаний и установить ее связь с частотным спектром совершенной решетки. Волнообразные колебания совершенной решетки дают, в принципе, дифференциальное сечение когерентного неупругого рассеяния при дискретных частотах, которые соответствуют законам сохранения энергии и волнового вектора, как это определено с помощью спектра частот. В присутствии примесей эти линии сдвигаются и уширяются при рассеянии волн в кристалле от разупорядоченной системы. Смещение и уширение рассчитываются в виде действительной и мнимой части значения собственной энергии фононов к первому порядку в концентрации "с" примесей. Ввиду некоторых дефектов резонансы происходят в полосе частот и они особенно хорошо определяются в отношении массы примесей, которые намного больше массы ядер кристалла. Смещение частот свидетельствует об изменении знака при изменении частот по обе стороны резонанса, а ширина показывает максимум. Эти эффекты должны быть заметными и служить прямым доказательством резонансного характера этих колебаний. Сечения некогерентного рассеяния отражают изменение вибрационных амплитуд атомов несовершенного кристалла и в большинстве случаев приводят к небольшим эффектам при низких концентрациях.

TEORIA DE LA DISPERSION NEUTRONICA POR VIBRACIONES RETICULARES EN CRISTALES IMPERFECTOS. Los autores deducen fórmulas teóricas para calcular la sección eficaz de dispersión inelástica monofonónica de neutrones en cristales que contienen una pequeña concentración de impurezas, partiendo del supuesto de que los átomos defectuosos sólo se diferencian de los átomos del cristal huésped en su masa, y de que las constantes de fuerza no sufren variación. Para masas defectuosas mucho más ligeras que el huésped, aparecen modos localizados a frecuencias muy superiores a las de la banda correspondiente a la red perfecta. En este caso, la evaluación de la sección eficaz de dispersión coherente demuestra que es posible determinar experimentalmente la extensión espacial de los modos localizados y de relacionarla con el espectro de frecuencias de la red perfecta. Los modos cuasi ondulatorios de la red perfecta presentan, en principio, una sección eficaz diferencial de dispersión inelástica coherente a frecuencias discretas que satisfacen el principio de la conservación de la energía y de los vectores de onda, conforme lo determina el espectro de frecuencias. En presencia de impurezas, esas líneas se desplazan y ensanchan a consecuencia de la dispersión de la onda reticular, causada por la disposición desordenada. Este desplazamiento y ensanchamiento se calculan respectivamente como la parte real e imaginaria de la energía propia de los fonones hasta el primer orden de la concentración c de impurezas. Para algunos defectos, aparecen modos de resonancia dentro de la banda de frecuencia, que resultan particularmente bien definidos para masas de impureza mucho mayores que las del cristal huésped. El desplazamiento de frecuencia cambia de signo al pasar de un lado a otro de la resonancia, siendo ahí donde la anchura es máxima, Estos efectos deben poder observarse y han de proporcionar prueba directa del carácter resonante de esos modos. Las secciones eficaces de dispersión incoherente reflejan el cambio producido en las amplitudes de vibración de los átomos de cristal imperfecto y, en la mayoría de los casos, ejercen escasos efectos cuando las concentraciones son bajas.

#### 1. INTRODUCTION

The vibrational modes of a crystal lattice are perturbed by the introduction of defects, and consequently all those properties of the crystal which depend on the vibrational motion are changed. These effects have recently

been the subject of extensive theoretical and experimental investigation [1]. Bulk crystal properties like the specific heat [2] and thermal resistance [3] may be measurably changed by a finite defect concentration. However, the most striking results are obtained in those experiments which use the defect as a probe, and to date the most detailed information has been obtained from defect-induced one-phonon optical absorption in covalent and ionic crystals [4]. Inelastic neutron scattering should be an even more sensitive experimental tool for the study of the effects of defects on individual phonons because the momentum and energy transfer from neutron to crystal can be measured simultaneously. For low defect concentrations the change from the perfect lattice is small, but it appears that there are some feasible neutron experiments which will give information about the vibrations that can be compared with well-established theories [1], and it is the purpose of this paper to draw attention to such possibilities. Most of our results are implicit in the work of Krivoglaz and Kagan quoted in Reference [5], but they do not emphasize the salient points where theory and experiment might meet. Some experimental results on the Pd-Ni system [6] and vanadium hydride [7] have been published. In this work it was the incoherent scattering of neutrons from these systems that was studied. Protons have such a large incoherent cross-section that if they are used as a defect, they tend to dominate the cross-section and weight the impurity atom scattering. Further experiments of the type described in Reference [7] should also prove very interesting. However, we shall see that it is coherent scattering experiments which provide the more detailed information.

For randomly disordered mixed crystals with high defect concentrations neutron scattering experiments will give important information. Several attempts at a theory of such systems have now been published [1, 8-10]. There are related experimental results on the order-disorder transition of  $\beta$ -brass [11]. All these types of experiment will be of particular value in metals where the vibrations cannot be so easily studied by other techniques.

Our calculations in this paper are confined to a low concentration of simple defects with changed mass and to the one-phonon scattering processes.

### 2. DEFECT VIBRATIONS

In the presence of an isolated defect the normal modes of a crystal are of two kinds. At frequencies outside the range of the allowed frequencies of the perfect lattice, localized modes may exist in which the vibrational amplitudes fall away faster than exponentially with distance from the defect [1]. These modes will have a point symmetry determined by the point symmetry of the defect. Inside the frequency range of the host lattice band modes still exist. At certain frequencies they may have a resonance character with greatly enhanced amplitude around the defect [12, 13]. Both of these important effects may be seen for the simplest defect, when a small concentration of atoms of mass M' are substituted at random in a Bravais lattice of atoms of mass M. It is convenient to define a mass defect parameter  $\varepsilon$  by

$$\epsilon = (M - M')/M. \tag{1}$$

Well-localized modes occur if  $M' \ll M$ , and sharp resonance modes occur at low frequencies if  $M' \gg M$ .

The one-phonon scattering cross-sections will be related in the next section to the time-dependent correlation functions between displacements

$$\langle u_{\alpha}(l,t)u_{\beta}(l',0)\rangle,$$
 (2)

where the brackets denote a thermal average.  $\alpha$ ,  $\beta$  are x, y or z giving the component of the displacement and 1 specifies the unit cell centred at  $\vec{x}(1)$ . The time Fourier transform of (2) is related to a Green function [14] by

$$\int_{-\infty}^{\infty} e^{i\omega t} \langle u_{\alpha}(1,t)u_{\beta}(1',0) \rangle dt = \lim_{\delta \to 0} \frac{i\hbar}{2\pi} \frac{1}{e^{\beta \omega} - 1} \left[ G_{\alpha\beta}(1,1';\omega+i\delta) - G_{\alpha\beta}(1,1';\omega-i\delta) \right], \qquad (3)$$

where  $\beta = \hbar/kT$ . The space Fourier transform of G is a convenient quantity to work with. We define

$$\frac{1}{N}\sum_{\mathbf{l},\mathbf{l}'}\sum_{\alpha\beta} \mathbf{e}_{\alpha}(\vec{\mathbf{k}},\mathbf{j}) \, \mathbf{e}^{-\mathbf{i}\vec{\mathbf{k}}\cdot\vec{\mathbf{x}}(\mathbf{l})} \, \mathbf{G}_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega) \, \mathbf{e}_{\beta}(\vec{\mathbf{k}'},\mathbf{j'}) \, \mathbf{e}^{\mathbf{i}\vec{\mathbf{k}'}\cdot\vec{\mathbf{x}}(\mathbf{l'})} = \mathbf{G}_{\mathbf{j}\mathbf{j}} \cdot (\vec{\mathbf{k}},\vec{\mathbf{k}'};\omega) \quad (\mathbf{4})$$

and also

$$\frac{1}{N}\sum_{\mathbf{l},\mathbf{l}'} \mathbf{G}_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega) e^{-i\vec{\mathbf{k}}\cdot\left[\vec{\mathbf{x}}(\mathbf{l})-\vec{\mathbf{x}}(\mathbf{l}')\right]} = \mathbf{G}_{\alpha\beta}(\vec{\mathbf{k}},\omega).$$
(5)

In the unperturbed crystal the latter function is

$$P_{\alpha\beta}(\vec{k},\omega) = \frac{1}{M} \sum_{j} \frac{e_{\alpha}(\vec{k},j) e_{\beta}(\vec{k},j)}{\omega^2 - \omega^2(\vec{k},j)}, \qquad (6)$$

where  $\omega(\vec{k}, j)$  is the frequency of the normal mode of the perfect crystal described by wave vector  $\vec{k}$  and branch index j, while  $e_{\alpha}(\vec{k}, j)$  is the associated

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eigenvector. Using the orthonormal properties of the eigenvectors we find that for a perfect lattice

$$P_{jj}, (\vec{k}, \vec{k'}; \omega) = \frac{1}{M} \delta_{jj}, \delta(\vec{k} \cdot \vec{k'}) \frac{1}{\omega^2 - \omega^2(\vec{k}, j)} .$$
(7)

For the perturbed lattice the equation for G is [15]

$$G_{\alpha\beta}(1,1';\omega) = P_{\alpha\beta}(1,1';\omega) + M\epsilon\omega^2 \sum_{\gamma,s} P_{\alpha\gamma}(1,s;\omega) G_{\gamma\beta}(s,1';\omega), \qquad (8)$$

where the sum on s runs over those sites with impurity atoms.

For a small concentration of defects which produces well-localized modes, the interference between pairs will be small and the results may be studied by examining the solution of Eq.(8) for an isolated defect. If this is at the origin the solution of Eq.(8) is

$$G_{\alpha\beta}(1,1';\omega) = P_{\alpha\beta}(1,1';\omega) + \frac{M\epsilon\omega^2 P_{\alpha\gamma}(1,0;\omega) P_{\gamma\beta}(0,1';\omega)}{1 - M\epsilon\omega^2 P_{\alpha\alpha}(0,0;\omega)}$$
(9)

for a cubic Bravais lattice where  $P_{\alpha\beta}(0,0;\omega)$  is diagonal in  $\alpha,\beta$  and is independent of  $\alpha$ . The extra response frequency of the system is given by the new pole of G at the local mode frequency  $\omega_1$  given by

$$\epsilon \omega_1^2 \int \frac{\nu(\omega') \, \mathrm{d}\omega'}{\omega_1^2 - \omega'^2} = 1, \tag{10}$$

where  $\nu$  is the density of modes per unit frequency range in the perfect crystal normalized so that  $J\nu(\omega')d\omega' \approx 1$ . The sum in Eq.(6) has been replaced by an integral since  $\omega_1$  lies outside the range of  $\nu$ . With a finite concentration of defects the local modes associated with each defect will interact and broaden this frequency into a band [8-10]. The relative width  $\Delta\omega/\omega$  is proportional to  $c^{\dagger}$  at small c [16] and would be hard to detect by neutron techniques. If the interference between modes on different defects is neglected the G for the whole crystal can be written in terms of Eq.(9) and multiplied by the number cN of defects.

For the band modes the solution is best described in terms of  $G_{\alpha\beta}(\vec{k},\omega)$ defined by Eq.(5) since the unperturbed  $P_{\alpha\beta}(\vec{k},\omega)$  in Eq.(6) leads directly to the frequency and momentum conservation familiar in one-phonon crosssections. This has been studied by TAYLOR [17] by iterating Eq.(8) and keeping only those terms which refer to a single sum over the defect sites s and hence are linear in the concentration. This gives

$$G_{\alpha\beta}(1,1';\omega) = P_{\alpha\beta}(1,1';\omega) + M\epsilon\omega \sum_{\gamma,s} \frac{P_{\alpha\gamma}(1,s;\omega) P_{\gamma\beta}(s,1';\omega)}{1 - M\epsilon\omega^2 P_{\alpha\alpha}(0,0;\omega)} .$$
(11)

Forming the transform, Eq.(4), and averaging over site positions s gives an expression for  $G_{jj}$ ,  $(\vec{k}, \vec{k'}; \omega)$  which in view of Eq.(7) is diagonal in j and  $\vec{k}$ . Abbreviating the notation we have

$$G_{j}(\vec{k},\omega) = P_{j}(\vec{k},\omega) + McV(\omega) P_{j}^{2}(\vec{k},\omega), \qquad (12)$$

where

$$V(\omega) = \epsilon \omega^2 [1 - M \epsilon \omega^2 P_{\alpha \alpha}(0, 0; \omega)]^{-1}.$$
(13)

This can be written to order c in the form

$$G_{j}(\vec{k},\omega) = \frac{1}{N} \frac{1}{\omega^{2} - \omega^{2}(\vec{k},j) - \Sigma(\vec{k},j,\omega)}$$
(14)

and

$$G_{\alpha\beta}(\vec{k},\omega) = \sum_{j} e_{\alpha}(\vec{k},j) e_{\beta}(\vec{k},j) G_{j}(\vec{k},\omega).$$
(15)

The last term in the denominator of Eq.(14) has the form of a self energy, and

$$\Sigma(\vec{k}, j, \omega) = cV(\omega).$$
(16)

The real part gives a shift of the characteristic frequencies of the lattice and the imaginary part represents the damping of the wave-like modes in the imperfect lattice. Self energies obtained by other authors [1, 9, 10] by other methods differ from Eq.(16) by a factor  $\omega^2(\vec{k}, j)/\omega^2$ . This makes essentially no difference for the width and shift in the low c case under consideration. The origin of the discrepancy is discussed elsewhere [17]. There is also a part of Eq.(9) which describes the local mode type of solution, for  $\Sigma$  becomes large even for small c near the frequency given by Eq.(10). The results obtained this way do not differ greatly from those we shall derive using Eq.(9).

#### 3. CROSS-SECTION FORMULAE

The differential scattering cross-section, per unit solid angle per unit interval of outgoing energy per nucleus, can be written as

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E}\right) = \frac{1}{2\pi\mathrm{N}\hbar} \frac{\mathrm{k}_2}{\mathrm{k}_1} \sum_{l=1}^{N} \mathrm{a}_l \mathrm{a}_{l'} \mathrm{e}^{-i\vec{\kappa}\cdot\vec{(x(l)}-\vec{x}(l'))} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{i\omega t} \langle \mathrm{e}^{-i\vec{\kappa}\cdot\vec{u}(l,t)} \mathrm{e}^{i\vec{\kappa}\cdot\vec{u}(l',0)} \rangle, \quad (17)$$

where  $\vec{k}_1$  and  $\vec{k}_2$  are the initial and final wave vectors of the neutron respec-

tively,  $\hbar \kappa = \hbar(\dot{k_1} - \dot{k_2})$  is the momentum transfer to the crystal, and  $\hbar \omega$  is the energy transfer to the crystal;  $a_1$  is the neutron scattering length of the 1-th atom. In the harmonic approximation, by use of standard transformations [1], Eq.(17) may be rewritten as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E} = \frac{\mathrm{k}_2}{2\pi\hbar\mathrm{k}_1} \,\mathrm{S}(\vec{\kappa},\omega),\tag{18}$$

where

$$S(\vec{\kappa},\omega) = \frac{1}{N} \sum_{l,l'} A_l A_{l'} e^{-i\vec{\kappa} \cdot [\vec{x}(l) - \vec{x}(l')]} \int_{-\infty}^{\infty} dt e^{i\omega t} \exp \langle \vec{\kappa} \cdot \vec{u}(l,t) \vec{\kappa} \cdot \vec{u}(l',0) \rangle.$$
(19)

Here A<sub>1</sub> is an effective temperature-dependent scattering length

$$A_1 = a_1 e^{-1/2 \left\langle [\vec{\kappa} \cdot \vec{u}(1)]^2 \right\rangle}$$
(20)

including the Debye-Waller factor. In a perfect crystal this is independent of 1, but in the non-ideal case it will vary from site to site depending on the impurity positions. This variation has been discussed in [5] and in more detail in a preprint by the authors of Reference [18]. At high  $T,\langle[\vec{\kappa}\cdot\vec{u}(1)]^2\rangle$  is the same for every atom in this case of uniform force constants and varying mass. We shall stick to the high T case and replace the Debye-Waller factor everywhere by  $e^{-2M_0}$ . The actual correlation function found in Eq.(19) turns out to be small even for relatively large  $\vec{\kappa}$ , in the third Brillouin zone, at temperatures comparable with the Debye temperature. The exponent may be expanded; the first term gives elastic scattering and the second the main result

$$S(\vec{\kappa},\omega) = \frac{e^{-2M_0}}{N} \sum_{\mathbf{1},\mathbf{1}^*} a_{\mathbf{1}}a_{\mathbf{1}^*} e^{i\vec{\kappa}\cdot[\vec{x}(\mathbf{1})-\vec{x}(\mathbf{1}^*)]} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \vec{\kappa}\cdot\vec{u}(1,t)\vec{\kappa}\cdot\vec{u}(1^*,0) \rangle.$$
(21)

This term represents the one-phonon cross-section which is of most direct interest.

In general  $a_1$  will vary from site to site even with the same atomic species. For each species we define a mean length as the coherent scattering length

$$\overline{\mathbf{a}} = \langle \mathbf{a} \rangle$$
, (22)

and a fluctuation about the mean gives an incoherent length  $\alpha$  defined by

$$\alpha^2 = \langle \mathbf{a}^2 \rangle - \langle \mathbf{a} \rangle^2 \,. \tag{23}$$

Denoting these quantities without a prime for the host atoms and with primes for the impurity, Eq.(21) can be divided into two parts. The first has the

same form as Eq. (21) with the coherent lengths  $\overline{a}_1$  substituted for  $a_1$ . This part tends to the coherent cross-section in the perfect lattice, but it now also contains a further incoherent part because of the random array of impurities. The division between coherent and incoherent thus becomes a little obscure; the division will be examined more closely in each particular case. There is also an entirely incoherent part.

$$S_{i}(\vec{k},\omega) = \frac{e^{-2M_{0}}}{2\pi N} \int_{-\infty}^{\infty} dt e^{i\omega t} \left( \sum_{l \neq s} \alpha^{2} + \sum_{l = s} \alpha^{\prime 2} \right) \langle \vec{k} \cdot \vec{u}(l,t) \vec{k} \cdot \vec{u}(l,0) \rangle, \qquad (24)$$

where again the label s denotes impurity site. In general the correlation function depends on 1, and when averaged over position in the sums, the self-correlation will be different at impurity and host sites.

#### 4. NEUTRON SCATTERING BY LOCALIZED MODES

The scattering of neutrons by localized modes has been considered at length in [18] to which the reader is referred for details. We quote here the essential results and comment briefly. Neglecting interference effects we may substitute Eq.(9) into Eq.(3) for the correlation function in Eq.(21). In the frequency range of interest  $P_{\alpha\alpha}(0,0;\omega+i\delta)$  has only an infinitesimal imaginary part, which leads to delta functions of the frequency at  $\pm \omega_1$ , the solutions of Eq.(10), which correspond to poles of G. The strength of the pole is obtained by differentiating the denominator.

$$\frac{\mathrm{d}}{\mathrm{d}\omega} \left[ 1 - \epsilon \omega^2 \mathbf{P}_{\alpha\alpha} \left( 0, 0; \omega \right) \right] \Big|_{\omega = \omega_1} = 2\epsilon \omega_1 \mathbf{B}(\omega_1^2) = 2\epsilon \omega_1 \int \frac{\omega^{12} \nu(\omega^1) \mathrm{d}\omega^1}{(\omega_1^2 - \omega^{1/2})^2} , \qquad (25)$$

after simplification with the use of Eq.(10). The Green's function giving the combination required in Eq.(21), assuming an impurity only at the origin is

$$\overline{\mathbf{a}}^{\mathbf{i}^{2}} \mathbf{G}_{\alpha\beta}(0,0;\omega_{1}) + \sum_{1=0}^{\infty} \overline{\mathbf{a}} \overline{\mathbf{a}}^{\mathbf{i}} \mathbf{G}_{\alpha\beta}(0,1;\omega_{1}) e^{-i\vec{\kappa}\cdot\vec{\mathbf{x}}(\mathbf{l})}$$

$$+ \sum_{1,1'\neq 0}^{\infty} \overline{\mathbf{a}}^{2} \mathbf{G}_{\alpha\beta}(1,1';\omega_{1}) e^{i\vec{\kappa}\cdot[\vec{\mathbf{x}}(1)-\vec{\mathbf{x}}(1')]}$$

$$= \left[\frac{\mathbf{a}'-\mathbf{a}}{\mathbf{M}\epsilon\omega_{1}^{2}} + \mathbf{a} \mathbf{P}_{\alpha\beta}(\vec{\kappa},\omega_{1})\right]^{2} \mathbf{M}\epsilon\omega_{1}^{2} \left[1 - \mathbf{M}\epsilon\omega_{1}^{2} \mathbf{P}_{\alpha\alpha}(0,0;\omega_{1})\right]^{-1}, \quad (26)$$

after some manipulation using Eq.(10).

### Finally, substituting these results back into Eqs. (21) and (17) we obtain

$$\begin{pmatrix} \frac{d^2\sigma}{d\Omega dE} \end{pmatrix} = \frac{k_2}{2k_1} \left\{ n_1 \delta(\omega + \omega_1) + (n_1 + 1) \delta(\omega - \omega_1) \right\} \frac{c\omega_1}{MB(\omega_1^2)} e^{-2M_0} \\ \times \sum_{j} [\vec{\kappa} \cdot \vec{e}(\vec{\kappa}, j)]^2 \left[ \frac{\vec{a}' - \vec{a}}{\epsilon \omega_1^2} + \frac{\vec{a}}{\omega_1^2 - \omega^2(\vec{\kappa}, j)} \right]^2,$$

$$(27)$$

where  $n_1$  is the equilibrium number of phonons, which enters from Eq.(3),

$$n_1 = (e^{\beta \omega} l - 1)^{-1}$$
 (28a)

. and

$$-n(-\omega) = n(\omega) + 1 .$$
 (28b)

The scattering cross-section takes a simple form when the vector  $\vec{\kappa}$  lies along one of the symmetry directions of a cubic crystal, namely the [100], [110] and [111] directions. The lattice waves propagating in these directions are purely longitudinal and purely transverse, so that  $\vec{\kappa} \cdot \vec{e}(\vec{\kappa}, j) = 0$  unless j refers to the longitudinal branch. In this case only this value of j occurs in the sum in Eq. (27). If the scattering is measured along a symmetry line perpendicular to  $\vec{n}$  (the direction of these longitudinal waves) which passes through a reciprocal lattice point so that  $\vec{\kappa}$  lies outside the first Brillouin zone, the cross-section is

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E} = \frac{\mathrm{k}_2}{2\hbar\mathrm{k}_1} \left[ n_1 \delta \left( \omega + \omega_1 \right) + \left( n_1 + 1 \right) \delta \left( \omega - \omega_1 \right) \right] \cdot \frac{\mathrm{c}\omega_1 \,\mathrm{e}^{-2M_0}}{\mathrm{MB}(\omega_1^2)}$$

$$\times \kappa^{2} \left\{ \sin^{2} \phi \left[ \frac{\overline{a}' - \overline{a}}{\epsilon \omega_{1}^{2}} + \frac{\overline{a}}{\omega_{1}^{2} - \omega^{2}(\overline{\kappa}, 1)} \right]^{2} + \cos^{2} \phi \left[ \frac{\overline{a}' - \overline{a}}{\epsilon \omega_{1}^{2}} + \frac{\overline{a}}{\omega_{1}^{2} - \omega^{2}(\overline{\kappa}, t)} \right]^{2} \right\},$$
(29)

where  $\phi$  is the angle between  $\vec{k}$  and  $\vec{n}$ , while t refers to a transverse mode whose polarization vector lies in the plane  $\vec{k}$  and  $\vec{n}$ . In this way effects associated with the transverse modes may be observed.

In principle a measurement of the intensity of inelastic scattering at  $\Delta E = \hbar \omega_1$  as a function of  $\vec{k}$  determines  $\omega(\vec{k})$  along symmetry directions for both longitudinal and transverse modes. The situation is reminiscent of that arising in the determination of phonon dispersion curves from the intensity of the thermal diffuse scattering of X-rays by one-phonon processes. The preceding result also allows a demonstration of the spatial localization of the modes. In fact  $P_{\alpha\beta}(\vec{k},\omega_1)$  appearing in Eq.(26) is related to the Fourier transform of the displacement field; the factor  $B(\omega_1^2)$  provides the normalization.

As an illustration we consider the special case of a face-centred cubic crystal with nearest-neighbour central forces between atoms. For  $\vec{\kappa}$  along the [100] direction the longitudinal mode frequency is [19]

$$\omega^2\left(\vec{\kappa}\right) = \omega_{\rm L}^2 \sin^2 \frac{1}{4} \, {\rm R}_0 \kappa_{\rm x} \, , \label{eq:main_state}$$

where  $\omega^{}_L$  is the maximum lattice frequency and  $\mathrm{R}^{}_0$  the lattice parameter. In this case

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E} = \frac{\mathrm{k}_2}{2\mathrm{k}_1} \left[ n_1\delta(\omega+\omega_1) + (n_1+1)\delta(\omega-\omega_1) \right] \frac{\omega_1\mathrm{c}\,\mathrm{e}^{-2M_0}}{\mathrm{MB}(\omega_1^2)} \left( \frac{4\overline{\mathrm{a}}}{\mathrm{R}_0\omega_1^2} \right)^2 \mathrm{F}(\mathbf{x}), \tag{30}$$

where

$$\mathbf{F}(\mathbf{x}) = \mathbf{x}^2 \left[ \frac{(\mathbf{a}'/\mathbf{a}) - 1}{\epsilon} + \frac{1}{1 - (\omega_L \sin \mathbf{x}/\omega_1)^2} \right]^2.$$
(31)

This function is plotted in Figs.1 and 2 for several values of  $\epsilon$  and  $(\overline{a'}/\overline{a})$ . The relation between  $\omega_1$  and  $\epsilon$  is taken from Table IV.1 of Reference [1]. There is some additional  $\vec{\kappa}$ -dependence in the cross-section, Eq.(30), through the Debye-Waller factor, which may reasonably be taken as constant under the conditions which allow us to use Eq.(21) for the one-phonon part of Eq.(19). From the results it is clear that the angular dependence is most striking for small  $\epsilon$  when the localized mode first appears above the band and is very extensive in space. In this situation interference effects between impurities will be more important. It will be noticed that the maximum of F(x) occurs for  $\vec{\kappa}$  near the zone boundary. The band modes of this type have relative motions of nearest neighbours which are essentially opposite and out of phase, and the motion of the local mode will be similar. Analysis of the curves shows an effective exponential decay of the localized mode displacement with distance from the origin, with an inverse decay length in the x-direction of

$$4\sqrt{2} \left[\omega_{1} / \omega_{m}\right]^{2} - 1 \left]^{1/2} / R_{0} , \qquad (32)$$

as may be obtained analytically by replacing sin x by  $1 - \frac{1}{2} \left(\frac{\pi}{2} - x\right)^2$  in Eq. (31).

#### 5. SCATTERING FROM BAND MODES

The cross-section in this case is most conveniently discussed in terms of the self-energy formulation in Eq. (14). Using this to obtain a correlation function from Eq. (3) to substitute in Eq. (19) gives

$$S(\vec{\kappa},\omega) = e^{-2M_0} \bar{a}^2 \sum_{j} \left[\vec{\kappa} \cdot \vec{e}(\vec{\kappa},j)\right]^2 \frac{c V_2(\omega)}{\left[\omega^2 - \omega^2(\vec{\kappa},j) - c V_1(\omega)\right]^2 + [c V_2(\omega)]^2} , \quad (33)$$


for different values of the mass defect parameter  $\epsilon$ . This function gives essentially the angular dependence of the one-phonon contribution to the differential scattering cross-section for the scattering of neutrons by a localized vibration mode when the momentum transfer from neutron to crystal is in the [100] direction.  $\overline{a'}/\overline{a=1}$ ,  $\overline{a'}$  and  $\overline{a}$  being the coherent neutron scattering lengths.

where for the moment we have put  $\overline{a} = \overline{a}$ . Here the real and imaginary parts of Eq.(13) are

$$V_{1}(\omega) + i V_{2}(\omega) = \frac{\epsilon \omega^{2} \left\{ \left[ 1 - \epsilon \omega^{2} P \int \frac{\nu(\omega') d\omega'}{\omega^{2} - \omega'^{2}} \right] + \frac{1}{2} i \pi \epsilon \omega \nu(\omega) \right\}}{\left[ 1 - \epsilon \omega^{2} P \int \frac{\nu(\omega') d\omega'}{\omega^{2} - \omega'^{2}} \right]^{2} + \frac{1}{4} \pi^{2} \epsilon^{2} \omega^{2} \nu^{2}(\omega)}, \quad (34)$$

where P denotes the principal valued integral. Thus for small c there is an effective frequency shift of the peak of the response

$$\Delta(\vec{\kappa}, j) = c V_1[\omega(\vec{\kappa}, j)] / 2\omega(\vec{\kappa}, j)$$
(35)

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and a width

$$\gamma(\vec{\kappa}, j) = c V_2 \left[ \omega(\vec{\kappa}, j) \right] / \omega(\vec{\kappa}, j).$$
(36)

This shift and width have an essentially resonance character. The width is a maximum when  $V_1 = 0$ ,

$$\gamma_r = 2c / \pi \nu(\omega_r) \,. \tag{37}$$

For a very heavy impurity  $\epsilon \ll 0$ , where the resonance appears at very low



frequencies, the result for a Debye model has some validity. Then the relative width is given by

$$\gamma_{\rm r}/\omega_{\rm r} = \frac{2c}{3\pi} \left(\frac{\omega_{\rm m}}{\omega_{\rm r}}\right)^3 \sim \frac{2c}{3\pi} \left[3\left(\frac{\rm M'}{\rm M}-1\right)\right]^{3/2} . \tag{38}$$

Specific calculations for Sn in Si and I in KCl show effective widths of this order [17]. It is probably beyond the limit of present neutron techniques

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except in especially favourable cases (e.g. Pb in Mg at concentrations of several per cent).

Numerical results for the shift and width of a phonon computed for the model of a face-centred cubic lattice introduced in the last section are shown



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The shift  $\Delta(\vec{k}, j)$  in the frequency of the normal mode  $(\vec{k}, j)$  of a perfect crystal owing to isotopic disorder is plotted as a function of the frequency of this mode, for a nearest-neighbour, central-force model of a face-centred cubic crystal. The parameter  $\epsilon$  is given by 1-(M<sup>\*</sup>/M), where M<sup>\*</sup> is the mass of an isotopic impurity, and M is the mass of an atom of the host crystal. The concentration of impurities is denoted by c, and  $\omega_L$  is the maximum frequency of the host crystal.



Fig.4

The width of the frequency of the normal mode  $(\vec{\kappa}, j)$  of a perfect crystal owing to isotopic disorder is plotted as a function of the frequency of this mode for a nearest-neighbour, central-force model of a face-centred cubic crystal. The parameter  $\epsilon$  is given by 1-(M<sup>\*</sup>/M), where M<sup>\*</sup> is the mass of an isotopic impurity, and M is the mass of an atom of the host crystal. The concentration of impurities is denoted by c, and  $\omega_L$  is the maximum frequency of the host crystal.

in Figs.3 and 4 for  $\epsilon$  appropriate to gold in copper. Both the shift and width are seen to have typical resonance character. At low frequencies the shift is that appropriate to the change in the mean mass of the crystal

$$\Delta(\vec{\kappa}, j) = c \in \omega(\vec{\kappa}, j)/2.$$
(39)

This shift changes sign at the resonance frequency, the change being more abrupt for sharper resonances. The relative frequency displacement across the resonance is crudely of the order of  $c\epsilon/2$ , and should be observable.

Note in Fig.3 that the shift is negative for large phonon frequencies. A larger shift of this sign has recently been confirmed experimentally [20] for longitudinal and transverse phonons at the Brillouin zone boundary in alloys of copper containing small concentrations of gold. It should be pointed out that the zone boundary values for the frequencies of transverse waves for the present model correspond to x = 0.707; 0.9239, 0.6533; 0.5, for waves propagating in the [100], [110], and [111] directions, respectively. For longitudinal waves the corresponding values are x = 1.0, 0.8536, 1.0, for waves propagating in the [100], [110], and [111] directions.

If the coherent scattering length  $\overline{a}$ ' is different from  $\overline{a}$  the intensity of the scattering given by Eq.(33) will be altered and an extra incoherent crosssection is to be expected. In passing from Eq.(11) to Eq.(12) we averaged over site positions with no weighting. To calculate Eq.(21) the weighted average

$$\sum_{\mathbf{l},\mathbf{l}'} \overline{\mathbf{a}}_{\mathbf{l}} \overline{\mathbf{a}}_{\mathbf{l}'} e^{i\vec{\kappa} \cdot [\vec{\mathbf{x}}(\mathbf{l}) - \vec{\mathbf{x}}(\mathbf{l}')]} G_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega)$$
(40)

is required. For the first term on the right hand side of Eq.(11) this gives

$$\langle \overline{a} \rangle^2 P_{\alpha\beta}(\vec{\kappa}, \omega) + [\langle \overline{a}^2 \rangle - \langle \overline{a} \rangle^2] P_{\alpha\beta}(0, 0; \omega),$$
 (41)

where

$$\langle \overline{a} \rangle = \overline{a} + c(\overline{a}' - \overline{a})$$
 (42)

and

$$\langle \overline{a}^2 \rangle - \langle \overline{a} \rangle^2 = c(1-c)(\overline{a}^1 - \overline{a})^2$$
. (43)

The two terms lead to the usual expressions for coherent and incoherent scattering in a perfect lattice. In the second term of Eq.(11) averaging over impurity configurations gives

$$\sum_{1} a_{1} e^{i\vec{\kappa}\cdot\vec{x}(l)} P_{\alpha\gamma}(1,s;\omega) = \langle \vec{a} \rangle P_{\alpha\gamma}(\vec{\kappa},\omega) + \langle \vec{a}' - \langle \vec{a} \rangle \rangle P_{\alpha\gamma}(0,0;\omega)$$
(44)

since s is always an impurity site. Expanding the result to order c gives for Eq.(40)

$$\left[\overline{\mathbf{a}^{2}} + \frac{2c\overline{\mathbf{a}}\left(\overline{\mathbf{a}'} - \overline{\mathbf{a}}\right) V(\omega)}{\epsilon \omega^{2}}\right] \mathbf{P}_{\mathbf{j}}\left(\vec{\kappa}, \omega\right) + \overline{\mathbf{a}^{2}} \operatorname{MeV}(\omega) \mathbf{P}_{\mathbf{j}}^{2}\left(\vec{\kappa}, \omega\right) + \frac{c(\overline{\mathbf{a}'} - \overline{\mathbf{a}})^{2} V(\omega) \mathbf{P}_{\alpha\alpha}\left(0, 0; \omega\right)}{\epsilon \omega^{2}}.(45)$$

In fact the last term is proportional to  $G(0, 0; \omega)$  at an isolated impurity site (cf. Eq.(9)) and gives the incoherent scattering appropriate to the vibration of an impurity site. This suggests that in the true incoherent cross-section, Eq.(24), the terms with 1 = s should also be multiplied by this same factor. The first part of Eq.(45) can be rewritten to first order in c as

$$\left[\overline{\mathbf{a}}^{2} + \frac{2c\overline{\mathbf{a}}\left(\overline{\mathbf{a}}' - \overline{\mathbf{a}}\right) V(\omega)}{\epsilon \omega^{2}}\right] \mathbf{G}_{\mathbf{j}}\left(\vec{\kappa}, \omega\right)$$
(46)

with the Green function of the perturbed lattice given by Eq.(14). This gives an effective scattering length dependent on the frequency. On taking the imaginary part of Eq.(46) to substitute in the cross-section it is found that the extra term divided by the term in Eq.(33) is

$$\frac{2\left(\overline{a}^{1}-\overline{a}\right)}{\overline{a}}\left[\frac{\omega^{2}-\omega^{2}\left(\vec{\kappa},j\right)}{\epsilon\omega^{2}}\right].$$
(47)

It has thus a very small effect in the vicinity of the peak in the cross-section and although it tends to produce an asymmetry it may usually be neglected.

#### 6. CONCLUSION

There are therefore two types of experiment in which inelastic neutron scattering could further elucidate the vibrations of crystals containing a low concentration of defects. The frequency of the localized modes and their spatial amplitude distribution could be determined. This might be of particular interest in a metal where other methods are not available. A study of the shift and width of the ordinary phonon scattering peaks would also give detailed information about the position of resonances in the band modes. Heavy defects like Au in Be, Pb in Mg or Ca, or Au in Cu are the most suitable for this purpose.

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### DISCUSSION

H. PALEVSKY: Could you give some estimate of the size of the expected multiphonon effects?

R.J. ELLIOTT: These will be of similar order to the two-phonon effects in a perfect crystal.

G. DOLLING: As far as I recall the results of Brockhouse's student Swenson, he did not observe the resonance effects you have described.

R.J. ELLIOTT: He did not look in the right frequency range.

G. DOLLING: Would you expect the same kind of localized mode theory to work in the case of an alkali halide, which displays a gap in the frequency distribution function, and when the "local" mode frequency falls in the gap?

R.J. ELLIOTT: Yes. Such modes have been observed in infrared absorption by Sievers of Cornell University.

P. EGELSTAFF: What effect does strain or lattice deformation in the region of the defect have on your results?

R.J. ELLIOTT: It does not change the qualitative picture of local and resonant modes, but it will affect the actual frequencies at which they occur.

J.A. JANIK: Do you know of any experiments, other than neutron experiments, which give evidence of localized modes in crystals?

R.J. ELLIOTT: There is a great deal of work on infrared absorption in semiconductors and ionic crystals. This shows up localized modes very well, e.g. B, Li, etc., in Si and III-V compounds which show effects of agglomeration, H and D in alkali halides and  $CaF_2$  which show anharmonic effects, and so on. Some work has been done on band modes, particularly in diamond, but the low frequency resonances are in a difficult spectral range. The effect of these resonances has been observed in thermal resistance, e.g. of I in KC1. Much of this work was reported and reviewed at the Conference on Lattice Dynamics<sup>\*</sup>.

B. BURAS (Chairman): I should like to add that a colleague of mine, Dr. Nazarewicz, in collaboration with Professor Balkanski's group at the Ecole Normale Supérieure in Paris, has recently studied the local modes of silicon doped with both lithium and boron, using infrared spectroscopy. He found some peaks which could be attributed to vibrations of  $\text{Li}^6-\text{B}^{10}$ ,  $\text{Li}^7-\text{B}^{11}$  and other complexes. Do you think that with inelastic neutron scattering one could see not only the local modes of single impurity atoms but also the vibrations of similar kinds of complexes?

R.J. ELLIOTT: I think so, especially in a favourable case. Using impurities with coherent cross-sections in a material with incoherent crosssections one could pick up the correlations between pairs quite strongly. I suppose vanadium could be used.

# INELASTIC NEUTRON SCATTERING FROM DOPED GERMANIUM AND SILICON

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### Abstract — Résumé — Аннотация — Resumen

INELASTIC NEUTRON SCATTERING FROM DOPED GERMANIUM AND SILICON. The normal modes of vibration of the pure semiconductors germanium and silicon have been extensively studied by means of coherent one-phonon scattering of slow neutrons from single-crystal specimens. The present paper describes similar experiments performed (i) on germanium heavily doped (~0.1%) with (a) arsenic and (b) gallium, and also (ii) on silicon doped with phosphorus. In each case, control experiments were carried out on highpurity crystals. All measurements were performed with the triple-axis crystal spectrometer at Chalk River. Nuclear Laboratories. The elastic constant  $C_{44}$  for germanium is known to be appreciably dependent on the dopant concentration, and so certain transverse acoustic (TA) modes of long wavelength were studied to see if such effects persisted into the dispersive region. Other TA modes whose frequencies could be measured with high precision were also studied in both materials to check as sensitively as possible for small effects which might be ascribed to the existence of excess electrons or holes. A particularly careful study was made of modes having the following wave vectors ( $at^2/2\pi$ , where a is the cubic unit cell side): (i) in germanium, (1, 0, 0), (ii) in silicon, (0.85, 0.85, 0) and (0.3, 0, 0). Such normal modes might be expected to show anomalous behaviour in the n-type crystals, since inter-valley scattering of electrons between adjacent conduction band minima would require their co-operation in order to conserve "crystal momentum".

The results in all cases were negative, i. e. no differences in phonon frequencies or energy widths between pure and doped specimens were observed, within the experimental accuracy. In the most favourable cases, this (relative) accuracy is about 0.5% in frequency, rising to 2.0% for certain longitudinal optic modes in silicon.

DIFFUSION INÉLASTIQUE DES NEUTRONS DANS DU GERMANIUM ET DU SILICIUM CONTENANT UNE «IMPURETÉ» L'auteur a étudié, à l'aide d'expériences de diffusion cohérente (à un phonon) de neutrons lents par des monocristaux, les modes normaux de vibration du germanium et du silicium purs. Le mémoire décrit des expériences semblables sur 1, du germanium contenant une «impureté»en assez forte proportion (~0,1%), cette «impureté» étant a) de l'arsenic, b) du gallium; et 2 du silicium contenant du phosphore. Dans chaque cas, des expériences de contrôle ont été faites sur des cristaux d'une grande pureté. Toutes les mesures ont été effectuées à l'aide du spectromètre à cristal triaxial de Chalk River. On sait que la concentration de l' «impureté» influe sensiblement sur la constante d'élasticité  $C_{44}$  du germanium; l'auteur a donc étudié certains modes acoustiques transversaux de grande longueur d'onde pour déterminer si ces effets persistent dans la région de dispersion. Il a également étudié, dans l'un et l'autre de ces semi-conducteurs, d'autres modes acoustiques transversaux dont les fréquences peuvent être mesurées avec une grande précision, afin de vérifier avec la plus grande sensibilité possible les effets mineurs pouvant être attribués à l'existence d'électrons ou de trous en excès. Un examen particulièrement approfondi a été effectué sur les modes ayant les vecteurs d'onde suivants (ad/2n, où a est la longueur de l'arête d'une cellule cubique unitaire): 1, dans le germanium (1,0,0); 2, dans le silicium (0,85, 0,85, 0) et (0,3, 0,0). On pouvait s'attendre que ces modes normaux présentent un comportement anormal dans les cristaux de type n, étant donné que la diffusion des électrons entre les minima des bandes de conduction adjacentes exigerait leur intervention de manière à assurer la conservation de la «quantité de mouvement du cristal».

Dans tous les cas, les résultats obtenus ont été négatifs, c'est-à-dire qu'on n'a observé, dans les limites de la précision expérimentale, aucune différence de fréquences de phonons ou de largeurs d'énergie entre les échantillons purs et les échantillons contenant une « impureté». Dans les cas les plus favorables, cette précision (relative) est d'environ 0, 5% pour la fréquence et elle atteint 2, 0% pour certains modes optiques longitudinaux dans le silicium.

НЕУПРУГОЕ РАССЕЯНИЕ НЕЙТРОНОВ НА ГЕРМАНИИ И КРЕМНИИ С ПРИСАД-КОЙ. Нормальные формы колебания чистых полупроводников германия и кремния широко изучались с помощью когерентного однофононного рассеяния медленных нейтронов на моно-кристаллических образцах. В данном докладе описываются аналогичные эксперименты, выполненные 1) с германием с большой присадкой (~0,1%) а)мышьяка и b) галия, а также 2) с кремнием с фосфорной присадкой. В каждом случае контрольные эксперименты проводились на кристаллах высокой чистоты. Все измерения выполнялись на трехосном кристаллическом спектрометре в лабораториях в Чок-Ривер. Как известно, постоянная упругости С44 для германия в значительной степени зависит от концентрации присадки, и поэтому некоторые поперечные акустические колебания (ТА) с большой длиной волны изучались с целью выяснения наличия таких эффектов в диспергирующей области. Другие ТА колебания, частоты которых можно измерять с высокой степенью точности, также изучались в обонх материалах с целью возможно более точной проверки небольших эффектов, которые можно было бы приписать наличию избытка электронов или дырок. Особенно тщательно изучались колебания со следующими волновыми векторами (аq̃/2 л, где а−сторона кубической элементарной ячейки): 1) в германии (1; 0; 0); 2) в кремнии (0.85; 0.85; 0) и (0.3; 0; 0). Можно было бы предположить, что такие нормальные колебания проявят необычные черты в кристаллах п-ного типа, поскольку для рассеяния электронов между соседними минимумами зон проводимости потребовалось бы взаимодействие для сохранения "импульса кристалла".

Результаты во всех случаях были отрицательными, т.е. в пределах точности экспериментов не наблюдалось никаких различий частот фононов или энергетических ширин между чистыми образцами и образцами с присадкой. В наиболее благоприятных случаях такая (относительная) точность составляет приблизительно 0,5% по частоте, с повышением до 2,0% для некоторых продольных оптических колебаний в кремнии.

DISPERSION INELASTICA DE NEUTRONES EN GERMANIO Y SILICIO DELIBERADAMENTE IMPURIFICADOS. Los modos normales de vibración de los semiconductores germanio y silicio puros se han estudiado ampliamente por dispersión monofonónica coherente de neutrones lentos en muestras monocristalinas. En la memoria se describen experimentos análogos realizados utilizando: 1) germanio deliberadamente impurificado (~0,1%) con a) arsénico y b) galio; 2) silicio impurificado con fósforo. Se realizaron siempre experimentos testigo con cristales de elevada pureza. Todas las mediciones se llevaron a cabo con el espectrometro triaxial de cristal instalado en los Chalk River Nuclear Laboratories. Como es sabido, la constante elástica C., correspondiente al germanio depende sensiblemente de la concentración de la impureza, por lo que se estudiaron ciertos modos acústicos transversales de onda larga para comprobar si tales efectos persistían en la región dispersiva. En ambos materiales se estudiaron también otros modos acústicos transversales de frecuencia susceptible de medirse con gran precisión, a fin de observar con el mayor detenimiento posible los leves efectos que pudiera atribuirse a la existencia de electrones o vacantes en exceso. Se estudiaron con particular cuidado los modos que tienen los vectores de onda  $(\overline{ad}/2\pi)$ , en donde a es la arista de la celdilla unidad cúbica): a) en el germanio (1,0,0), y b) en el silicio (0, 85, 0, 85, 0) y (0, 3, 0, 0). Cabría esperar que estos modos normales tuviesen un comportamiento anómalo en los cristales de tipo n, pues la dispersión intervalle de electrones entre mínimos adyacentes de bandas de conducción exigiría su cooperación para conservar « el impulso del cristal»,

Los resultados fueron negativos en todos los casos, esto es, no se observó diferencia alguna de frecuencias fonónicas ni de amplitudes de energía entre muestras puras e impurificadas, dentro del margen de error experimental. En los casos más favorables, esta exactitud (relativa) alcanza al 0,5% del valor de la frecuencia, y llega hasta 2,0% tratándose de algunos modos ópticos longitudinales en el silicio.

### 1. INTRODUCTION AND THEORY

In recent years the normal modes of vibration of the pure semiconductors germanium [1, 2] and silicon [3, 4] have been extensively studied by means of slow neutron inelastic scattering techniques [5]. The interatomic force systems [4, 6] and electronic band structures [7] of these materials are now fairly well understood, at least in broad outline. This paper describes attempts to detect changes in the vibrational properties of Ge and Si when relatively large concentrations (about 0.1%) of dopant material are added. Specifically, a number of normal mode frequencies have been measured at 296°K for three single crystal specimens of germanium (a) pure, (b) doped with arsenic (n-type) and (c) doped with gallium (p-type), and for two specimens of silicon (a) pure and (b) doped with phosphorus (n-type). A brief report of the measurements on silicon has been given elsewhere [8]. All of the measurements were made by means of a triple-axis crystal spectrometer at the NRU reactor, Chalk River, and consisted of observations of the energy distributions of neutrons scattered from the single-crystal specimens by coherent one-phonon processes involving neutron energy loss, and under conditions of constant neutron momentum transfer (constant- $\vec{Q}$ method [5]).

That such changes in the normal mode frequencies might be expected is shown, for example, by the fact [9] that the elastic constant  $C_{44}$  of heavily doped n-type germanium at 4.2°K is 5% lower than that of the pure material. (The other elastic constants are substantially the same.) It is of interest to ascertain whether these effects persist into the dispersive region of the frequency-wave vector characteristic,  $\nu(\vec{q})$ , and if possible to describe any observed changes in terms of some modification of the effective interatomic potential. There is also the possibility of observing certain special effects in the n-type crystals, associated with the phenomenon of intervalley scattering of the "excess" electrons between adjacent conduction band minima\*. The locations in reciprocal space of these minima are known: for Ge [7] at wave vectors  $a\vec{q}/2\pi = (0.5, 0.5, 0.5)$ , (0.5, 0.5, -0.5), etc., and for Si [10] at wave vectors  $a\vec{q}/2\pi = (\zeta, 0, 0)$ , where  $\zeta \approx 0.85$ . The selection rules governing these intervalley scattering processes have been enumerated by LAX and HOPFIELD [11]. For such scattering to occur, the momentum and energy changes suffered by the electron must be balanced by the creation or annihilation of a suitable phonon. Figures 1 and 2 illustrate for the case of n-type germanium and n-type silicon, respectively, how these conservation



WAVE-VECTOR TRANSFER Q = (0,0,1.0)

Energy-wave vector diagram for "conduction" electrons in n-type germanium, showing how intervalley electron scattering may involve a phonon of wave vector  $a\vec{q}/2\pi = (1, 0, 0)$ 

Fig.1

<sup>\*</sup> This possibility was suggested by Dr. P.J. Price.



Fig.2

Energy-wave vector diagram for "conduction" electrons in n-type silicon, showing how intervalley electron scattering may involve a phonon of wave vector  $a\overline{q}/2\pi = (1, 0, 0)$ 

conditions restrict the possible wave vectors of the phonon concerned. The ability of the electrons to adjust themselves to the changing nuclear positions during a lattice vibration might well be significantly affected by these processes. Consequently, one might expect changes in the frequency and perhaps also the frequency widths of the particular modes shown in Figs. 1 and 2.

The location of the conduction band minimum is much less accurately known in silicon than in germanium. Furthermore, many of the normal mode frequencies of silicon are rather too high for convenient and easy determination. We therefore describe in some detail (section 2) the more favourable case of germanium, and restrict discussion of the experiments on silicon (section 3) to a presentation of the results.

## 2. EXPERIMENTS ON GERMANIUM

The three germanium specimens were very similar in size and shape (cylinders, 2 in long and 1 in in diameter), and of the same orientation (cylinder axis parallel to the  $(1\overline{10})$  crystallographic direction). The approximate dopant concentrations were (a)  $< 5 \times 10^{13}$  atoms/cm<sup>3</sup> for the pure specimen, (b)  $3.5 \times 10^{19}$  arsenic atoms/cm<sup>3</sup> for the n-type specimen and (c)  $3 \times 10^{19}$  gallium atoms/cm<sup>3</sup> for the p-type specimen. All three were similarly mounted so that the  $(1\overline{10})$  axis was in each case perpendicular to the plane containing the incident and scattered neutron beams of the spectrometer. A number of modes of vibration were selected and scattered neutron groups arising from appropriate coherent one-phonon processes were observed, from which the normal mode frequencies were determined. The triple-axis spectrometer was operated in such a way that the energy distribution of scattered neutrons could in each case be measured for a fixed value of the wave vector of the normal mode concerned. Certain low frequency transverse acoustic (TA) modes were chosen for study, in view of the known dependence [9] of the elastic constant C<sub>44</sub> upon dopant concentration. Other TA modes, whose frequencies could for experimental reasons be measured with high precision, were studied in an attempt to detect relatively small changes in the effective interatomic potential. The possibility of special

effects arising from intervalley scattering of conduction electrons in the n-type specimen was investigated by observing various modes with wave vectors in the vicinity of the zone boundary in the  $\Delta$ -direction, i.e.  $a\vec{q}/2\pi = (1, 0, 0)$  where a is the lattice constant. The optic mode of zero wave vector (Raman mode) was also studied for this reason. If the electron wave vectors appropriate to two conduction band minima are  $\vec{k}_1$  and  $\vec{k}_2$ , then the condition of conservation of "crystal momentum" may be expressed by

$$\vec{k}_{1} - \vec{k}_{2} = \vec{Q} = 2\pi \vec{\tau} + \vec{q}$$
,

where  $\vec{q}$  is the reduced wave vector of a normal mode of vibration and  $\vec{\tau}$  a vector of the reciprocal lattice. For example, for  $a\vec{k}_1/2\pi = (0.5, 0.5, 0.5)$  and  $a\vec{k}_2/2\pi = (-0.5, 0.5, 0.5)$ , Eq.(1) may be satisfied if the phonon wave vector is  $a\vec{q}/2\pi = (1, 0, 0)$ . The selection rules [11] indicate that only the longitudinal (L) mode may participate in such an electron scattering process. Nevertheless, measurements of the TA and TO mode frequencies were also made in an attempt to check whether these selection rules were indeed satisfied.

The complete results for the three specimens (at 296°K) are given in Table I. The errors quoted are <u>relative</u> rather than absolute, and have been estimated on the assumptions (a) that the instrumental calibration remained the same during the entire experiment and (b) that the specimen orientations were the same to within 0.05°. Assumption (a) was checked by making several repeat measurements, with changes of specimen between each repeat, and also by measuring the energy distribution of neutrons scattered by a polycrystalline vanadium sample before and after the experiments. The specimen orientations were determined by careful observation of several independent "Bragg reflections". This method is capable of the above-mentioned relative accuracy  $(0.05^{\circ})$  provided that extinction effects are similar in the three crystals. If this is so, the mean position in the crystal from which the incident neutrons are Bragg reflected, and hence the effective angle of scattering, will be the same in all cases. Measurement of the mosaic spread and Bragg reflection intensity for the present specimens showed that while the pure and gallium-doped crystals were very similar in these respects, the arsenic-doped crystal displayed a substantially larger mosaic spread and "Bragg reflecting power". This may lead to an error in crystal orientation and effective scattering angle sufficient to produce an appreciable change in the measured frequency of a mode for which the gradient  $\nabla_{q} \nu$  is large. In the case of the LA modes of wave vectors near (1, 0, 0), for example, it is estimated that this effect may be as much as 0.3% in frequency (that is, the measured LA frequencies for the arsenic-doped crystal are up to 0.3% too low). This effect is of course negligible for many of the modes studied in these experiments, since  $\nabla_a \nu$ is usually small or zero.

The lattice constant a of germanium was taken to be 5.6575 Å. Measurements of a by means of neutron diffraction experiments showed that it was indeed the same for all three crystals, to within 0.08%. If the lattice constant of the arsenic-doped crystal is as much as 0.08% larger than that of the pure material, then the resultant error in q may be similar (0.3%) to that involved in the orientation error mentioned above.

## G. DOLLING

#### TABLE I

| Wave vector   | Mode | Frequency<br>(10 <sup>12</sup> c/s) |                          |              |
|---------------|------|-------------------------------------|--------------------------|--------------|
| co-ordinate ζ |      | (i) Pure Ge                         | (ii) As-Ge               | (iii) Ga-Ge  |
| 1.00          | TA   | 2.37 ± 0.01                         | 2.37 ± 0.01              | 2.36 ± 0.01  |
| 0.95          | ТА   | 2.37 ±0.01                          | 2.37 ± 0.01              | 2.37 ± 0.01  |
| 0, 90         | ТА   | 2.37 ± 0.01                         | 2.37 ±0.01               | 2.36 ± 0.01  |
| 0,20          | TA   | 1.175 ± 0.01                        | 1.18 ± 0.01              | 1.18 ± 0.01  |
| 0.24          | TA   | 1.36 <sub>5</sub> ± 0.01            | 1.35 <sub>5</sub> ± 0.01 | 1.365 ± 0.01 |
| 0.28          | TA   | 1.53 ±0.01                          | 1.53 ±0.01               | 1.53 ± 0.01  |
| 0.00          | О    | 8.94 <sup>a</sup>                   | 8.98 ± 0.10              |              |
| 0.05          | то   |                                     | 9.00 ± 0.10              |              |
| 0.10          | то   |                                     | 8.97 ± 0.10              |              |
| 0.85          | то   | 8.13 ± 0.08                         | 8.12 ± 0.08              | 8.10 ± 0.08  |
| 0.88          | ОТ   | 8.10 ± 0.08                         | 8.15 ± 0.08              | 8.10 ± 0.08  |
| 0.90          | то   | 8.11 ± 0.08                         | 8.18 ± 0.08              | 8.13 ± 0.08  |
| 0.93          | то   | 8.16 ± 0.08                         | 8.20 ± 0.08              | 8.08 ± 0.08  |
| 0.95          | то   | 8.20 ± 0.08                         | 8.11 ± 0.08              | 8.07 ± 0.08  |
| 0.98          | то   | 8.11 ± 0.08                         | 8.12 ± 0.08              | 8.14 ± 0.08  |
| 1.00          | то   | 8.11 ± 0.08                         | 8.18 ± 0.08              | 8.13 ± 0.08  |
| 1.00          | L    | 7.12 ± 0.05                         | 7.11 ± 0.05              | 7.12 ± 0.06  |
| 0,95          | LA   | 6.92 ± 0.04                         | 6.89 ±0.04               | 6,92 ± 0,05  |
| 0.90          | LA   | 6.66 ± 0.04                         | 6.64 ± 0.04              | 6.65 ± 0.05  |
| 0,95          | LO   | 7.32 ± 0.06                         | 7.30 ± 0.06              | 7.33 ± 0.06  |
| 0,90          | LO   | 7.52 ± 0.07                         | 7.50 ± 0.07              | 7.51 ± 0.07  |

## FREQUENCIES OF NORMAL MODES PROPAGATING ALONG THE [500] DIRECTION IN PURE AND DOPED GERMANIUM AT 296°K

<sup>a</sup> Interpolated from Reference [2] (not checked in the present experiments).

Figure 3 shows the scattered neutron groups observed under identical conditions for the three specimens, and associated with (a) the TA mode (1, 0, 0) and (b) the LA mode (0.95, 0, 0). Part of the discrepancy between the measured frequency of this LA mode in the arsenic-doped crystal and those in the other two crystals is no doubt due to the orientation-error effect described above. The experimental points in Fig.4 represent the results



Fig. 3

Neutron groups observed in experiments at 296°K on the three germanium specimens (i) pure, (ii) n-type and (iii) p-type corresponding to normal modes (a) TA(1, 0, 0) and (b) LA(0.95, 0, 0) Wave vector co-ordinates are given in reciprocal lattice units.

Neutron groups (b) are superposed on a sloping "background" arising partly from fast neutrons and partly from incoherent scattering from the specimens.

for the arsenic-doped crystal, while the dashed and dotted curves refer to the pure crystal at 296°K. Those parts of the dispersion curves, which have not been measured in pure germanium at 296°K, have been estimated by interpolation from data at 100°K and 700°K [2, 12].

Consideration of Table I and Figs. 3 and 4 shows that in no case is there any significant difference between the normal mode frequencies in the three specimens. In the L modes near (1, 0, 0) for example, any effect due to intervalley electron scattering must be less than 1% and is probably less than 0.5%. There is perhaps a suggestion of a discontinuity ( $\approx 1\%$ ) near  $a\vec{q}/2\pi = (1, 0, 0)$  in the transverse optic (TO) branch of  $\nu(\vec{q})$  for the arsenic-doped specimen, though measurements of higher resolution would be needed to prove its existence. No significant differences between the three specimens were observed as regards the <u>widths</u> of the scattered neutron groups.

## 3. EXPERIMENTS ON SILICON

Two specimens were employed, having the same shape and crystal orientation as the germanium crystals described in section 2: (a) a pure specimen, approximately 1 in in diameter and (b) a phosphorus-doped specimen



Fig.4

Dispersion curves for the [500] direction in germanium at 296°K. The dotted (dashed) curves represent transverse (longitudinal) modes in pure germanium, while the experimental points (circles and triangles refer to transverse and longitudinal modes, respectively) were obtained for n-type germanium. The results for p-type closely resemble these and are not shown.

 $(3 \times 10^{19} \text{ phosphorus atoms/cm}^3)$ , 1.4 in in diameter. The measurements were performed at 296°K with the  $(1\overline{10})$  crystallographic direction perpendicular to the plane of the incident and scattered neutron beams. Most of the results for the pure specimen have been reported previously [4]. A small number of additional measurements were made to check the earlier work and excellent agreement was obtained. The normal mode frequencies measured in the n-type crystal at 296°K are given in Table II and plotted in Fig.5 (as experimental points). Most of the acoustic mode points are the mean values of three or more independent measurements, while the optic mode points generally represent only one or two measurements each. The dashed and dotted curves in Fig. 5 represent the results for pure silicon at 296°K for comparison. The most accurate results are those for the low frequency acoustic modes; any differences between the two specimens would appear to be substantially less than 1% for these modes. The optic mode frequencies have been determined with a relative accuracy of only about 2%, from which we conclude that any differences here must be less than about 3% in frequency. There are suggestions of possible depression of the optic mode frequencies in the n-type specimen, although considerably more work would be needed to examine these possibilities in more detail, owing to the difficulty of measuring such high frequency modes. As in the case of germanium, no significant changes in the widths of the neutron groups were observed in the experiments on silicon.

## TABLE II

## FREQUENCIES OF NORMAL MODES PROPAGATING ALONG THE [\$00] AND [0\$\$] DIRECTIONS IN PURE<sup>a</sup> AND DOPED SILICON AT 296°K

| Wave vector   | Mode            | Frequency<br>(10 <sup>12</sup> c/s) |                      |  |
|---------------|-----------------|-------------------------------------|----------------------|--|
| co-ordinate ζ |                 | P-Si                                | Pure Si <sup>a</sup> |  |
|               | [500] Direction | •                                   |                      |  |
| 1.0           | TA              | 4.47 ± 0.03                         | 4.49 ± 0.03          |  |
| 0.9           | TA              | $4.50 \pm 0.03$                     | 4.47 ± 0.03          |  |
| 0.6           | TA              | 4.21 ± 0.03                         | 4.27 ± 0.04          |  |
| 0.5           | TA              | 3.91 ± 0.02                         | 3.92 ± 0.03          |  |
| 0.3           | TA              | 2.86 ± 0.02                         | -                    |  |
| 1.0           | то              | 13.85 ± 0.17                        | 13.90 ± 0.17         |  |
| 0.0           | 0               | 15.30 ± 0.18                        | 15.53 ± 0.13         |  |
| 1.0           | L               | 12.36 ± 0.10                        | 12.36 ± 0.10         |  |
| 0.9           | LA              | 11.65 ± 0.10                        | -                    |  |
| 0.4           | LA              | 6.10 ± 0.08                         | $6.10 \pm 0.08$      |  |
| 0.35          | LA              | 5.46 ± 0.07                         | -                    |  |
| 0.3           | LA              | 4.62 ± 0.05                         | 4.65 ± 0.05          |  |
| 0,25          | LA              | 3,90 ± 0,05                         | 3.90 ± 0.05          |  |
| 0.2           | LA              | 3.17 ± 0.05                         | 3.20 ± 0.05          |  |
| 0.9           | LO              | 13.03 ± 0.20                        | -                    |  |
| 0.3           | LO              | 15.10 ± 0.20                        | $15.20 \pm 0.30$     |  |
| 0,25          | LO              | 15.25 ± 0.20                        | -                    |  |
| 0.2           | LO              | 15.45 ± 0.20                        | 15,55 ± 0.25         |  |
|               | [055] Direction |                                     |                      |  |
| 0.9           | ПА              | 5.15 ± 0.06                         | 5.10 ± 0.06          |  |
| 0.85          | ПА              | 5.65 ± 0.06                         | 5.60 ± 0.06          |  |
| 0.8           | ПА              | 6.22 ± 0.06                         | 6.19 ± 0.06          |  |
| 0.9           | по              | 14.12 ± 0.20                        | 14.15 ± 0.25         |  |
| 0.85          | ПО              | 14.09 ± 0.20                        | 14.20 ± 0.20         |  |
| 0,8           | по              | 14.10 ± 0.20                        | 14.35 ± 0.25         |  |
| 0,75          | по              | 14.30 ± 0.20                        | 14.40 ± 0.25         |  |
| 0.7           | ПО              | 14.65 ± 0.20                        | 14.60 ± 0.25         |  |
| 0.6           | по              | 14.60 ± 0.20                        | · -                  |  |
| 0.5           | по              | 14.63 ± 0.20                        | 14.55 ± 0.25         |  |

<sup>a</sup> Taken from [4] and other unpublished work by the present author. Estimated <u>relative</u> errors are quoted.

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Fig.5

Dispersion curves for the [ $\zeta$ 00] and [ $0\zeta\zeta$ ] directions in silicon at 296°K. The notation is similar to that of Fig. 4, except that the modes are not strictly longitudinal or transverse in the [ $0\zeta\zeta$ ] direction.

The experimental points refer to n-type silicon, and the dashed and dotted curves to pure silicon.

#### 4. SUMMARY

A search has been made for changes in the vibrational properties of pure germanium and silicon at 296°K, as a result of the introduction of excess electrons (or holes) by suitable doping. No significant changes of any kind were observed in either material. It would be interesting to make a theoretical calculation of the expected magnitude of any such effects, as a check on the experimental results, though this has not been attempted in the present paper.

## ACKNOWLEDGEMENTS

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### DISCUSSION

R.J. ELLIOTT: Your experiment reminds me of a different effect one might hope to see in a material with a many-valley band structure, namely, scattering of the neutron off the conduction electrons with a momentum change corresponding to the intervalley distance. Such a cross-section would be small, but it would be concentrated at particular K-values. A favourable substance might be the semi-metal bismuth, which is known to have small electron and hole pockets near the edge of the zone and which also has a large electron magnetic moment because of the large spin-orbit coupling.

J.L. WARREN: I talked briefly with Dr. Koenig of IBM Watson Laboratories on the way to the meeting. He was not too surprised at the negative results of your experiment. If I understood him correctly, the change in the constant  $C_{44}$  in n-type materials is due to a sort of electron screening effect for lattice vibrations associated with intervalley scattering. The relaxation time for this effect is of the order of  $10^{-12}$  s and hence this effect would not be operative for the high frequencies observed by inelastic neutron scattering.

G. DOLLING: Dr. Koenig's explanation of the change in  $C_{44}$  is very interesting. This type of effect will naturally be much smaller for the higher frequency modes. However, I think that the kind of effect which we were hoping to detect at certain specific wave vectors is quite distinct from that discussed by him.

# A STUDY OF INELASTIC NEUTRON SCATTERING BY ANHARMONIC CRYSTALS WITH THE DAMPING THEORY<sup>\*</sup>

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### Abstract — Résumé — Аннотация — Resumen

A STUDY OF INELASTIC NEUTRON SCATTERING BY ANHARMONIC CRYSTALS WITH THE DAMPING THEORY. The damping theory is developed in terms of projection operators, and an expression for the transition probability per unit time which is suitable to line shape studies in general is obtained. This expression replaces the usual energy-conserving delta function by a Lorentzian distribution whose width is equal to the difference of the widths of the initial and final states. Using this expression, a formula for the scattering cross-section of slow neutrons by an anharmonic crystal is derived. Expressions for the width and shift of lines corresponding to multiphonon events in general, and to a one-phonon event as a special case, are obtained and investigated in the zero and high temperature limits. The results are compared to those obtained previously. It is found that the inverse of phonon lifetime is expressible in terms of the difference of the widths of the crystal states, as obtained by Brout. The shift formula is shown to be in agreement at all temperatures with that obtained by Maradudin and Fein and others. The width formula agrees with theirs only in the zero temperature limit. In the high temperature limit, the present formula predicts a quadratic temperature dependence in contrast with the linear dependence predicted by theirs. This discrepancy is discussed in terms of the concept of phonon lifetime. The present theory predicts a larger width at high temperatures by a factor  $(2/\beta\hbar\omega_0)$ , and therefore is expected to yield a better agreement with the large experimental widths observed by Brockhouse et al. than that reported by Maradudin and Fein.

ÉTUDE, AU MOYEN DE LA THÉORIE DE L'AMORTISSEMENT, DE LA DIFFUSION INÉLASTIQUE DES NEUTRONS DANS DES CRISTAUX ANHARMONIQUES. En développant la théorie de l'amortissement en fonction des opérateurs de projection, les auteurs obtiennent une expression de la probabilité de transition par unité de temps, qui convient de manière générale pour des études sur la forme des raies. Cette expression remplace la fonction delta habituelle de conservation de l'énergie par une distribution lorentzienne dont la largeur est égale à la différence entre les largeurs des états initial et final. A partir de cette expression, les auteurs établissent une formule de la section efficace de diffusion des neutrons lents par un cristal anharmonique. Ils obtiennent des expressions de la largeur et du déplacement des raies correspondant à des événements à plusieurs phonons en général et à un événement à un phonon dans un cas particulier, expressions qu'ils étudient à une température nulle et à haute température. Les résultats sont comparés à ceux qui ont été obtenus auparavant. On constate que l'inverse de la durée de vie d'un phonon peut s'exprimer en fonction de la différence entre les largeurs des états cristallins, établie par Brout. La formule du déplacement concorde, à toutes les températures, avec celle de Maradudin, Fein et d'autres chercheurs. La formule de la largeur ne concorde avec la leur qu'à la limite correspondant à une température nulle. A la limite correspondant à une température élevée, la formule actuelle laisse prévoir une variation quadratique en fonction de la température, par opposition avec la variation linéaire que prévoit leur formule. Les auteurs discutent cette divergence entre les résultats en se fondant sur la notion de durée de vie des phonons. La présente théorie laisse prévoir une largeur plus grande d'un facteur  $(2/\beta\hbar\omega_0)$  à de hautes températures et devrait donc mieux concorder avec les grandes largeurs observées par Brockhouse et ses collaborateurs lors de leurs expériences, qu'avec celles indiquées par Maradudin et Fein,

ИЗУЧЕНИЕ НЕУПРУГОГО РАССЕЯНИЯ НЕЙТРОНОВ НА НЕГАРМОНИЧЕСКИХ КРИ-СТАЛЛАХ С ПОМОЩЬЮ ТЕОРИИ ЗАТУХАНИЯ. Теория затухания разрабатывается с учетом операторов предсказанного значения случайных величин, и авторы выводят выражение вероятности перехода на единицу времени, пригодное в целом для изучения формы спектраль-

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ных линий. Это выражение заменяет обычную дельта-функцию сохранения энергии с помощью распределения Лоренца, ширина которого равна разнице между размерами ширины первоначального и конечного состояний. С помощью этого выражения выводится формула для поперечного сечения рассеяния медленных нейтронов на негармонических кристаллах. Выводятся и изучаются при пределах нулевой температуры и высокотемпературных пределах выражения для ширины и смещения линий, соответствующих многофононным явлениям в целом и однофононному явлению в частном случае. Результаты сравниваются с ранее полученными результатами. Устанавливается, что обратная величина времени жизни фононов может быть выражена в отношении разницы между размерами ширины при разных состояниях кристалла, как это выведено Браутом. Показывается, что формула смещения согласуется при любой температуре с формулой, полученной Марадюдином, Файном и др. Формула ширины согласуется с их формулой только при пределе нулевой температуры. При высокотемпературном пределе нынешняя формула предсказывает квадратическую температурную зависимость в противоположность линейной зависимости, предсказываемой их формулой. Такое расхождение обсуждается в рамках концепции времени жизни фонона. Нынешняя теория предсказывает больший размер ширины при высоких температурах на фактор (2/ $\beta$  h $\omega$ .), и поэтому, как предполагается, она приводит к лучшему согласованию с большими экспериментальными значениями ширины, отмеченными Брокхаузом и др., чем теория, предложенная Марадюдином и Файном.

ESTUDIO DE LA DISPERSIÓN INELASTICA DE NEUTRONES EN CRISTALES ANARMONICOS, APLICANDO LA TEORÍA DEL AMORTIGUAMIENTO. Los autores desarrollan la teoría del amortiguamiento en función de los operadores de proyección, y obtienen para la probabilidad de transición por unidad de tiempo una expresión que, por lo general, resulta adecuada para los estudios sobre la forma de las curvas. Esta expresión sustituye a la habitual función delta de conservación de la energía por una distribución lorentziana cuya amplitud es igual a la diferencia entre las amplitudes correspondientes a los estados inicial y final. Haciendo uso de esta expresión, los autores deducen una fórmula para la sección eficaz de dispersión de los neutrones lentos en un cristal anarmónico. Obtienen expresiones para la amplitud y el desplazamiento de las rayas correspondientes a los procesos multifonónicos, en general, y como caso particular, a un proceso monofonónico, y estudian esas expresiones para temperaturas que tienden a cero y para temperaturas elevadas. Comparan los resultados con los obtenidos previamente, y comprueban que la inversa de la vida media del fonón puede expresarse en función de la diferencia entre las amplitudes de los estados del cristal, calculadas por Brout. La fórmula obtenida para el desplazamiento concuerda, para todas las temperaturas, con la propuesta por Maradudin y Fein, y por otros investigadores. En cuanto a la fórmula para la amplitud, concuerda con las de esos investigadores sólo para el límite de temperatura cero. Para el límite superior, la nueva fórmula prevé una variación con el cuadrado de la temperatura, en contraste con la variación de tipo lineal establecida en la de aquéllos. Los autores examinan esta discrepancia atendiendo al concepto de vida media del fonón. La teoría de los autores prevé una mayor amplitud de un factor  $(2/\beta\hbar\omega_0)$  a altas temperaturas y, por ello, es de suponer que concuerde en forma más satisfactoria con los elevados valores de amplitud observados experimentalmente por Brockhouse y sus colaboradores, que con los dados a conocer por Maradudin y Fein.

### I. INTRODUCTION

The aim of this paper is to study the inelastic scattering of slow neutrons by anharmonic crystals with the damping theory. The latter was presented by Heitler in References [1,2] some time ago, as a perturbation theory of transition rates between decaying states, and was used extensively to investigate the natural broadening of optical lines. However, the potential of the damping theory as a tool for calculating the shapes of spectral lines in photon emission and neutron scattering experiments in the presence of medium effects does not seem to have been investigated. The present work is a step in this direction.

The following section contains an extension of the damping theory to include the decay of the final state. Such an extension is essential for the

application of the theory to the inelastic neutron scattering by anharmonic crystals because the lifetime of the final crystal state is comparable to that of the initial state, and hence cannot be neglected as is often done in the optical line shape problems. The remaining sections are devoted to the calculation of the spectrum of the slow neutrons inelastically scattered by anharmonic crystals.

### II. DAMPING THEORY

The quantum-mechanical interpretation of a large class of experiments involves the quantity

$$W_{mn} = |U_{mn}(t)|^2/t$$
 (2.1)

where U(t) is the "time-evolution" operator which is given by U(t) =  $e^{-itH}$ when the Hamiltonian H of the system is time-independent (units are chosen so that  $\hbar = 1$ ). The representation {|n>} is generated by H<sub>0</sub> which is the part of H = H<sub>0</sub> + V for which the eigenvalue problem

$$(H_0 - E_n) | n > = 0$$
 (2.2)

can be solved. The numerator in Eq.(2.1) is the probability of finding the physical system in a state  $|m\rangle$  at time t, knowing that it was in the state  $|n\rangle$  at t = 0. The quantity  $W_{mn}$  is in general time-dependent. However, in certain time intervals, it can be approximated by some time-independent quantity, and thus interpreted as "transition probability per unit time" from the initial state  $|n\rangle$  into the final state  $|m\rangle$ . Such an approximation can be obtained by using Heitler's damping theory [1,2]. The following treatment of the damping theory differs from Heitler's original derivation in two respects: First, it is developed in terms of projection operators and second, it employs a different iteration procedure. It is an extension of the quantum theory of decaying states by MESSIAH [3] to the cases where the decay of the final state cannot be ignored [4].

The first step is to compute the diagonal and off-diagonal matrix elements, namely,  $U_{nn}(t)$  and  $U_{mn}(t)$ , of the time-evolution operator in Eq.(2.1). Since U(t) is the inverse Laplace transform of the resolvent of H, i.e. G(z) =(z-H)<sup>-1</sup>, one tries to compute  $G_{nn}(z)$  and  $G_{mn}(z)$ . For this purpose, one introduces two new operators  $\mathcal{G}_{nn}(z)$  and  $\mathcal{G}_{mn}(z)$  which are defined by

$$\mathcal{G}_{nn}(z) \equiv P_n G(z) P_n$$
,  $\mathcal{G}_{mn}(z) = P_m G(z) P_n$ , (2.3)

where  $P_n$  and  $P_m$  are projection operators onto the subspaces spanned by the eigenvectors belonging to the eigenvalues  $E_n$  and  $E_m$ . If the states  $|n\rangle$ are non-degenerate, then  $P_n$  implies projection on the eigenvector  $|n\rangle$ . The projection operator on the complementary subspace will be denoted by  $Q_n$ , namely  $Q_n = 1 - P_n$ . Following Messiah, one divides H into two parts as H =  $H_1 + H_2$ , where  $H_1$  and  $H_2$  are defined by A.Z. AKCASU and R.K. OSBORN

$$H_1 \equiv P_n HP_n + Q_n HQ_n = H_0 + P_n VP_n + Q_n VQ_n, \qquad (2.4)$$

$$\mathbf{H}_{2} \equiv \mathbf{P}_{n} \mathbf{H} \mathbf{Q}_{n} + \mathbf{Q}_{n} \mathbf{H} \mathbf{P}_{n} = \mathbf{P}_{n} \mathbf{V} \mathbf{Q}_{n} + \mathbf{Q}_{n} \mathbf{V} \mathbf{P}_{n} .$$
 (2.5)

The following commutation relations are needed in the subsequent analysis:

$$[H_1, P_n] = [H_1, Q_n] = 0$$
 (2.6)

$$P_n H_2 = H_2 Q_n$$
,  $Q_n H_2 = H_2 P_n$ , (2.7)

$$\mathbf{P}_{n}\mathbf{H}_{0} = \mathbf{E}_{n}\mathbf{P}_{n} = \mathbf{H}_{0}\mathbf{P}_{n} . \tag{2.8}$$

The resolvent G(z) can be expressed in terms of  $H_1$  and  $H_2$  as follows:

G(z) = 
$$\frac{1}{z-H_1} + \frac{1}{z-H_1} H_2G(z)$$
 (2.9a)

$$= \frac{1}{z-H_1} + \frac{1}{z-H_1} H_2 \frac{1}{z-H_1} + \frac{1}{z-H_1} H_2 \frac{1}{z-H_1} H_2 G(z).$$
 (2.9b)

One can now obtain an expression for  $\mathcal{G}_{nn}(z)$  by operating on both sides of Eq. (2.9b) by  $P_n$ , and observing that the second term vanishes by virtue of Eq.(2.7). The result is

$$G_{nn}(z) = [z - E_n - \Gamma_n(z)]^{-1} P_n,$$
 (2.10)

where the operator  $\Gamma_n$  (z) is defined by

$$\Gamma_{n}(z) \equiv P_{n}[V + VQ_{n}(z - Q_{n}HQ_{n})^{-1}V]P_{n}. \qquad (2.11)$$

A similar expression for  $\mathcal{G}_{mn}(z)$  is obtained by operating on Eq. (2.9a) by  $P_m$  on the left, and by  $P_n$  on the right:

$$\mathcal{G}_{mn}(z) = P_m(z - Q_n HQ_n)^{-1} Q_n V \mathcal{G}_{nn}(z). \qquad (2.12)$$

Using  $Q_n \equiv \sum_{r \neq n'} P_r = P_m + \sum_{r \neq n, m} P_r$ , one can express Eq. (2.12) as follows:

$$\mathcal{G}_{mn}(z) = P_m(z - Q_n HQ_n)^{-1} P_m V \mathcal{G}_{nn}(z) + \sum_{r \neq n, m} P_m(z - Q_n HQ_n)^{-1} P_r V \mathcal{G}_{nn}(z).$$
(2.13)

It is noted that Eqs. (2.10) and (2.13) for  $\mathcal{G}_{nn}(z)$  and  $\mathcal{G}_{mn}(z)$ , respectively, are exact. However, they contain the operator  $(z-Q_nHQ_n)^{-1}$  whose matrix elements in the representation  $\{|n\rangle\}$  are not known. Messiah approximates this operator by  $(z-H_0)^{-1}$  by ignoring  $Q_nVQ_n$  in  $Q_nHQ_n = Q_n(H_0+V)Q_n$ , and thereby obtains a closed form for  $\mathcal{G}_{mn}(z)$  and  $\mathcal{G}_{nn}(z)$ . This approximation excludes automatically the width and shift of the final state  $|m\rangle$ , and therefore is not suitable to line shape studies in all cases. A more

accurate approximation can be obtained by repeating the foregoing procedure in the complementary subspace defined by  $Q_n$ , for the following operator

$$G'(z) \equiv (z - \mathcal{H})^{-1}Q_n$$
, (2.14)

where  $\mathcal{M} \equiv Q_n H Q_n$ . In Eq. (2.14), and below, a single prime denotes an operator restricted to the subspace  $Q_n$ . One splits  $\mathcal{M}$  as  $\mathcal{M} = \mathcal{M}_0 + \mathscr{V}$  where  $\mathcal{M}_0 \equiv Q_n H_0 Q_n$  and  $\mathscr{V} \equiv Q_n V Q_n$ . Clearly, the representation  $\{|m\rangle\}$  diagonalizes  $\mathcal{M}_0$ , i.e.  $P_m \mathcal{M}_0 = E_m P_m = \mathcal{M}_0 P_m$  holds. The operator  $\mathcal{C}'_{mm}(z) \equiv P_m G'(z) P_m$  appearing in the first term in Eq. (2.13) can be readily obtained from Eq. (2.10) by replacing  $H_0$  and V by  $\mathcal{M}_0$  and  $\mathscr{V}$ , respectively:

$$G'_{mm}(z) = [z - E_m - \Gamma'_m(z)]^{-1} P_m,$$
 (2.15)

where

$$\Gamma'_{m}(z) \equiv P_{m}[V + VQ_{n}Q_{m}(z - Q_{m}Q_{n}HQ_{n}Q_{m})^{-1}V]P_{m}.$$
 (2.16)

The operators  $\mathcal{G}_{mr}(z) \equiv P_m G'(z)P_r$  appearing in the restricted summation in Eq. (2.13) can be written, according to Eq. (2.12), as

$$G'_{mr}(z) = G'_{mm}(z) \mathscr{V}Q_m(z - Q_m \mathcal{M}Q_m)^{-1} P_r$$
, (2.17)

or, replacing  $\mathbf{Q}_m$  by  $\sum_{s\, \ddagger\, m,\, n} \mathbf{P}_s$  , one finds

$$\mathcal{G}'_{\mathrm{mr}}(z) = \mathcal{G}'_{\mathrm{mm}}(z) \nabla \mathcal{G}''_{\mathrm{rr}}(z) + \sum_{s \neq r, m} \mathcal{G}'_{\mathrm{mm}}(z) \mathscr{V} \mathcal{P}_{s} \mathrm{G}''(z) \mathcal{P}_{r}, \qquad (2.18)$$

where  $G''(z) = (z - Q_m \mathcal{H}Q_m)^{-1}Q_mQ_n$ , and where  $\mathcal{G}''_{Ir}(z)$  is defined in a similar fashion as  $\mathcal{G}_{nn}(z)$  in Eq. (2.10), or  $\mathcal{G}'_{mm}(z)$  in Eq. (2.15). Operators with double prime are restricted to the subspace obtained by deleting the subspaces  $P_m$  and  $P_n$  from the original Hilbert space. The first iteration is effected by substituting  $\mathcal{G}'_{mr}(z)$  from Eq. (2.18) into Eq. (2.13). The result is

$$\mathcal{G}_{mn}(z) = \mathcal{G}_{mm}(z) \vee \mathcal{G}_{nn}(z) + \sum_{r \neq m, n} \mathcal{G}_{mm}(z) \vee \mathcal{G}_{rr}(z) \vee \mathcal{G}_{nn}(z) + \dots \quad (2.19)$$

It is observed that Eq. (2.19) is an expansion, in a sense, in powers of V. It expresses the non-diagonal operator  $\mathcal{G}_{mn}(z)$  in terms of the diagonal operators  $\mathcal{G}_{nn}(z)$ ,  $\mathcal{G}'_{mm}(z)$ ,... The first term corresponds to the direct transition from the initial subspace into the final subspace; the second term represents transitions through an intermediate subspace, and so on. It is noted [cf. Eqs. (2.10) and (2.15)] that the diagonal operators  $\mathcal{G}_{nn}(z)$ ,  $\mathcal{G}'_{mm}(z)$ , ... still contain G(z), G'(z),..., through  $\Gamma_n(z)$ ,  $\Gamma'_m(z)$ ,... However, one may now approximate  $\Gamma_n(z)$ ,  $\Gamma'_m(z)$ ... by replacing H in their expression [cf. Eqs. (2.11) and (2.16)] by H<sub>0</sub>:

$$\Gamma_{n}(z) \approx P_{n} [V + VQ_{n}(z - H_{0})^{-1}V] P_{n},$$
 (2.20)

$$\Gamma'_{m}(z) \sim P_{m}[V + VQ_{n}Q_{m}(z-H_{0})^{-1}V]P_{m}.$$
 (2.21)

It is noted that the width and the shift of the final state are included in this approximation in contrast to the approximation made by replacing H by  $H_0$  in Eq.(2.13) directly.

When the eigenvalues of  $H_0$  are non-degenerate, the projection operators  $P_n$ ,  $P_m$ , etc., in the foregoing formulas can be replaced by their corresponding eigenvectors. The operators  $\mathcal{G}_{mn}(z)$  and  $\mathcal{G}_{nn}(z)$  then reduce to the matrix elements  $G_{mn}(z)$  and  $G_{nn}(z)$ , respectively, and Eqs. (2.19), (2.10), (2.20), and (2.21) become:

$$\mathbf{G}_{mn} = \mathbf{G}_{mm}^{\prime} \mathbf{V}_{mn} \mathbf{G}_{nn} + \sum_{r \neq n, m} \mathbf{G}_{mm}^{\prime} \mathbf{V}_{mr} \mathbf{G}_{rr}^{*} \mathbf{V}_{rn} \mathbf{G}_{nn} + \dots \qquad (2.22)$$

$$G_{nn}(z) = [z - E_n - \Gamma_n(z)]^{-1}$$
, (2.23a)

$$G'_{mm}(z) = [z - E_m - \Gamma_m'(z)]^{-1}$$
, (2.23b)

$$\Gamma_{n}(z) = V_{nn} + \sum_{r \neq n} |V_{rn}|^{2} (z - E_{r})^{-1},$$
 (2.24a)

$$\Gamma_{\rm m}'(z) = V_{\rm mm} + \sum_{\rm r \neq m,n} |V_{\rm rm}|^2 (z - E_{\rm r})^{-1}. \qquad (2.24b)$$

These results are identical to those obtained by ARNOUS and HEITLER [1] except for the fact that  $\Gamma'_m$  in Eq.(2.23b), which represents the width and shift of the final state excludes the transition back to the initial state, as well as the transition into itself. Consequently, the initial and final states do not enter the formulas symmetrically in the present derivation whereas  $G_{mn}(z)$  is symmetric with respect to the initial and final states in Heitler's derivation. The foregoing refinement over Heitler's results does not seem to be of any significance in the application of the damping theory to neutron scattering by crystals discussed in section III. However, it may be of importance in the study of natural broadening of the optical lines.

When the unperturbed Hamiltonian  $H_0$  of the system can be expressed as  $H_0 = H_0^a + H_0^p$ , where  $H_0^a$  has a degenerate discrete spectrum, and  $H_0^r$  has a continuous spectrum, the choice of the representation  $|n\rangle$  and the definition of  $P_n$  require closer attention. This situation is encountered in the study of optical line shape where the emitting atom has a discrete spectrum, and the surrounding medium has a continuous spectrum. In this case, the base vectors can be written as  $|n\rangle = |a\mu\rangle |\beta\rangle$ , where  $|\alpha\mu\rangle$  are internal states of the emitter with energy  $E_a$ , and  $|\beta\rangle$  describe the states of the surrounding medium, as well as the external states of the emitter. Accordingly, the projection operator  $P_n$  becomes  $P_n = P_a P_\beta$ . In this case, one chooses  $P_a$  as the projector onto the finite dimensional subspace spanned by  $|a\mu\rangle$  so that the shift functions which ultimately appear in the formulas remain finite. The shift function is the same as the second-order perturbation calculation of the correction to the energy of a level, and this choice of  $P_a$  eliminates the vanishing denominators. The operator  $P_\beta$  is chosen as the projector on  $|\beta\rangle$ . As will be seen presently, one is actually interested in the non-hermitian operators  $G(x^+)$ ,  $\Gamma_n(x^+)$ ,  $\Gamma'_m(x^+)$ , etc., which are defined as

$$\Gamma_{n}(\mathbf{x}^{+}) = \lim \ \Gamma_{n}(\mathbf{x} + i\epsilon) \equiv S_{n}(\mathbf{x}) - \frac{i}{2} \gamma_{n}(\mathbf{x}), \qquad (2.25)$$

where

$$S_n(x) \equiv P_n[V + VQ_n(x - H_0)_p^{-1} V] P_n$$
 (2.26)

$$\gamma_{n}(\mathbf{x}) \equiv 2\pi P_{n} V Q_{n} \delta(\mathbf{x} - H_{0}) V P_{n}, \qquad (2.27)$$

and where  $(x - H_0)_P^{-1}$  indicates principal value of  $(x - H_0)^{-1}$ . Then, the matrix element of  $G(x^+)$  between  $|n\rangle = |a\mu\rangle|\beta\rangle$  and  $|m\rangle = |b\nu\rangle|\gamma\rangle$  can be written as

$$G_{mn}(\mathbf{x}^{\dagger}) = \sum_{\mu'\nu'} \left[ \left\{ \mathbf{b}\nu \right\} \left[ \mathbf{x} - \mathbf{E}_{m} - \left\langle \gamma \right\rangle \left[ \Gamma_{m}'(\mathbf{x}^{\dagger}) \right] \gamma \right\} \right]^{-1} \left| \mathbf{b}\nu' \right\rangle \left\langle \mathbf{b}\nu' \right| \nabla_{\gamma\beta} \left| \mathbf{a}\mu' \right\rangle \right] \\ \left\{ \mathbf{a}\mu' \left[ \left[ \mathbf{x} - \mathbf{E}_{n} - \left\langle \beta \right\rangle \left[ \Gamma_{n}'(\mathbf{x}^{\dagger}) \right] \beta \right]^{-1} \left| \mathbf{a}\mu \right\rangle \right] + \dots \right] \right\}$$

$$(2.28)$$

Let it be assumed that the operators  $\langle \gamma | \Gamma_{\rm m}^{\prime}(x^{*}) | \gamma \rangle$  and  $\langle \beta | \Gamma_{\rm n}(x^{*}) \beta \rangle$  operating on  $|a\mu\rangle$  and  $|b\nu\rangle$ , respectively, can be diagonalized in the subspaces  $E_a$  and  $E_b$ . Then, the summations on  $\mu'$  and  $\nu'$  in Eq. (2.28) disappear, and the form of Eq. (2.28) reduces to that in Eq. (2.22) obtained for the nondegenerate case. It follows that the Eqs. (2.22), (2.23), and (2.24) can be used also in the present case provided the representation  $\{|n\rangle\}$  is chosen properly as illustrated.

One is now in a position to compute the matrix elements of the timeevolution operator U(t) as the inverse Laplace transform of G(z). First consider the diagonal matrix element  $U_{nn}(t)$ , which can be written as

$$U_{nn}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dx \ e^{-ixt} \frac{\gamma_n(x)}{[x - E_n - S_n(x)]^2 + (1/4)\gamma_n^2(x)},$$

where  $S_n(x)$  and  $\gamma_n(x)$  are defined by Eqs. (2.26) and (2.27) respectively. This integral can be evaluated approximately by treating  $S_n(x)$  and  $\gamma_n(x)$  as a constant. This is justified because  $S_n(x)$  and  $\gamma_n(x)$  are slowly varying in the neighbourhood of  $x = E_n$  where the integrand attains its maximum value, and because the dominant contribution to the value of the integral comes from this region. The constant value of  $S_n(x)$  and  $\gamma_n(x)$  can be taken as their value at  $x = E_n$ . Thus, one obtains the well-known result

$$U_{nn}(t) = \exp[-it(E_n + \Gamma_n)],$$
 (2.29)

where

$$\Gamma_{n} \equiv S_{n}(E_{n}) - \frac{i}{2} \gamma_{n} (E_{n}).$$
 (2.30)

Next consider the off-diagonal element of  $U_{mn}(t)$ . According to Eq. (2.22), it is the inverse Laplace transform of the products  $G'_{mm}(z)G_{nn}(z)$ ,  $G'_{mm}(z)$   $G''_{rr}(z)G_{nn}(z)$ , etc. Hence, it can be expressed as

$$U_{mn}(t) = V_{mn} \int_{0}^{t} U'_{mm}(\tau) U_{nn}(t-\tau) d\tau + \dots , \qquad (2.31)$$

where  $U_{lmm}(t)$  is the inverse Laplace transform of  $G_{lmm}(z)$ . Henceforth, only the first term in Eq. (2.31) will be retained because the approximation made by ignoring higher order terms corresponding to transitions via an intermediate state is found to be sufficiently accurate to include the dominant features of the line-broadening phenomenon. The integration in Eq. (2.31) can be performed approximately by using the approximate expression for  $U_{nn}(t)$  from Eq. (2.29), and the similar expression for  $U_{lmm}(t)$ , i.e.  $U'_{mm}(t) = \exp[-it(E_m + \Gamma'_m)]$ . The result can be expressed

$$\left| U_{mn}(t) \right|^{2} = \frac{\left| V_{mn} \right|^{2}}{\left| (E_{m} + \Gamma_{m}') - (E_{n} + \Gamma_{n}) \right|^{2}} \left| e^{-it(E_{n} + \Gamma_{n})} - e^{-it(E_{m} + \Gamma_{m}')} \right|^{2} (2.32)$$

which is the basic result of the damping theory.

The next task is to obtain an approximate formula for the transition probability per unit time from  $|n\rangle$  into  $|m\rangle$ , using Eqs. (2.29) and (2.32). According to Eq. (2.29), the states decay exponentially as  $|U_{nn}(t)|^2 = \exp[-\gamma_n t]$ , indicating that  $\gamma_n$  is actually the probability of decay per unit time. This suggests that one may express  $W_{mn}$  in Eq. (2.1) as

$$W_{\rm mn} = \gamma_{\rm n} \mathscr{P}_{\rm mn}, \qquad (2.33)$$

where  $\mathscr{P}_{mn}$  is the probability that the transition from  $|n\rangle$ , when it occurs, will be <u>towards</u>  $|m\rangle$ , and attempt to determine  $\mathscr{P}_{mn}$  rather than  $W_{mn}$ . Combining this probability concept with the fact that the states decay exponentially, one can obtain an alternative expression for  $|U_{mn}(t)|^2$ :

$$|U_{mn}(t)|^{2} = \int_{0}^{t} e^{-\gamma_{n}t} \gamma_{n} dt' \mathscr{P}_{mn} e^{-\gamma_{m}'(t-t')}, \qquad (2.34a)$$

or

$$\left|U_{mn}(t)\right|^{2} \approx \frac{\gamma_{n}}{\gamma_{n} - \gamma_{m}^{\prime}} \left(e^{\gamma_{m}^{\prime}t} - e^{-\gamma_{n}^{\prime}t}\right) \mathscr{P}_{mn}. \qquad (2.34b)$$

The factor  $\exp \left[-\gamma_{n} t^{\prime}\right] \gamma_{n} dt^{\prime}$  in Eq. (2.34a) is the probability that a transition will occur in dt' about t',  $\mathscr{P}_{mn}$  is the probability that this transition will be towards  $|m\rangle$ , and the last factor is the probability that the system will remain in  $|m\rangle$  in the time interval  $(t-t^{\prime})$ . Comparing Eqs. (2.34b) and (2.32) in the time interval  $|\gamma'_{m} - \gamma_{n}| t \gg 1$ , one finds the following expression for  $\mathscr{P}_{mn}$ :

$$\mathcal{P}_{mn} = \frac{2}{\gamma_n} |V_{mn}|^2 \frac{|\gamma_{mn}|}{(E_m - E_n + S_{mn})^2 + \gamma_{mn}^2}, \qquad (2.35)$$

where we have introduced

$$S_{mn} = S'_m - S_n$$
,  $\gamma_{mn} = (\gamma'_m - \gamma_n)/2$ . (2.36)

Combining Eqs. (2.33) and (2.35) yields

$$W_{mn} = 2 \left| V_{mn} \right|^2 \frac{|\gamma_{mn}|}{(E_m - E_n + S_{mn})^2 + \gamma_{mn}^2}$$
(2.37)

which will be the starting point of the line shape theory developed in the subsequent section. One notes that Eq. (2.37) reduces to the conventional expression for the transition probability per unit time when  $\gamma_{mn}$  and  $S_{mn}$  tend to zero because the last factor approaches  $\pi\delta(E_m - E_n)$  as  $\gamma_{mn} \rightarrow 0$ .

The following alternative derivation of Eq. (2.37) may reflect more clearly the nature of the approximations inherent in  $W_{mn}$ . One starts with  $W_{mn} = |U_{mn}(t)|^2/t$  and substitutes  $|U_{mn}(t)|^2$  from Eq. (2.32). Since U(t) and U'(t) are unitary, one has  $\sum_{\gamma} |U_m(t)|^2 = 1$  and  $\sum_{\gamma} |U'_{rm}(t)|^2 = 1$ . Using these, and multiplying the numerator and denominator by  $||U_{nn}(t)|^2 - |U'_{mm}(t)|^2|$ , one can write  $W_{mn}$  as

$$W_{mn} = \frac{|U_{mn}|^2}{|U_{nn}|^2 - |U_{mm}|^2|} \left| \sum_{r \neq n} \frac{|U_{rn}|^2}{t} - \sum_{r \neq m} \frac{|U'_{rm}|^2}{t} \right|, \qquad (2.38)$$

where the argument of U(t) and U'(t) are omitted. Equation (2.38) is still exact. The approximation which has to be made to obtain Eq. (2.37) consists of evaluating the first factor using Eqs. (2.29) and (2.32) for large times, i.e.  $|\gamma'_m - \gamma_n| t \gg 1$ , and of evaluating the second factor first letting  $\gamma_n$  and  $\gamma'_m$  tend to zero and then taking the limit as  $t \rightarrow \infty$ . The second factor gives rise to  $|\gamma'_m - \gamma_n|$  in Eq. (2.37). The novelty about Eq. (2.37) is that it takes into account the decay of the final states, without which the application of the damping theory to the study of a large class of line shape problems<sup>\*</sup>, e.g. phonon line shape, would be impossible.

### III. NEUTRON SCATTERING BY ANHARMONIC CRYSTALS

As an application of the damping theory, scattering of slow neutrons by a macroscopic system, in particular by an anharmonic crystal, are discussed in this section. The differential scattering cross-section per unit solid angle and per unit final neutral energy  $\epsilon_f = (\hbar^2 k_f^2/2m)$ , can be written as (units are chosen in this section such that  $\hbar \neq 1$ )

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}\epsilon_{\mathrm{f}}} = \frac{1}{(2\pi\hbar)^3} \frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{k}_{\mathrm{i}}} \frac{\mathrm{m}^2}{2\mathrm{N}} \sum_{\mu_{\mathrm{i}},\tau_{\mathrm{i}}} P_{\mu_{\mathrm{i}}} \sum_{\mu_{\ell},\tau_{\mathrm{f}}} |U_{n_{\mathrm{f}}n_{\mathrm{i}}}(t)|^2 / t, \qquad (3.1)$$

where ki and kf are the initial and final neutron wave numbers, misneutron mass, N is the number of nuclei in the scattering medium,  $|\tau_i\rangle$  and  $|\tau_f\rangle$ are the initial and final neutron spin states,  $|\mu_i\rangle$  and  $|\mu_i\rangle$  are the initial and final states of the scatterer including spins,  $P_{\mu i}$  is the probability of finding the scatterer in  $|\mu_i\rangle$ , and finally the last factor is the transition probability per unit time which is discussed in section II. The representation  $|n\rangle = |\mu\rangle |\tau\rangle |\vec{k}\rangle$  is generated by  $H_0 = H^n + \mathcal{M}^s$  where  $H^n$  is the kinetic energy of neutron and  $\mathcal{H}^{s}$  is an appropriate portion of the Hamiltonian H<sup>s</sup> of the scatterer. In the case of a crystal as the scattering medium,  $\mathcal{H}^s$  will be the harmonic part of the crystal Hamiltonian. In deriving Eq. (3.1) one ignores the off-diagonal matrix elements of density operator D in  $\{|n>\}$ , and replaces  $P_{n_j} \equiv D_{n_j n_i}$  by  $P_{\mu_i} \xrightarrow{P_{k_j}} P_{\underline{\tau}_j}$ , where  $P_{k_i}$  and  $P_{\tau_j}$  are the probability of finding the neutron initially in  $|\vec{k}_i > |\tau_i >$ . In an experiment with a monoenergetic unpolarized beam,  $P_{k_i} = 1$  and  $P_{\tau_i} = 1/2$ . The main approximation of the present theory of neutron scattering is made by replacing  $|U_{nfn}(t)|^2/t$ by Eq. (2.37). The perturbation V appearing in Eq. (2, 37) is given by  $V = H' + V^n$  where  $H' = H^s - \mathcal{J}^s$  and  $V^n$  is the interaction between the neutron and the scatterer. In the case of a crystal, H' denotes the anharmonic potential energy. Approximating  $V^n$  by the Fermi pseudo potential one obtains the starting formula of the present theory:

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}\epsilon_{\mathrm{f}}} = \frac{\mathrm{k}_{\mathrm{f}}}{2\pi\mathrm{N}\mathrm{k}_{\mathrm{i}}} \sum_{\tau_{\mathrm{i}}, \tau_{\mathrm{f}}\mu_{\mathrm{i}}\mu_{\mathrm{f}}} \sum_{\mu_{\mathrm{i}}} \left| \mu_{\mathrm{f}}\tau_{\mathrm{f}} \right| \\ \times \sum_{\mathrm{i}=1}^{\mathrm{N}} a_{\mathrm{i}} e^{i\vec{\kappa}\cdot\vec{R}_{\mathrm{i}}} \left| \mu_{\mathrm{i}}\tau_{\mathrm{i}} \right|^{2} \times \frac{\left| \gamma_{\mathrm{n}_{\mathrm{f}}n_{\mathrm{i}}} \right|}{(\mathrm{E}_{\mu_{\mathrm{i}}} - \mathrm{E}_{\mu_{\mathrm{f}}} + \epsilon - \mathrm{S}_{\mathrm{n}_{\mathrm{f}}n_{\mathrm{i}}})^{2} + \gamma_{\mathrm{n}_{\mathrm{f}}n_{\mathrm{i}}}^{2}}, \quad (3.2)$$

\* Equation (2.37) does not apply to the natural line width problems of a multi-level atom where the width of a line in a transition  $a \rightarrow b$  is equal to  $\gamma_a + \gamma_b$ , rather than the difference of the widths  $\gamma_a$  and  $\gamma_b$  of the levels [5]. The reason for this, as pointed out by BROUT [12], is that the sequence of transitions between the excited states are not statistically independent. The present theory applies to the systems where the decay of the final state is predominantly caused by the system Hamiltonian rather than the radiation (or the neutron interaction, in the case of neutron scattering problems). where  $\vec{\kappa}$  and  $\epsilon$  are the momentum and energy transfer, respectively, from the neutron to the scatterer, namely  $\vec{k} = \vec{k}_i - \vec{k}_f$  and  $\epsilon = \hbar^2(\vec{k}_i^2 - \vec{k}_f^2)/2m$ ,  $a_1$ is the spin-dependent scattering length of the l-th nucleus located at  $\vec{R}_1$ , and finally  $S_{n_fn_i}$  and  $\gamma_{n_fn_i}$  are defined [cf. Eqs. (2.36), (2.30), (2.26), and (2.27)] by

$$S_{n_{f}n_{i}} - i\gamma_{n_{f}n_{i}} = \lim_{\epsilon \to 0} [\Gamma_{n_{f}} - \Gamma_{n_{i}}] , \qquad (3.3)$$

$$\Gamma_{n_{i}} = \langle n_{i} | V^{n} + H^{\dagger} | n_{i} \rangle + \sum_{n \neq n_{i}} |\langle n | V^{n} + H^{\dagger} | n_{i} \rangle |^{2} [E_{n_{i}} - E_{n} + i\epsilon]^{-1}. \quad (3.4)$$

The expression for  $\Gamma_{n_f}$  is obtained by replacing  $(n_i)$  in Eq. (3.4) by  $(n_f)$ . Here, we ignore the distinction between  $\Gamma'_m$  and  $\Gamma_m$  as discussed earlier, because the number of available states into which the system can decay from the final state is large in a crystal. The exclusion of the transition back to the initial state corresponds to deleting one term from a large number of terms.

Equation (3.2) is the scattering cross-section for slow neutrons which includes line structure that may be present in the energy spectrum of the inelastically scattered neutrons. It expresses the cross-section as a superposition of a sequence of Lorentzian distributions. It is observed that the line shape problem has already been reduced to computational form in Eq. (3.2). When H' in Eq. (3.4) is spin-dependent, and when the eigenstates  $|\mu>$  of the scatterer can be written as the product of spin state |s> and position state |r>, the cross terms arising from the squared matrix element in Eq. (3.4) vanish. Then,  $\Gamma_{ni}$  can be written as  $\Gamma_{ni} = \Gamma_{ni}^{n} + \Gamma_{i}$ , where

$$\Gamma_{n_{i}}^{n} \equiv V_{n_{i}n_{i}}^{n} + \sum_{n \neq n_{i}} |V_{n_{i}n}^{n}|^{2} (E_{n_{i}} - E_{n} + i\epsilon)^{-1}, \qquad (3.5)$$

$$\Gamma_{i} = H_{ii}^{i} + \sum_{\substack{r \neq i}} |H_{ri}^{i}|^{2} (E_{i} - E_{r} + i\epsilon)^{-1} . \qquad (3.6)$$

In these formulas  $|i\rangle$  is the initial position state with energy  $E_i$  of the scatterer. The quantity  $\Gamma_{n_i}^n$  in Eq. (3.5) represents the broadening and the shift due to the transitions caused by neutron interaction. The quantity  $\Gamma_i$  is due to transitions caused by H'. In the case of a crystal  $\Gamma_i$  represents the shift and the broadening in the energy of the harmonic crystal states  $|i\rangle$  as a result of the anharmonic potential. In scattering experiments, it is legitimate to ignore  $\Gamma_{n_i}^n$  as compared to  $\Gamma_i$ . Then, one finds that  $S_{nfn_i}$  and  $\gamma_{nfn_i}$  in Eq. (3.2) become independent of neutron states and the spin state of the scatter, and the summation on the final spin states  $|\tau_f\rangle|_{S_f}\rangle$  can be performed. This enables one to separate the coherent scattering cross-section as

$$\frac{d^{2}\sigma_{coh}}{d\Omega d\epsilon_{f}} = \frac{a_{c}^{2}k_{f}}{\pi Nk_{i}} \sum_{f i} P_{i} | < f | \sum_{i} e^{i\vec{\kappa}\cdot\vec{R}_{i}} |i>|^{2} \frac{|\gamma_{fi}|}{(\epsilon + E_{i} - E_{f} - S_{fi})^{2} + \gamma_{fi}^{2}}, \quad (3.7)$$

where  $a_c$  is the coherent scattering length [6, 7] and  $P_i$  is the probability of finding the scatterer in the position state |i>. The final position state is denoted by |f>. The foregoing discussion indicates that the spindependence of the neutron-nucleus interaction does not affect the line shape if the Hamiltonian of the scatterer is spin-independent, and if  $\Gamma_{H_i}^n$  is ignored.

The general scattering cross-section formula of Eq. (3.7) will now be applied to neutron scattering by an anharmonic crystal. For the sake of simplicity, a simple Bravais crystal will be considered. The result can be cast into the following form

$$\frac{d^{2}\sigma_{coh}}{d\Omega d\epsilon_{f}} = \frac{a_{c}^{2}}{\pi} \frac{k_{f}}{k_{i}} \left[ \prod_{\lambda=1}^{3N} \sum_{\substack{m_{\lambda}=\infty \\ m_{\lambda}=\infty}}^{+\infty} \sum_{\substack{n_{\lambda}=0 \\ n_{\lambda}=0}}^{\infty} (1-y_{\lambda}^{2})y_{\lambda}^{2n}\lambda F(m_{\lambda},\vec{\kappa})\mathcal{F}(m_{\lambda},n_{\lambda},X_{\lambda}) \right] \times \frac{|\gamma_{fi}|}{(\epsilon-\sum_{\lambda} \hbar w_{\lambda} m_{\lambda}-S_{fi})^{2}+\gamma_{fi}^{2}}, \quad (3.8)$$

where

$$y_{\lambda} = \exp\left[-(\hbar w_{\lambda}/2kT)\right], \qquad (3.9a)$$

$$\mathbf{F}(\mathbf{m}_{\lambda},\vec{\kappa}) = \frac{1}{N} \sum_{\mathbf{1}\mathbf{1}'} \exp[\mathbf{i}(\vec{\kappa} - \mathbf{m}_{\lambda}\vec{\mathbf{q}}) \cdot (\vec{\mathbf{l}} - \vec{\mathbf{1}'})], \qquad (3.9b)$$

$$\mathcal{F}(n, m, x) \equiv x^{m} \frac{n!}{(n+m)!} e^{x} [L_{n}^{m}(x)]^{2},$$
 (3.9c)

$$X_{\lambda} = (\hbar/2MNw_{\lambda}) |\vec{e}_{\lambda} \cdot \vec{\kappa}|^{2}. \qquad (3.9d)$$

In these equations,  $\lambda = (\vec{q}, j)$  describes a normal mode with a wave vector  $\vec{q}$ , polarization index j(j = 1, 2, 3), direction of polarization  $\vec{e}_{\lambda}$ , and frequency  $w_{\lambda}$ ;  $n_{\lambda}$  and  $n_{\lambda} + m_{\lambda}$  are the occupation numbers of the  $\lambda$ -th mode in the initial and final states, respectively;  $\vec{l}$  is the equilibrium position of the 1-th nucleus; M is the mass of the nuclei, and finally  $L_{n}^{m}(x)$  is the associated Laguerre polynomial. The main steps in arriving at Eq. (3.8) are reproduced in the Appendix. In computing  $\gamma_{fi}$  and  $S_{fi}$  through Eq. (3.4), one has to know the relative magnitudes of the various anharmonic potentials, in particular those of the cubic ( $H^{(3)}$ ) and quartic ( $H^{(4)}$ ) harmonic potentials, for a consistent scheme of approximation. It is pointed out by VAN HOVE <u>et al.</u> [8] and also by MARADUDIN and FEIN [9] that the anharmonic potential can be written schematically as

$$H' = \mu H^{(3)} + \mu^2 H^{(4)} + \dots$$

where  $\mu$  measures the relative order of magnitude of the anharmonic terms

and is equal to the ratio of the averaged atomic displacement to the nearest-neighbour separation in the lattice. Then,  $\Gamma_i$  reads in the lowest order as

$$\Gamma_{i} = H_{ii}^{(4)} - \langle i | H^{(3)}(\mathcal{H}^{s} - E_{i} + i\epsilon)^{-1} H^{(3)} | i \rangle, \qquad (3.10)$$

where  $H_{ii}^{(3)} = 0$  is used. Using the usual expressions for the quartic and cubic anharmonic potentials in terms of creation and destruction operator, one finds  $\Gamma_i$  as follows:

$$\Gamma_{i} = \frac{1}{2} \sum_{\overline{1,2}}^{2} G_{1,-1,2,-2}(n_{1}n_{2}+n_{1}+n_{2}+3) \\ -\frac{1}{3!\tilde{n}} \sum_{1,2,3} |G_{1,2,3}|^{2} \left\{ \frac{(1+n_{-1})(1+n_{-2})(1+n_{-3})}{w_{1}+w_{2}+w_{3}+i\epsilon} - \frac{n_{1}n_{2}n_{3}}{w_{1}+w_{2}+w_{3}-i\epsilon} + 3 \frac{n_{1}(1+n_{-2})n_{3}}{-w_{1}+w_{2}-w_{3}+i\epsilon} + 3 \frac{(1+n_{1})n_{-2}(1+n_{3})}{w_{1}-w_{2}+w_{3}+i\epsilon} \right\}, \quad (3.11)$$

where  $n_i$  and  $w_i$  are the occupation number and the frequency of the mode  $\lambda_i$ , and where the negative subscripts (-i) refer to the mode whose wave vector has the opposite sign to that of mode  $\lambda_i$ . The symbol  $G_{1,2,3}$  is defined by

$$G_{1,2,3} = (\hbar/2M)^{3/2} (Nw_{\lambda_1}w_{\lambda_2}w_{\lambda_3})^{-1/2} \delta(\vec{g}, \vec{q}_1 + \vec{q}_2 + \vec{q}_3)$$

$$\times \sum_{h_1, h_2} \exp \left[i(\vec{q}_2 \cdot \vec{h}_1 + \vec{q}_3 \cdot \vec{h}_2)\right] \sum_{\alpha, \alpha', \alpha''} U_{0\alpha, h_1\alpha', h_2\alpha''} e_{\lambda_1\alpha} e_{\lambda_2\alpha'} e_{\lambda_3\alpha''},$$

where the symbols have their conventional meanings [10]<sup>\*</sup>. The expression for  $\Gamma_f$  can be obtained by replacing  $n_{\lambda}$  in Eq. (3.11) by  $(n_{\lambda} + m_{\lambda})$ . Then  $S_{fi}$  and  $\gamma_{fi}$  in Eq. (3.8) follows from

$$S_{fi} - i\gamma_{fi} = \lim_{\epsilon \to 0} (\Gamma_f - \Gamma_i)$$

as

$$S_{fi} = \frac{1}{2} \sum_{1,2} G_{1,-1,2,-2} m_{1}(2n_{1}+1+m_{2})$$

$$-\frac{1}{2\tilde{h}} \sum_{1,2,3} |G_{1,2,3}|^{2} \left\{ \frac{m_{1}(1+n_{2}+n_{3})+m_{1}m_{2}}{w_{1}+w_{2}+w_{3}} + \frac{2m_{1}(n_{3}-n_{-2})-m_{-2}(1+n_{1}+n_{3})-2m_{1}m_{-2}+m_{1}m_{3}}{w_{2}-w_{1}-w_{3}} \right\}_{p}, \quad (3.12)$$

<sup>\*</sup> The symmetric properties of  $G_{1,2,3}$ , namely,  $G_{1,2,3} = G_{1,3,2} = G_{2,1,3} = G_{1,2,-3}$  and  $G_{1,2,2} = 0$ , have been used many times in Reference [10].

$$\gamma_{\rm fi} = \frac{\pi}{2\hbar} \sum_{1.2.3} |G_{1,2,3}|^2 [2m_1(n_3 + n_{-2} + 2n_{-2}n_3) + m_{-2}(1 + n_1 + n_3 + 2n_1n_3) + m_1 m_{-2}(2n_3 + 1) + m_1 m_3 (2n_{-2} + 1) + 2m_1 m_{-2} m_3] \delta(w_1 - w_2 + w_3).$$
(3.13)

In the case of creation or annihilation of phonons of one kind, the above formulas simplify considerably. Denoting the mode which interacts with the neutron by  $\lambda_0$ , and the change in the occupation number by  $m_0$ , and substituting  $m_{\lambda} = 0$  for  $\lambda \neq \lambda_0$  and  $m_{\lambda} = m_0$  for  $\lambda = \lambda_0$  in Eqs. (3.12) and (3.13), one obtains

$$S_{fi} = \frac{m_0}{2} \sum_{1}^{n} G_{0,-0,1,-1}(2n_1+1)$$

$$-\frac{m_0}{2\hbar} \sum_{1,2}^{n} |G_{0,1,2}|^2 \left\{ \frac{1+n_1+n_2}{w_0+w_1+w_2} + 2\frac{n_{-1}-n_2}{w_0-w_1+w_2} - \frac{1+n_{-1}+n_{-2}}{w_0-w_1-w_2} \right\}_p, \quad (3.14)$$

$$\gamma_{fi} = \frac{\pi}{2\hbar} m_0 \sum_{1,2}^{n} |G_{0,1,2}|^2 \left\{ [(1+n_{-1})(1+n_{-2}) + n_{-1}n_{-2}]\delta(w_0-w_1-w_2) \right\}_p$$

+ 2[(1+n<sub>-1</sub>)n<sub>2</sub>+n<sub>-1</sub>(1+n<sub>2</sub>)] 
$$\delta$$
 (w<sub>0</sub>-w<sub>1</sub>+w<sub>2</sub>) . (3.15)

### IV. DISCUSSION OF THE CROSS-SECTION FORMULA

In this section, some of the important features of the cross-section formula of Eq. (3.8) are discussed. First, it will be shown that Eq. (3.8) reduces to the scattering cross-section for a harmonic crystal when  $\gamma_{\rm fi}$  and  $S_{\rm fi}$  tend to zero. Indeed, where  $\gamma_{\rm fi} = S_{\rm fi} = 0$ , the last factor in Eq. (3.8) approaches a delta function, and becomes independent of the initial occupation numbers. Then the thermal average of the factor  $\mathcal{T}(m_{\lambda}, n_{\lambda}, X_{\lambda})$  can be worked out (see Appendices):

$$\sum_{\substack{n_{\bar{\lambda}} \ 0}}^{\infty} (1 - y_{\lambda}^{2}) y_{\lambda}^{2n_{\lambda}} \mathcal{F}(m_{\lambda}, n_{\lambda}, X_{\lambda}) = y_{\lambda}^{-m_{\lambda}} e^{2W_{\lambda}} I_{m_{\lambda}}(P_{\lambda}), \qquad (4.1)$$

where

$$2W_{\lambda} \equiv X_{\lambda}(1+y_{\lambda}^{2})/(1-y_{\lambda}^{2}),$$
 (4.2a)

$$P_{\lambda} \equiv 2X_{\lambda} y_{\lambda} / (1 - y_{\lambda}^{2}), \qquad (4.2b)$$

and where  $I_{\,m_{\lambda}}(P_{\lambda})$  is the modified Bessel function of the first kind. The

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factor exp[-2W] is the usual Debye-Waller factor. Substituting Eq. (4.1) in Eq. (3.8) gives:

$$\frac{d^2 \sigma_{\text{coh}}}{d \Omega d\epsilon_{f}} = a_{c}^{2} \frac{k_{f}}{k_{i}} e^{-2W} \sum_{m=-\infty}^{+\infty} \delta(\epsilon - \sum_{\lambda} \hbar w_{\lambda} m_{\lambda}) \prod_{\lambda} F(m_{\lambda}, \vec{\kappa}) y_{\lambda}^{-m_{\lambda}} I_{m_{\lambda}}(P_{\lambda}), \quad (4.3)$$

where m denotes the set  $(m_1, m_2, \ldots m_{3N})$ , and where a given set of values of  $m_{\lambda}$ 's give rise to a term in the summation. This formula is identical to the differential cross-section formula for a harmonic crystal obtained elsewhere [6,7]. The novelty about Eq. (4.3) is that it is obtained without resorting to Bloch's theorem, by using the identities proved in the Appendices.

Second, the zero temperature limit of Eq. (3.8) will be considered. In this limit all the initial occupation numbers are zero, and the crystal is in the ground state. The cross-section in this limit follows from Eq. (3.8) as

$$\frac{\mathrm{d}^{2}\sigma_{\mathrm{coh}}}{\mathrm{d}\Omega\mathrm{d}\epsilon_{\mathrm{f}}} = \frac{a_{\mathrm{c}}^{2}}{\pi} \frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{k}_{\mathrm{i}}} e^{-2W(0)} \left[ \prod_{\lambda}^{3N} \sum_{m_{\lambda}=-\infty}^{\infty} F(m_{\lambda},\vec{\kappa}) \frac{X_{\lambda}^{m_{\lambda}}}{(m_{\lambda})!} \right]$$

$$\times \frac{|\gamma_{\mathrm{fi}}(m,o)|}{\left[\epsilon - \sum_{\lambda} \hbar w_{\lambda} m_{\lambda} - S_{\mathrm{fi}}(m,o)\right]^{2} + \gamma_{\mathrm{fi}}^{2}(m,0)}, \qquad (4.4)$$

where  $\mathscr{F}(m_{\lambda}, 0, X_{\lambda}) = \exp(-X_{\lambda})(X_{\lambda}^{m_{\lambda}}/m_{\lambda}!)$  was used. In this formula  $S_{fi}(m, 0)$ and  $\gamma_{fi}(m, 0)$  are to be obtained from Eqs. (3.12) and (3.13), respectively, by setting  $n_1 = n_2 = n_3 = 0$  everywhere. It is noted that Eq. (4.4) contains only the positive values of  $m_{\lambda}$  as a result of  $m_{\lambda}!$  in the denominator. Physically, this implies that the crystal cannot give energy to neutrons when it is in the ground state. The cross-section for one-phonon excitation, which is perhaps the most interesting case from the experimental point of view, can be obtained from Eq. (4.4) by setting  $m_{\lambda} = 1$  for  $\lambda = \lambda_0$  and zero otherwise. The result is

$$\frac{\mathrm{d}^2 \sigma_{\mathrm{coh}}}{\mathrm{d}\Omega \mathrm{d}\epsilon_{\mathrm{f}}} = \frac{a_{\mathrm{ch}}^2 \mathrm{h}}{2\pi \mathrm{M}} \frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{k}_{\mathrm{i}}} \,\delta(\vec{\mathrm{g}},\vec{\kappa}-\vec{\mathrm{q}}_{0}) \mathrm{e}^{-2\mathrm{W}(0)} \sum_{j_0} \frac{\left|\vec{\kappa}\cdot\vec{\mathrm{e}}_{0}\right|^2}{\mathrm{w}_{0}} \frac{\left|\gamma_{0}\right|}{(\epsilon-\mathrm{h}\mathrm{w}_{0}-\mathrm{S}_{0})^2 + \gamma_{0}^2}, \qquad (4.5)$$

where  $\gamma_0$  and  $S_0$  are obtained from Eqs. (3.14) and (3.15), respectively, by setting  $m_0 = 1$ ,  $n_{\lambda} = 0$  for all  $\lambda$ .

$$S_{0} = \frac{1}{2} \sum_{1} G_{0,0,1,-1} + \frac{1}{2} \sum_{1,2} |G_{0,1,2}|^{2} \left[ \frac{1}{w_{0} - w_{1} - w_{2}} - \frac{1}{w_{0} + w_{1} + w_{2}} \right]_{P}, \quad (4.6)$$

$$\gamma_{0} = \frac{\pi}{2\hbar} \sum_{1,2} |\mathbf{G}_{0,1,2}|^{2} \delta (\mathbf{w}_{0} - \mathbf{w}_{1} - \mathbf{w}_{2}). \qquad (4.7)$$

Apart from differences in notations, this formula is identical to that obtained by MARADUDIN and FEIN [9] and KOKKEDEE [11].

We now consider the cross-section at a finite temperature. Equation (3.8) expresses the cross-section as a weighted superposition of a sequence of Lorentzian distributions with different widths and shifts. For each initial and final state there corresponds a Lorentzian distribution. For a specified final state, the average of the appropriate Lorentzian distributions over initial states gives a peaked curve which corresponds to an observed line in the neutron spectrum. Although the individual distributions have a Lorentzian form, their thermal average will not in general be a Lorentzian distribution. However, as an approximation, one may replace the resultant curve by a Lorentzian distribution with an average width and shift. Denoting the average width and shift by  $\widehat{\Gamma}(m)$  and  $\widehat{S}(m)$ , one obtains the following cross-section formula:

$$\frac{d^{2}\sigma_{coh}}{d\Omega d\epsilon_{f}} = \frac{a_{c}^{2}}{\pi} \frac{k_{f}}{k_{i}} e^{-2W} \sum_{m=-\infty}^{+\infty} \frac{\overline{\Gamma}(m)}{\left[\epsilon - \Sigma \hbar w_{\lambda} m_{\lambda} - \overline{S}(m)\right]^{2} + \overline{\Gamma}^{2}(m)}$$

$$\prod_{\lambda} F(m_{\lambda}, \vec{\kappa}) y_{\lambda}^{-m_{\lambda}} I_{m_{\lambda}}(P_{\lambda}) . \qquad (4.8)$$

The average shift and width are to be obtained from Eqs. (3.12) and (3.13) respectively by replacing the occupation numbers  $n_{\lambda}$  by their mean values, namely,  $\pi_{\lambda} = y_{\lambda}^{2}/(1-y_{\lambda}^{2})$ . Note that the approximation made in obtaining Eq. (4.8) from Eq. (4.3) is equivalent to replacing the average of a function by the function of the averaged variables. The cross-section for one normal mode interaction is obtained again by choosing the set  $m = m_{1}, m_{2} \dots m_{3N}$  in Eq. (4.8) as  $m = (0, 0, \dots, m_{0}, 0, \dots)$ . The result is

$$\frac{\mathrm{d}^{2}\sigma_{\mathrm{coh}}}{\mathrm{d}\Omega\mathrm{d}\epsilon_{\mathrm{f}}} = \frac{\mathrm{a}_{\mathrm{c}}^{2}\,\mathrm{k}_{\mathrm{f}}}{\pi\,\mathrm{k}_{\mathrm{i}}}\,\mathrm{e}^{-2\mathrm{W}}\,\mathrm{F}(\mathrm{m}_{0},\vec{\kappa})\mathrm{y}_{0}^{-\mathrm{m}_{0}}\mathrm{I}_{\mathrm{m}_{0}}(\mathrm{P}_{0}\,)\frac{\overline{\Gamma}(|\mathrm{m}_{0}|)}{[\epsilon-\mathrm{hm}_{0}\mathrm{w}_{0}-\mathrm{S}(\mathrm{m}_{0})]^{2}+\mathrm{F}^{2}(|\mathrm{m}_{0}|)}\prod_{\lambda\neq\lambda_{0}}\mathrm{I}_{\lambda_{0}}(\mathrm{P}_{\lambda}),$$

$$(4.9)$$

where

$$\overline{S}(m_{0}) = \frac{m_{0}}{2} \left\{ \sum_{1}^{1} G_{0,-0,1,-1} \left( 2\overline{n}_{1} + 1 \right) - \frac{1}{\overline{n}} \sum_{1,2}^{1} \left| G_{0,1,2} \right|^{2} \times \left[ \frac{1 + \overline{n}_{1} + \overline{n}_{2}}{w_{0} + w_{1} + w_{2}} + 2 \frac{\overline{n}_{1} - \overline{n}_{2}}{w_{0} - w_{1} + w_{2}} - \frac{1 + \overline{n}_{1} + \overline{n}_{2}}{w_{0} - w_{1} - w_{2}} \right]_{p} \right\}.$$

$$(4.10)$$

$$\overline{\Gamma} \left( \left| \mathbf{m}_{0} \right| \right) = \frac{\pi}{2\hbar} \left| \mathbf{m}_{0} \right| \sum_{1,2} \left| \mathbf{G}_{0,1,2} \right|^{2} \left\{ \left[ (1+\overline{n}_{1})(1+\overline{n}_{2}) + \overline{n}_{1}\overline{n}_{2} \right] \delta \left( \mathbf{w}_{0} - \mathbf{w}_{1} - \mathbf{w}_{2} \right) + 2 \left[ (1+\overline{n}_{1})\overline{n}_{2} + \overline{n}_{1}(1+\overline{n}_{2}) \right] \delta \left( \mathbf{w}_{0} - \mathbf{w}_{1} + \mathbf{w}_{2} \right) \right\}.$$

$$(4.11)$$
Equation (4.10) can be further simplified in many applications by using the asymptotic value of  $I_m(x)$  for small arguments, i.e.,

$$I_{m}(x) \sim (x/2)^{|m|} \frac{1}{|m|!}$$

as follows:

$$\frac{d^{2}\sigma_{coh}}{d\Omega d_{f}} = \frac{a_{c}^{2}}{\pi} \frac{k_{f}}{k_{i}} e^{-2W} F(m_{0},\vec{\kappa}) \frac{1}{|m_{0}|!} \left[\frac{\hbar}{2MNw_{0}} |\vec{\kappa} \cdot \vec{e}_{0}|^{2}\right]^{|m_{0}|} \\ \times \frac{e^{-\beta\hbar w_{0}} (|m_{0}|-m_{0})/2}{(1-e^{-\beta\hbar w_{0}})^{|m_{0}|}} \frac{\overline{\Gamma}(|m_{0}|)}{[\epsilon - \hbar w_{0}m_{0} - \overline{S}(m_{0})]^{2} + \overline{\Gamma}^{2}(|m_{0}|)}$$
(4.12)

In the zero temperature limit, this cross-section vanishes when  $m_0 < 0$  as a result of the factor exp $[-\beta\hbar w_0(|m_0|-m_0)/2]$ . This result is in agreement with Eq. (4.4). As a matter of fact, Eq. (4.12) reduces exactly to Eq. (4.4) when the temperature approaches zero, although it involves one more approximation over Eq. (4.4), i.e. replacing the width and the shift by their mean values. The reason for this is that the latter approximation becomes exact in the zero temperature limit.

The dependence of the cross-section on  $m_0$ , i.e. the number of phonons exchanged between the crystal and the neutron, is exhibited by Eq. (4.12). Because of the exponential factor in the numerator, the cross-section for the energy transfer from the neutron to the crystal is greater than the crosssection for an energy transfer to the neutron by a factor  $\exp[-\beta \hbar w_0 | m_0 |]$ . At high temperatures, both processes become equally probable. The shape of the peaks in the neutron spectrum depends on  $|m_0|$ . Hence, the shape is the same for both the creation and annihilation of phonons. Furthermore, since the width is proportional to  $|m_0|$ , the peaks are broadened and reduced in height when the energy exchange gets larger. The shift of the lines is proportional to  $m_0$ , and thus depends on the direction of the energy transfer. There will be two identical peaks in the neutron spectrum on both sides of the incident neutron energy, corresponding to the creation and annihilation of equal number of photons.

The asymptotic values of the shift and the width in the high temperature limit can be obtained from Eqs. (4.10) and (4.11) by replacing the mean occupation numbers by  $kT/\hbar w_{\lambda}$ . One finds

$$\overline{S}(m_{0}) = \frac{m_{0}}{2\hbar} kT \left\{ 2 \sum_{\hat{1}} \frac{G_{0,-0,1,-1}}{w_{1}} - \sum_{\hat{1},\hat{2}} \frac{|G_{0,1,2}|^{2}}{\hbar w_{1}w_{2}} \right\}$$

$$\times \left[ \frac{w_{1} + w_{2}}{w_{0} + w_{1} + w_{2}} + 2 \frac{w_{2} - w_{1}}{w_{0} - w_{1} + w_{2}} - \frac{w_{1} + w_{2}}{w_{0} - w_{1} - w_{2}} \right]_{p} \right\}, \quad (4.13)$$

$$\widetilde{\Gamma}(|\mathbf{m}_{0}|) = \pi |\mathbf{m}_{0}| \frac{(\mathbf{k}T)^{2}}{\widetilde{n}^{3}} \sum_{\mathbf{1},2} \frac{|\mathbf{G}_{0,1,2}|^{2}}{\mathbf{w}_{1}\mathbf{w}_{2}} [\delta(\mathbf{w}_{0} - \mathbf{w}_{1} - \mathbf{w}_{2}) + 2\delta(\mathbf{w}_{0} - \mathbf{w}_{1} + \mathbf{w}_{2})].$$
(4.14)

It is observed that the shift is proportional to T at high temperatures where- as the width is proportional to  $T^2\,.$ 

#### V. CONCLUSIONS

The present study of neutron scattering by anharmonic crystal is essentially a straightforward application of the damping theory. The width and shifts of the phonon lines are expressed as the difference of the widths and shifts of the initial and final crystal states. This conclusion is in agreement with BROUT's results [12]. The cross-section formula in the zero temperature limit is obtained directly from the results of the damping theory without requiring any additional approximation. At finite temperatures, an approximation of a statistical nature had to be made to replace the superposition of a sequence of Lorentzian distributions corresponding to a given multiphonon event by an averaged Lorentzian distribution.

The shift formula for a one-phonon line agrees exactly with those reported in the previous studies [9, 11, 13] at all temperatures. The width formulas, however, agree only in the zero temperature limit. The discrepancy at finite temperature arises from the difference in the sign of the terms in  $\bar{n}_1\bar{n}_2$  and  $\bar{n}_1(1+\bar{n}_2)$  in Eq. (4.11) (see also Eq. (3.15)). These terms correspond to transitions in which a phonon with ( $\vec{q}_0$ ,  $j_0$ ) is created whereas the remaining two terms in Eq. (4.11) correspond to transitions in which a phonon with ( $\vec{q}_0$ ,  $j_0$ ) is annihilated. Thus, the observed width of a one-phonon line in the present work is proportional to the sum of the averaged probabilities of all the transitions involving the mode ( $\vec{q}_0$ ,  $j_0$ ) which interacts with the neutron, namely

$$(\vec{q}_0, j_0) \stackrel{\leftarrow}{\leftarrow} (-\vec{q}_1, j_1) + (-\vec{q}_2, j_2),$$
  
 $(\vec{q}_0, j_0) + (\vec{q}_2, j_2) \stackrel{\leftarrow}{\leftarrow} (-\vec{q}_1, j_1).$ 

In other words, any transition involving a change in the number of phonons in the mode  $(\vec{q}_0, j_0)$  contributes additively to the observed width. The width formula of the cited references can be obtained from Eq. (4.11) if the sign of the second and fourth terms is reversed [14], i.e.

$$\overline{\Gamma}(|\mathbf{m}_0|) = \frac{\pi}{2\bar{n}} |\mathbf{m}_0| \sum_{\mathbf{1},\mathbf{2}} |\mathbf{G}_{0,\mathbf{1},\mathbf{2}}|^2 \{ [(1+\bar{n}_1)(1+\bar{n}_2) - \bar{n}_1\bar{n}_2] \delta(\mathbf{w}_0 - \mathbf{w}_1 - \mathbf{w}_2) + 2 [(1+\bar{n}_1)\bar{n}_2 - \bar{n}_1(1+\bar{n}_2)] \delta(\mathbf{w}_0 - \mathbf{w}_1 + \mathbf{w}_2) \}.$$

According to this formula, the observed width is proportional to the difference of the averaged transition probabilities for the creation and annihilation of a phonon  $(\vec{q}_0, j_0)$ . Physically, this implies that the observed width is related to the rate of net change in the number of phonons in the  $(\vec{q}_0, j_0)$ , in contrast to Eq. (4.11) which expresses the width as the averaged probability per unit time that the occupation number of  $(\vec{q}_0, j_0)$  will change by one, or, as the frequency of fluctuations in the occupation number. A consequence of this discrepancy is that the present theory predicts a quadratic temperature dependence at high temperatures in contrast to linear dependence predicted by the previous investigators except for BROUT [12]. Furthermore, the present theory predicts a larger width at high temperature by a factor  $2/\beta\hbar w_0$ , and therefore may yield a better agreement with the large widths measured by BROCKHOUSE <u>et al</u>. [15] in scattering from lead at high temperatures, than the agreement reported by MARADUDIN and FEIN [9]. The short lifetimes of the order of a period, or even less, obtained from the width of the observed one-phonon peak may be interpreted more satisfactorily in terms of the frequency of fluctuations rather than the decay time of a normal mode.

It is worth mentioning that the present formalism includes the broadening and the shift due to the transitions caused by neutron interaction, although they are neglected in the final width formula on the ground that their numerical value is small as compared to the width and the shift caused by the phonon-phonon interaction. This effect corresponds to the natural broadening of the optical spectral lines.

It is also interesting to note that the cross-section formula of Eq. (4.8) at finite temperatures, which is obtained with the statistical approximation, is identical to the cross-section formula for harmonic crystal [cf. Eq. (4.3)] with the exception that the energy conserving delta functions in the latter are replaced by a Lorentzian function. There is no correction to the Debye-Waller factor arising from the anharmonicity of the crystal within the limitations of the statistical approximation. This result seems to be in agreement with the conclusion reached by THOMPSON [13].

The shift and width given by Eqs. (3.14) and (3.15) respectively can be related to each other by a certain dispersion relation which is derived in Appendix B.

The authors were unable to explain the origin of the discrepancy between the width formula obtained with the damping theory, which is in agreement with that by Brout, and the width formula of the cited references. However, they believe that this discrepancy is of a fundamental nature, and presumably arises from the techniques used for handling infinite series involved in width calculations. The damping theory provides an iteration procedure thus eliminating the summation of infinite series. The relative merits of these two results will probably remain to be judged by more refined experiments.

#### APPENDIX A

#### COMPUTATION OF THE MATRIX ELEMENTS OF $exp[i\vec{k},\vec{x}_1]$

In obtaining the formula of Eq. (3.8), one encounters the matrix element  $I_1 \equiv \langle f | \exp[i\vec{x} \cdot \vec{x}_1] | i \rangle$  where  $\vec{x}_1$  is the displacement from the equilibrium of the l-th nucleus. In terms of creation and destruction operators,  $\vec{x}_1$  can be written as

$$\vec{k} \cdot \vec{x}_1 = \sum_{\lambda} (\alpha^*_{\lambda 1} a^+_{\lambda} + \alpha_{\lambda 1} a_{\lambda}),$$

where

$$\alpha_{\lambda 1} \equiv (\hbar/2MNw_{\lambda})^{1/2} (\vec{e}_{\lambda} \cdot \vec{\kappa}) \exp(i\vec{q} \cdot \vec{l}).$$

The matrix element to be computed is

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$$I_1 = \langle f | \prod_{\lambda} \exp \left[ i(\alpha_{\lambda 1}^* a_{\lambda}^+ + \alpha_{\lambda 1} a_{\lambda}) \right] | i \rangle.$$

Using the operator identity

$$e^{A + B} = e^{A}e^{B}e^{-(1/2)[A, B]}$$

where A and B are operators satisfying [A, [A, B]] = [B, [A, B]] = 0, and expressing the initial and final states in terms of occupation numbers, one gets

$$I_{1} = \prod_{\lambda} e^{-X_{\lambda}/2} < m_{\lambda} + n_{\lambda} | e^{i\alpha_{\lambda} a^{+}} e^{i\alpha_{\lambda} a^{a}} | n_{\lambda} > , \qquad (A.1)$$

where  $X_{\boldsymbol{\lambda}}$  denotes

$$X_{\lambda} \equiv |\alpha_{\lambda 1}|^{2} = (\hbar/2MNw_{\lambda}) |\vec{e}_{\lambda} \cdot \vec{\kappa}|^{2}. \qquad (A.2)$$

Note that  $X_{\lambda}$  is independent of 1. To compute the matrix element in Eq.(A.1), one uses the following relations:

$$e^{i\alpha a} |n\rangle = \sum_{s=0}^{n} \frac{(i\alpha)^{s}}{s!} \sqrt{\frac{n!}{(n-s)!}} |n-s\rangle,$$
$$e^{i\alpha^{*}a^{+}} |n-s\rangle = \sum_{t=0}^{\infty} \sqrt{\frac{(n-s-t)!}{(n-s)!}} \frac{(i\alpha^{*})^{t}}{t!} |n-s+t\rangle$$

The result is

$$I_{1} = \prod_{\lambda} e^{-\mathbf{X}} \sqrt{2} \sum_{t=0}^{\infty} \sum_{s=0}^{\infty} \frac{(i\alpha_{\lambda 1})^{s}}{s!} \frac{(i\alpha_{\lambda 1}^{*})^{t}}{t!} \frac{\sqrt{n_{\lambda}! (n_{\lambda} - s + t)!}}{(n_{\lambda} - s)!} \delta_{n_{\lambda} + m_{\lambda}, n_{\lambda} - s + t}$$

 $\mathbf{or}$ 

$$I_{1} = \prod_{\lambda} e^{-X_{\lambda}/2} (i\alpha_{\lambda 1}^{*})^{m_{\lambda}} \sqrt{n_{\lambda}! (n_{\lambda} + m_{\lambda})!} \sum_{s=0}^{n_{\lambda}} \frac{(-X_{\lambda})^{s}}{s! (n_{\lambda} - s)! (m_{\lambda} + s)!}.$$

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The last expression can be written in a compact way by recalling the definition of associate Laguerre polynomials, namely,

$$L_{n}^{m}(x) \equiv \sum_{s=0}^{n} \frac{(n+m)!}{(n-s)!(n+s)!} \frac{(-x)^{s}}{s!},$$

as

 $I_{1} = \prod_{\lambda} e^{-X_{\lambda}/2} (i\alpha_{\lambda 1}^{*})^{m_{\lambda}} \sqrt{\frac{n_{\lambda}!}{(n_{\lambda} + m_{\lambda})!}} L_{n_{\lambda}}^{m_{\lambda}} (X_{\lambda}), \qquad (A.3)$ 

which is the desired formula.

The product  $I_1 I_1^{*}$  which appears in Eq. (3.7) follows from Eq. (A.3) as

$$I_{l}I_{l'\bar{\psi}}^{*}\prod_{\lambda}e^{im_{\lambda}\bar{\psi}\cdot(\vec{l}'-\vec{l})}\mathcal{F}(n_{\lambda}, m_{\lambda}, X_{\lambda}),$$

where

$$\mathcal{T}(n, m, x) \equiv x^{m} \frac{n!}{(n+m)!} e^{-x} [L_{n}^{m}(x)]^{2}.$$
 (A.4)

We shall now calculate the thermal average of  $\mathcal{T}(n_{\lambda}, m_{\lambda}, X_{\lambda})$  with respect to the initial occupation numbers, i.e.

$$\langle \mathscr{T}(n_{\lambda}, m_{\lambda}, X_{\lambda}) \rangle \equiv (1 - y_{\lambda}^{2}) \sum_{n_{\lambda}=0} y_{\lambda}^{2n_{\lambda}} \mathscr{T}(n_{\lambda}, m_{\lambda}, X_{\lambda}),$$
 (A.5)

where

$$y_{\lambda} \equiv e^{-(\hbar w_{\lambda}/2kT)}$$

Dropping the subscripts and arguments, and combining Eqs. (A.4) and (A.5), one finds

$$\langle \mathscr{T} \rangle = (1 - y^2) x^m e^{-x} \sum_{n=0}^{\infty} y^{2n} \frac{n!}{(n+m)!} [L_n^m(x)]^2.$$

To compute the summation in the last expression, one may use the following expansion, given by MAGNUS and OBERHETTINGER [16]

$$\frac{n!}{(n+m)!} [L_n^m(x)]^2 = \sum_{s=0}^{\infty} \frac{x^{2s}}{s! (m+s)!} L_{n-s}^{m+2s}(2x).$$

The result is

$$<\mathcal{F}>=(1-y^2)x^m e^{-x} \sum_{s=0}^{\infty} \frac{x^{2s}}{s!(m+s)!} \sum_{n=0}^{\infty} L_{n-s}^{m+2s}(2x)y^{2n}.$$
 (A.6)

The summation on n can be performed by using the generating function for the associated Laguerre polynomials [17], namely,

$$\frac{e^{-xt/(1-t)}}{(1-t)m+1} = \sum_{n=0}^{\infty} L_n^m(x)t^n,$$

as follows:

$$\sum_{n=0}^{\infty} L_{n-s}^{m+2s} (2x) y^{2n} = y^{2s} \quad \frac{e^{-2xy^2/(1-y^2)}}{(1-y^2)^{m+2s+1}} .$$

Inserting the last formula into Eq. (A.6), one finally obtains

$$\langle \mathcal{T} \rangle = y^{-m} e^{-x(1+y^2)/(1-y^2)} I_m \left(\frac{2xy}{1-y^2}\right),$$
 (A.7)

where  $I_m(x)$  is the modified Bessel function of the first kind.

#### APPENDIX B

#### A DISPERSION RELATION

The shift and width formulas given by Eqs. (3.14) and (3.15), respectively, can be written as

$$\begin{split} \mathbf{S}_{\mathrm{fi}} &= \mathrm{Re}\left[\mathbf{G}_{\mathrm{f}}\left(\mathbf{E}_{\mathrm{f}}\right) - \mathbf{G}_{\mathrm{i}}\left(\mathbf{E}_{\mathrm{i}}\right)\right] \\ \gamma_{\mathrm{fi}} &= \mathrm{Im}\left[\mathbf{G}_{\mathrm{f}}\left(\mathbf{E}_{\mathrm{f}}\right) - \mathbf{G}_{\mathrm{i}}\left(\mathbf{E}_{\mathrm{i}}\right)\right], \end{split}$$

where the functions  $G_i(x)$  and  $G_f(x)$  are defined by

$$G_{i}(x) \equiv H_{ii}^{(4)} + \lim_{\epsilon \to 0} < i | H^{(3)} \frac{1}{(x - H^{s} - i\epsilon)} H^{(3)} | i > .$$

Observing

•

$$\operatorname{Im}[G_{i}(E_{i})] = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} \frac{\operatorname{Re}[G_{i}(x)] - H_{ii}}{x - E_{i}} dx$$

one finds

$$\gamma_{fi} = \frac{1}{\pi} P \int_{-\infty}^{\infty} \left\{ \frac{\text{Re}[G_{f}(x)] - H_{ff}^{(4)}}{x - E_{f}} - \frac{\text{Re}[G_{i}(x)] - H_{ii}^{(4)}}{x - E_{i}} \right\} dx$$
$$= \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{dy}{y} \left[ \text{Re}[G_{f}(E_{f} + y) - G_{i}(E_{i} + y)] - (H_{ff}^{(4)} - H_{ii}^{(4)}) \right].$$

Define a new function  $G_{fi}(y, w_0)$  as

$$\mathbf{G}_{\mathrm{fi}}\left(\mathbf{y}, \mathbf{w}_{0}\right) \equiv \mathbf{G}_{\mathrm{f}}(\mathbf{E}_{\mathrm{f}} + \mathbf{y}) - \mathbf{G}_{\mathrm{i}}(\mathbf{E}_{\mathrm{i}} + \mathbf{y}),$$

where the subscript zero refers to the mode that interacts with the neutron. This function can be obtained explicitly as follows:

$$G_{fi}(y, w_{0}) = \frac{1}{2} \sum_{1}^{n} G_{0, -0, 1, -1}(2n_{1}+1) - \frac{1}{2\hbar} \sum_{1, 2}^{n} |G_{0, 1, 2}|^{2}$$

$$\lim_{\epsilon \to 0} \left\{ \frac{(1+n_{1})(1+n_{2})}{y+w_{0}+w_{1}+w_{2}+i\epsilon} - \frac{n_{1}n_{2}}{y-w_{0}-w_{1}-w_{2}+i\epsilon} + 2\frac{(1+n_{-1})n_{2}}{y-w_{0}+w_{1}-w_{2}+i\epsilon} + 2\frac{n_{-1}(1+n_{2})}{y+w_{0}-w_{1}+w_{2}+i\epsilon} + \frac{n_{-1}n_{-2}}{y+w_{0}-w_{1}-w_{2}+i\epsilon} + \frac{(1+n_{-1})(1+n_{-2})}{y-w_{0}+w_{1}+w_{2}+i\epsilon} \right\}.$$

It is clear from the definition of  $G_{fi}(y, w_0)$  that

$$S_{fi} = Re [G_{fi}(0, w_0)],$$
  
 $\gamma_{fi} = Im [G_{fi}(0, w_0)].$ 

The thermal average of  $G_{\rm fi}(y, w_0)$ , denoted by  $G(y, w_0, T)$ , is obtained by replacing the occupation numbers in its expression by their mean values. Then, the averaged width and shift are given by

 $\gamma (w_0, T) = \text{Im} [G(0, w_0, T)]$ S(w\_0, T) = Re[G (0, w\_0, T)],

which, in view of the foregoing remarks, satisfy the following relation:

Im G(0, w<sub>0</sub>, T) = 
$$\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Re}[G(y, w_0, T)] - A}{y} dy$$
,

where

$$A \equiv < H_{ff}^{(4)} - H_{ii}^{(4)} > T.$$

One observes from the expression of  $G(y, w_0, T)$  that  $\operatorname{Re}[G(y, w_0, T)]$  is, for large values of T, a quadratic function of T for all  $y \neq 0$ , and a linear function of T when y = 0. Similarly,  $\operatorname{Im}[G(y, w_0, T)]$  is a quadratic function of T for all y. It follows that the width  $\gamma(w_0, T) = \operatorname{Im}[G(0, w_0, T)]$  may depend on T quadratically while the shift  $S(w_0, T) = \operatorname{Re}[G(0, w_0, T)]$  is a linear function of T for large T, in spite of the fact that the real and imaginary parts of  $G(y, w_0, T)$  are related to each other by the foregoing transform.

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## THE NATURE OF THE PHONON SPECTRUM AND THE ANALYSIS OF LATTICE THERMAL CONDUCTIVITY

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#### Abstract — Résumé — Аннотация — Resumen

THE NATURE OF THE PHONON SPECTRUM AND THE ANALYSIS OF LATTICE THERMAL CONDUCTIVITY. An analysis of lattice thermal conductivity is presented, wherein a more realistic phonon spectrum is utilized than the usual Debye-like phonon spectrum consisting of one average acoustic branch. We have first used an anisotropic continuum dispersive model in our calculation of the temperature dependence of the lattice thermal conductivity of germanium. The approach that we have utilized in this calculation is a modified version of Callaway's formulation. Houston's six- and three-term integration procedures are used in evaluating rather formidable integrals over lattice frequencies. Suitable prevalent expressions for relaxation times for boundary and impurity scatterings and three-phonon normal and Umklapp processes are used. A good fit to the experimental data of Holland and Slack and Glassbrenner is obtained for germanium from 2 to 1000°K by adjusting the four constants occurring in the integrals.

On the face of reliable neutron spectroscopic evidence, we know that germanium has very disperse transverse branches and for them an anisotropic continuum dispersive model also yields a poor representation. We therefore thought it appropriate to utilize the very elaborate shell model for the lattice dynamics of germanium put forth by Cochran. With a proper adjustment of the parameters entering in our formulation for the calculation of lattice thermal conductivity, we again find a good fit with the experimental data. We are led to a conclusion that the nature of the phonon spectrum does not greatly influence the analysis of lattice thermal conductivity data according to current approaches and the niceties of the phonon spectrum are lost in the adjustment of the various parameters involved. It is felt that instead of putting too much labour in evaluating the tedious integrals for more realistic lattice dynamical models, it is better to investigate the validity of various relaxation time assumptions that have gone into these integrals.

NATURE DU SPECTRE DES PHONONS ET ANALYSE DE LA CONDUCTIBILITÉ THERMIQUE DU RÉSEAU. Les auteurs présentent les résultats d'une étude sur la conductibilité thermique des réseaux effectuée au moyen d'un spectre de phonons plus précis que le spectre de phonons analogue au modèle de Debye, utilisé d'ordinaire, qui est constitué par une seule branche acoustique moyenne. Pour calculer les variations en fonction de la température de la conductibilité thermique du réseau du germanium, ils ont utilisé tout d'abord un modèle anisotrope de dispersion en continu et suivi comme méthode une version modifiée de la formulation de Callaway. Pour effectuer la sommation d'intégrales complexes sur les fréquences du réseau, ils ont appliqué la méthode d'intégration à six et trois termes de Houston. On utilise les expressions appropriées des temps de relaxation pour les diffusions à la frontière et les diffusions dues aux impuretés ainsi que pour le processus normal à trois phonons et le processus Umklapp. Pour le germanium entre 2 et 1000°K, on obtient une concordance satisfaisante avec les données expérimentales de Holland et de Slack et Glassbrenner en ajustant les quatre constantes présentes dans les intégrales.

D'après des données de spectroscopie des neutrons dignes de foi, on sait que le germanium comporte des branches transversales très dispersées et qu'un modèle anisotrope de dispersion en continu en donne aussi une mauvaise représentation. Les auteurs ont donc jugé bon d'utiliser le modèle des couches très complexes pour la dynamique de réseau du germanium présenté par Cochran. En ajustant les paramètres entrant dans la formulation qu'ils ont utilisée pour le calcul de la conductibilité thermique du réseau, ils ont également obtenu des résultats concordant avec les données expérimentales. Ceci leur a donné à penser que la nature du spectre des phonons n'a pas une grande influence sur l'analyse des données relatives à la conductibilité thermique du réseau suivant les méthodes actuelles, et que le spectre des phonons per de sa précision en raison de l'ajustement des différents paramètres entrant dans les calculs. Les auteurs estiment qu'au lieu de s'attarder à effectuer la sommation d'intégrales complexes pour des modèles de la dynamique de réseau plus proches de la réalité. il vaudrait mieux étudier la validité des différentes hypothèses relatives au temps de relaxation prises comme base pour l'établissement de ces intégrales. ХАРАКТЕР ФОНОННОГО СПЕКТРА И АНАЛИЗ ТЕПЛОПРОВОДНОСТИ РЕШЕТКИ. Дается анализ теплопроводности решетки, в котором используется более реалистичный фононный спектр, чем обычный дебаевский фононный спектр, состоящий из одной средней акустической ветви. Впервые использована дисперсионная модель анизотропного сплошного спектра в ресчете зависимости теплопроводности решетки германия от температуры. Примененный путь решения в этом расчете представляет собой измененный вариант выражения Коллуэйя. Для оценки довольно значительных интегралов выше частот решетки используется процедура интеграции шести и трех членов уравнения Хаустона. Применяются наиболее подходящие распространенные выражения для времени релаксации для рассеяния на границе и на примеси, а также для трех фононных нормальных процессов и процесса Умклаппа. При правильном подборе четырех постоянных, имеющихся в интегралах, получается хорошее соответствие с экспериментальными данными Холланда, Слака и Глассбреннера для германия от 20 до 1000°К.

Благодаря надежным данным нейтронной спектроскопии мы знаем, что германий имеет очень разбросанные поперечные ветви, и дисперсионная модель анизотропного сплошного спектра также дает о них плохое представление. Поэтому мы считаем необходимым использовать очень хорошо отработанную модель оболочки для динамики решетки германия, предложенную Кохраном. При соответствующем подборе параметров, входящих в наше выражение для расчета теплопроводности решетки, мы вновь получаем хорошее соответствие с экспериментальными данными. Мы пришли к выводу, что характер фононного спектра не влияет сильно на анализ данных теплопроводности решетки существующими методами, и точность фононного спектра теряется в результате подгонки различных входящих сюда параметров. Есть мнение, что вместо того, чтобы тратить слишком много времени на расчет трудоемких интегралов для более реалистичных динамических моделей решетки, лучше изучить справедливость различных предположений о времени релаксации, входящих в эти интегралы.

NATURALEZA DEL ESPECTRO FONÓNICO Y ANALISIS DE LA CONDUCTIVIDAD TERMICA RETICULAR. Los autores analizan la conductividad térmica reticular utilizando para ello un espectro fonónico más realista que el habitual espectro fonónico tipo Debye, consistente en una rama acústica media. Para calcular la influencia de la temperatura sobre la conductividad térmica reticular del germanio, emplean en primer término un modelo dispersivo continuo de carácter anisotrópico. Aplican a tal efecto una versión modificada de las fórmulas de Callaway. Utilizan el método de integración de seis y tres términos de Houston para determinar integrales sumamente complejas que abarquen las frecuencias reticulares, y emplean las expresiones actualmente más adecuadas para los tiempos de relajación correspondientes a la dispersión en los bordes y a la dispersión por impurezas, así como procesos trifonónicos normales y procesos de «Umklapp». En el caso del germanio se obtiene una concordancia satisfactoria con los datos experimentales de Holland y de Slack y Glassbrenner, entre 2 y 1000°K, ajustando las cuatro constantes que aparecen en las integrales.

Como se sabe por los resultados fidedignos obtenidos por espectroscopia neutrónica, el germanio tiene ramas transversales muy dispersas, y un modelo dispersivo continuo de tipo anisotrópico tampoco constituye una representación satisfactoria de las mismas. Por tanto, los autores han estimado oportuno utilizar el complejo modelo de capas propuesto por Cochran para la dinámica reticular del germanio. Ajustando adecuadamente los parámetros que figuran en la fórmula utilizada por los autores para calcular la conductividad térmica de la red, se obtiene también una concordancia satisfactoria con los datos experimentales. Se llega, pues, a la conclusión de que, según los criterios actuales, la naturaleza del espectro fonónico no ejerce inferencia acusada en el análisis de los datos relativos a la conductividad térmica reticular, y de que las sutilezas propias del espectro fonónico se pierden con el ajuste de los diversos parámetros que intervienen. A juicio de los autores, en lugar de preocuparse demasiado por determinar las laboriosas integrales correspondientes a modelos de dinámica reticular más realistas, es preferible investigar la validez de las diferentes hipótesis referentes al tiempo de relajación que intervienen al formular dichas integrales.

#### I. INTRODUCTION

In simple dielectric crystals thermal energy is transported by lattice vibrations. A finite thermal conductivity results from interactions between phonons and from the scattering of phonons by crystal imperfections. Analysis of lattice thermal conductivity as a means of studying phonon-phonon and phonon-defect interactions has been attracting increasing attention in recent years. Although an exact calculation of lattice thermal conductivity is possible in principle, lack of knowledge of crystal vibration spectra and of anharmonic forces in crystals and the difficulty of obtaining an exact solution of the Boltzmann equation are formidable barriers to progress. In order to make a calculation a number of assumptions have been introduced in the general theory. The usual approach is the relaxation time approximation for solving the Boltzmann equation. Further, it is often necessary to work with the Debye approximation for the lattice dynamics of the solid. Under these assumptions it is possible to find a reasonably good agreement between theory and experiment in certain temperature ranges. A simple model for the lattice thermal conductivity was proposed by CALLAWAY [1]. He assumed a Debye phonon spectrum and made several assumptions as to the form of the three-phonon scattering times. The low temperature thermal conductivity of a number of materials can be fitted under this formulation [2-10]. As a small concession to reality, Holland has tried an analysis of lattice thermal conductivity of germanium and silicon by making some gross assumptions about the nature of the phonon dispersion. HOLLAND [11] has shown that an analysis, which considers the transport of heat by transverse and longitudinal phonons separately, gives a good fit to the data on germanium over a wide range of temperature.

The assumptions contained in the Debye model of lattice thermal conductivity can be summarized in the following five points: (1) Debye density of states, (2) no distinction of polarizations, (3) constant sound velocity, (4) relaxation time and (5) additivity of reciprocal relaxation times. The validity of all these assumptions is open to question. The frequency and temperature dependence of the three-phonon relaxation times is strongly dependent on the actual phonon branch and on the dispersion of the lattice waves. With the detailed theoretical and experimental information now available about the lattice dynamics of solids, it would be interesting to attempt to eliminate some of the restrictive assumptions enshrined in the Debye model. We have here attempted an analysis of the lattice thermal conductivity utilizing more realistic phonon spectra than the Debye one. The motivations for such calculations were two fold. First, one would like to know whether thermal conductivity and its temperature dependence, as calculated from more realistic lattice dynamical models than the Debye one, did in fact improve agreement with experiment or not. Secondly, it would be interesting to find whether thermal conductivity data can be used as a test of a lattice dynamical model. In the present calculation of the lattice thermal conductivity of germanium we have utilized two lattice dynamical models, the anisotropic continuum dispersive model [12] and Cochran's shell model [13].

#### II. THEORY

In the relaxation time approximation, the lattice thermal conductivity per unit volume,  $\kappa$ , of a dielectric material is given by [14]

$$\kappa = \frac{1}{(2\pi)^3} \sum_{\lambda} \int \tau_{q,\lambda} C_{ph}(\omega_{q,\lambda}) v_{q,\lambda}^2 \cos^2\theta \, d^3 \vec{q} , \qquad (1)$$

where  $\vec{q}$  represents the phonon wave vector,  $\lambda$  the polarization index,  $\vec{v}_{q,\lambda} = d\omega_{q,\lambda}/d\vec{q}$  is the phonon group velocity ( $\omega_{q,\lambda}$  being the lattice frequency),  $\theta$  is the angle between  $\vec{v}_{q,\lambda}$  and the direction of temperature gradient and  $C_{ph}(\omega_{q,\lambda})$  is the heat capacity per normal mode given by

$$C_{\rm ph}(\omega) = \frac{(\hbar \omega)^2}{kT^2} \exp\left(\frac{\hbar \omega}{kT}\right) \left[\exp\left(\frac{\hbar \omega}{kT}\right) - 1\right]^{-2}.$$
 (2)

The integration over  $\bar{q}$  is to be taken over the whole of the first Brillouin zone. Using the transformation  $d^3q = q^2 dq d\Omega_q$  and then changing from integration over q to integration over  $\omega$ , we can write Eq.(1) in the following form:

$$\kappa = \frac{k}{(2\pi)^3} \sum_{\lambda} \int \int \frac{\mathrm{d}\,\omega}{\mathrm{d}q} \cos^2\theta \,\tau_{q,\lambda} \,\frac{(\hbar\,\omega/kT)^2 \,e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1\right)^2} q^2 \,\mathrm{d}\omega \,\mathrm{d}\Omega_q. \tag{3}$$

Our calculation of  $\kappa$ , on the basis of this equation, was for two lattice dynamical models: the anisotropic continuum dispersive model and the shell model. The choice of these models was dictated by the following facts. The anisotropic continuum dispersive model is a very simple though crude model and its usefulness for a calculation of a physical property has already been vindicated [12, 15, 16]. A shell model is an elaborate model which gives nice agreement with the experimentally observed dispersion relations [13], and may be taken as giving us a realistic picture of the lattice dynamics of germanium. We further discuss our calculation for these models separately.

#### Anisotropic continuum dispersive model

In the anisotropic continuum dispersive model, the lattice frequencies are given by

$$\omega_{q,\lambda} = C_{\lambda} \frac{2Q}{\pi} \sin\left(\frac{\pi q}{2Q}\right), \qquad (4)$$

where  $C_{\lambda}(\theta, \phi)$  are the velocities of sound waves with different polarizations given by the three roots of the third-order Christoffel equation for a particular direction  $(\theta, \phi)$  of the propagation vector  $\vec{q}$ . The Brillouin zone is replaced by a sphere of radius  $Q = (6\pi^2 N)^{\frac{1}{2}}$ , where N is the number of unit cells per unit volume. Combining Eqs.(3) and (4) we find

$$\kappa = bQ \sum_{\lambda} \int \int \tau_{q,\lambda} X_{\lambda}(\omega) d\omega d\Omega_{q}, \qquad (5)$$

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where

$$b = \frac{k}{4\pi^4}$$
$$X_{\lambda}(\omega) = (a^2 - \omega^2)^{\frac{1}{2}} \frac{(\hbar\omega/kT)^2 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \sin^{-1}(\omega/a_{\lambda})$$

and

$$a_{\lambda}(\theta,\phi) = \frac{2Q}{\pi} C_{\lambda}(\theta,\phi).$$
 (6)

When the phonon scattering processes are taken to be independent, the combined relaxation time  $\tau_{q,\lambda}$  in Eq. (5) is obtained by the reciprocal addition of all the relaxation times present, so that

$$\tau^{-1} = \sum_{j} \tau_{j}^{-1}, \qquad (7a)$$

where  $\tau_j$  is the relaxation time for a single scattering process. If in addition to the normal three-phonon scattering with relaxation time  $\tau_N$ , we consider Umklapp processes, scattering by impurities and boundary scattering (relaxation time  $\tau_{II}$ ,  $\tau_{I}$  and  $\tau_{h}$  respectively) then

$$\tau^{-1} = \tau_{\rm b}^{-1} + \tau_{\rm L}^{-1} + \tau_{\rm N}^{-1} + \tau_{\rm U}^{-1} . \tag{7b}$$

 $\tau_b^{-1}$  is as usual approximated by v/LF, where v is average phonon velocity; L gives equivalent sample size and F is a geometric factor. The customary expression for  $\tau_I^{-1}$  is Aw<sup>4</sup> where A =  $(\Omega_0/4\pi v^3) \Sigma f_i [1 - M_i/M]^2$  and M =  $\Sigma f_i M_i$ ;

 $\Omega_0$  is the volume per atom;  $M_i$  is the mass of the i-th type of atom, these being a fraction  $f_i$  of the total number of atoms. This form assumes that the scattering is entirely due to mass difference, which is true for isotropic disorder. For the normal processes HERRING [17] has classified the relaxation times according to crystal class and polarization and has given expressions for  $\tau_N$ . According to Herring we should expect to find at low temperatures

$$\tau_{LN}^{-1} = B_L \omega^2 T^3$$
 and  $\tau_{TN}^{-1} = B_T \omega T^4$ .

The subscripts L and T indicate the longitudinal and transverse modes, respectively. In the case of Umklapp processes HOLLAND [11] has deduced the following expression for highly dispersive transverse phonons

Here  $\omega_2$  is the frequency of the transverse acoustic modes at the zone boundary and  $\omega_1$  the frequency of these very modes for a wave vector of half the magnitude of the maximum wave vector along that direction in the zone. This form of  $\tau_{\rm TU}$  indicates that low-frequency phonons with frequency less than  $\omega_1$  do not participate in Umklapp processes.

The summation over  $\lambda$  in Eq.(5) is for the quasi-longitudinal mode and the two quasi-transverse modes. We can therefore write

$$\kappa = \kappa_{\mathrm{L}} + \kappa_{\mathrm{T}} = \kappa_{\mathrm{L}} + \kappa_{\mathrm{T}_{1}} + \kappa_{\mathrm{T}_{2}}$$
(9)

with

$$\kappa_{\rm L} = bQ \int \int \tau_{\rm L} X_{\rm L}(\omega) d\omega d\Omega_{\rm q}$$

and

$$\kappa_{\rm T} = b \mathbf{Q} \sum_{\rm T} \int \int \tau_{\rm T} \mathbf{X}_{\rm T}(\omega) \, d\omega \, d\Omega_{\rm q} \,. \tag{10}$$

On the basis of reasons mentioned earlier, the expressions for the relaxation times  $\tau_L$  and  $\tau_T$  are given by:

$$\tau_{\rm L}^{-1} = \frac{\rm v}{\rm FL} + {\rm A}\omega^4 + {\rm B}_{\rm L}\omega^2{\rm T}^3$$
(11)
$$\tau_{\rm T}^{-1} = \frac{\rm v}{\rm FL} + {\rm A}\omega^4 + {\rm B}_{\rm T}\omega{\rm T}^4 + \tau_{\rm TU}^{-1} .$$

We assume that  $\tau_T$  is given by the same expression for both the transverse modes. Because of the form of  $\tau_{TU}$  (Eq.(8)), the component  $\kappa_T$  can be further split to give

$$\kappa = \kappa_{\rm L} + \kappa_{\rm TO} + \kappa_{\rm TU}, \tag{12}$$

 $\kappa_{TO}$  is the contribution of low-frequency transverse modes with  $\omega < \omega_1$  and  $\kappa_{TU}$  is due to transverse modes with frequencies lying between  $\omega_1$  and  $\omega_2$ . Eqs. (9)-(12) finally lead to the expressions

$$\kappa_{\rm L} = bQ \int_{\Omega} \int_{0}^{\omega_{\rm L}} \frac{X_{\rm L}(\theta, \phi)}{(1/\tau_{\rm b}) + A\omega^4 + B_{\rm L}\omega^2 T^3} d\omega d\Omega_{\rm q}$$

$$\kappa_{\rm TO} = bQ \sum_{\rm T} \int_{\Omega} \int_{0}^{\omega_1} \frac{X_{\rm T}(\theta, \phi)}{(1/\tau_{\rm b}) + A\omega^4 + B_{\rm T}\omega{\rm T}^4} \, d\omega \, d\Omega_{\rm q}$$
(13)

$$\kappa_{\rm TU} = bQ \sum_{\rm T} \int_{\Omega} \int_{\omega_1}^{\omega_2} \frac{X_{\rm T}(\theta, \phi)}{(1/\tau_{\rm b}) + A\omega^4 + B_{\rm TU}\omega^2/\sinh{(\hbar\omega/kT)}} \, d\omega \, d\Omega_{\rm q}$$

In  $\kappa_{TU}$  we have neglected the small N-process term  $B_T\omega T^4$  and the whole analysis neglects U-processes for the longitudinal modes.

#### Shell model

In the light of reliable neutron spectrometric investigations [18], we realize that germanium has very dispersive transverse branches and the anisotropic continuum dispersive model yields a poor representation for the lattice dynamics of this solid. We therefore thought it appropriate to utilize the very elaborate shell model put forth by Cochran for a calculation of  $\kappa$ . In Cochran's model the ion is not treated as rigid. A spherical shell of outer electrons can move rigidly with respect to the core. There is isotropic coupling between each core and its shell as well as shell-shell, shell-core and core-core short range interactions between nearest neighbours. On the basis of this model the frequency-wave vector relations can be reasonably well accounted for with only two disposable parameters.

The lattice vibrational frequencies  $\omega_{q,\lambda}$  entering in the thermal conductivity expression are given by Eqs. (2.11) and (3.3) of COCHRAN's paper [13] for wave vectors lying along symmetry directions [100] and [111]. An expression for the group velocity  $d\omega/dq$  along these directions can be obtained from expression for  $\omega$ . Along other off-symmetry directions, an evaluation of group velocity became a terribly involved process because of the complexity of the model. The relaxation time expressions were exactly the same as utilized in the case of the anisotropic continuum dispersive model, and the process employed for evaluating  $\kappa$  was also similar to the one used for the anisotropic continuum dispersive model. The explicit expressions for  $\kappa_{L}$ ,  $\kappa_{TO}$ ,  $\kappa_{TU}$  are too lengthy and involved to be reproduced here.

#### III. CALCULATION AND RESULTS

It is convenient to discuss the evaluation of  $\kappa$  separately for the anisotropic continuum dispersive model and the shell model.

#### Anisotropic continuum dispersive model

The integrations over  $\Omega_q$  in Eq. (13) were carried out using modified Houston's spherical six-term integration method as developed by BETTS <u>et al.</u> [19]. The applicability of Houston's method has been discussed by many workers [20-24]. If we wish to evaluate

$$\mathbf{J} = \int \mathbf{I}(\boldsymbol{\theta}, \boldsymbol{\phi}) \, \mathrm{d}\boldsymbol{\Omega},$$

where the integrand is invariant under the operations of the complete cubic symmetry group, we will require the value of  $I(\theta, \phi)$  in the following six directions:

These will be written  $I_A$ ,  $I_B$  etc. The expansion of the integrand in cubic harmonics retaining six terms leads to the following expression for J:

$$J = \frac{4\pi}{1\,081\,080} \left[ 117\,603 \,I_{A} + 76\,544 \,I_{B} + 17\,496 \,I_{C} + 381\,250 \,I_{D} + 311\,040 \,I_{E} + 177\,147 \,I_{F} \right].$$
(14)

During our calculation we found that the three-term formula

$$J = \frac{4\pi}{35} \left[ 10 I_{A} + 16 I_{B} + 9 I_{C} \right]$$

gives results not much different from the six-term formula and it is economic to use three-term procedure during the process of adjustment of parameters in Eqs. (13). The  $C_{\lambda}(\theta, \phi)$  were expressed in terms of the elastic constants through the solutions of the Christoffel equation for the propagation of the elastic waves in a continuum for six directions [001], [101], [111], [102], [112], and [212]. We have taken into account the observed temperature variation of the elastic constants and the lattice parameter. The elastic constants are taken from McSKIMIN [25] whose measurements are extrapolated towards lower temperatures by assuming a temperature variation of the type observed by FINE [26]. The integrations over  $\omega$  were performed numerically.

Arbitrary parameters  $\tau_b$ ,  $B_{TU}$ ,  $B_L$  and  $B_T$  appearing in Eqs. (13) were adjusted to such values as to give a good agreement of the calculated value of  $\kappa$  with the experiment.  $\tau_b$  is adjusted to fit the data at 2°K.  $\kappa_{TU}$  is obtained from 700°K data with the assumption that mainly transverse modes contribute at this temperature through three-phonon Umklapp processes.  $B_{TU}$  was thus obtained by fitting 700°K data.  $B_L$  was obtained from 300°K



Thermal conductivity of germanium Solid lines are the result of the calculation on the basis of the anisotropic continuum dispersive model.

O - Measurements of Slack and Glassbrenner
 □ - Measurements of Holland

Separate contributions are also shown.

data with the values of  $\kappa_{TU}$  taken into account,  $\kappa_{TO}$  will be insignificant at this temperature.  $B_T$  was then obtained from the best fit for 40°K data, with  $\kappa_{TU}$  and  $\kappa_L$  taken into account. The final values of the parameters used in the analysis are:

$$\tau_{b}^{-1} = 5.2 \times 10^{6} \text{ s}^{-1}$$

$$B_{TU} = 12.6 \times 10^{-18} \text{ s}$$

$$B_{L} = 8.4 \times 10^{-24} \text{ s} (^{\circ}\text{ K})^{-3}$$

$$B_{T} = 8.0 \times 10^{-11} (^{\circ}\text{ K})^{-4}$$

The isotropic scattering parameter A is taken as  $2.4 \times 10^{-44}$  s<sup>3</sup>, the value given by SLACK and GLASSBRENNER [27]. Lattice thermal conductivity calculated by this formulation is plotted in Fig. 1, where we have also shown the contributions  $\kappa_{TU}$ ,  $\kappa_{TO}$  and  $\kappa_{L}$ . The experimental data is from HOLLAND [11] for low temperatures (1.7 to 200°K) and from SLACK and GLASSBRENNER [28] for higher temperatures (200°K to the melting point).

#### Shell model

In the calculation of lattice frequencies and  $d\omega/dq$  for wave vectors along [100] and [111] directions, the same constants as those given by Cochran were used. The three-term integration procedure of Houston was used to effect an integration over  $\Omega_q$  Since  $\omega$  and  $d\omega/dq$  were not calculated for the [110] direction in this model it was necessary to approximate them. Fortunately their contributions may be very well approximated by giving their weights, in the integrand, to the longitudinal and transverse [100] modes. BIENENSTOCK [29] had earlier used this sort of approach for evaluating integrals over spherical Brillouin zone in a calculation of the thermal expansion of germanium.

For the evaluation of parameters  $\tau_{\rm b}$ ,  $B_{\rm TU}$ ,  $B_{\rm L}$  and  $B_{\rm T}$ , exactly the same procedure was adopted as was utilized in the case of the anisotropic continuum dispersive model. The values of the parameters are

$$\tau_{b}^{-1} = 5.95 \times 10^{6} \text{ s}^{-1}$$

$$B_{TU} = 4.00 \times 10^{-18} \text{ s}$$

$$B_{L} = 8.4 \times 10^{-24} \text{ s} (^{\circ}\text{K})^{-3}$$

$$B_{T} = 8.0 \times 10^{-11} (^{\circ}\text{K})^{-4}$$

The value of A is the same as given earlier. The contribution of the optical modes to the thermal conductivity is limited by their low group velocity. To estimate their contribution in a crude way we used the same relaxation time expressions as for the acoustic modes with corresponding polarizations, and the parameters  $B_L$ ,  $B_T$ , etc. were given the values listed above. The contribution of these modes to  $\kappa$  was found quite negligible. The calculated values of thermal conductivity along with the experimental data are shown in Fig.2.

#### IV. DISCUSSION

From Figs. 1 and 2 it is evident that the agreement of the calculated values with the experiment is quite good over a very large temperature range for both the lattice dynamical models for germanium. The constants needed to fit the two models are quite different and at a particular temperature the relative contributions  $\kappa_{TO}$ ,  $\kappa_L$  and  $\kappa_{TU}$  are also quite different. The highly dispersive nature of the shell model phonon spectrum shifts the  $\kappa_{TH}$  peak to lower temperatures. The study indicates that though the thermal conductivity analysis seems to depend on the type of the model used for the lattice dynamics of the solid, the presence of many adjustable parameters in the theory washes off such effects from the ultimate result of a calculation of  $\kappa$ . The niceties of the phonon spectrum are lost in the adjustment of the various parameters involved.

In the present analysis we have not considered the four-phonon Umklapp processes, and electrons and holes as possible carriers of heat. The elec-

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Fig. 2



○ - Measurements of Slack and Glassbrenner
 □ - Measurements of Holland

Separate contributions are also shown.

tronic contribution to  $\kappa$  becomes important at the very highest temperatures, when the number of thermally generated carriers becomes very large. Our analysis of low temperature data leads to a value of  $\tau_b^{-1}$  higher than the Casimer's expression v/LF. This implies increased boundary scattering. There is always the possibility that the increased boundary scattering is due to large-scale crystal defects. In this analysis we have not taken different relaxation times for N-processes in low and high temperature regions. The three-phonon N-processes are important mainly in the temperature range  $0-300^{\circ}$ K, for which the use of the low temperature expression for relaxation time may not lead to much error.

We are also aware of the insufficiencies in the existing thermal conductivity formulations. In discussing phonon scattering problems, is it at all possible to use the relaxation time approximation in the Boltzmann equation describing the phonon flow? Furthermore, since there are usually several phonon scattering processes active simultaneously, can one get the combined relaxation through Eq. (7a)? This equation means that the scattering processes are essentially independent of each other, which is not quite true.

We thus realize that the Callaway scheme or its modifications have proved extremely successful phenomenological schemes for the calculation of the thermal conductivity and it is not surprising that they have shown certain weaknesses on closer examination. It is doubtful that better methods of comparable simplicity will be available in the near future, because of the inherent complexity of the processes involved in lattice thermal conduction. Our study shows that instead of putting too much labour in evaluating the tedious integrals for more realistic phonon spectra, it is better to scrutinize the assumptions that have gone into these integrals.

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#### DISCUSSION

R. SRINIVASAN: The constant  $B_{TU}$ , indicating the Umklapp process effect, is three times less for the shell model than for the anisotropic dispersive continuum model. What feature of the phonon dispersion curves in the shell model is responsible for the difference?

S.K. JOSHI: The transverse branches in the shell model are very dispersive as compared with the anisotropic continuum dispersive model and this leads to the difference in  $B_{TU}$  values.

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### ANHARMONIC EFFECTS AND THE SCATTERING OF NEUTRONS FROM A CRYSTAL

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#### (Presented by G. Dolling)

#### Abstract — Résumé — Аннотация — Resumen

ANHARMONIC EFFECTS AND THE SCATTERING OF NEUTRONS FROM A CRYSTAL. The effects of the anharmonic interactions between the normal modes of vibration of a crystal on the inelastically scattered neutron distributions have been discussed by several authors. It is well known that they give rise to temperaturedependent widths and frequencies for the scattered neutron groups. It is less well known that both the frequency and the lifetime of a normal mode depend not only on the temperature, but also on the "applied" frequency used to study the normal mode. As a result of this frequency dependence, the scattered neutron groups may have a more complex structure than a simple Lorentzian shape. Furthermore, if the eigenvectors of the normal mode are not completely determined by the symmetry of the crystal they cannot be considered as independent. The interference between them will depend on both the temperature and the applied frequency. In most crystals these effects are small at temperatures well below the melting point. However, in certain crystals, ferroelectrics for example, some of the modes are anomalously temperature dependent so that these effects may be larger. Calculations have been made of these effects using a model of strontium titanate. The results, which give reasonable agreement with the temperature dependence of the modes, the infrared reflectivity and thermal expansion, show that the effects of the frequency dependence of the modes and of the interference of the different normal modes are by no means negligible.

EFFETS ANHARMONIQUES ET DIFFUSION DES NEUTRONS PAR UN CRISTAL, Plusieurs auteurs ont analysé les effets des interactions anharmoniques entre les modes normaux de vibration d'un cristal sur les distributions de neutrons diffusés inélastiquement. C'est un fait bien connu que ces interactions donnent lieu, pour les groupes de neutrons diffusés, à des largeurs et des fréquences qui dépendent de la température. C'est un fait moins bien connu que la fréquence comme la durée de vie d'un mode normal sont fonction non seulement de la température, mais aussi de la fréquence «appliquée» que l'on utilise pour l'étude du mode normal. Du fait de cette influence de la fréquence, il se peut que les groupes de neutrons diffusés aient une structure plus complexe que celle d'une forme lorentzienne simple. En outre, si les vecteurs propres du mode normal ne sont pas complètement déterminés par la symétrie du cristal, ils ne peuvent être considérés comme indépendants. Leur interférence dépendra à la fois de la température et de la fréquence appliquée. Dans la plupart des cristaux, ces effets sont restreints à une température très inférieure au point de fusion. Toutefois, dans certains cristaux, par exemple les ferroélectriques, certains des modes dépendent dans une mesure anormale de la température, de sorte que ces effets peuvent être plus importants. L'auteur a calculé ces effets au moyen d'un modèle de titanate de strontium. Les résultats, qui concordent dans une mesure raisonnable avec l'influence de la température sur les modes, la réflectivité infrarouge et la dilatation thermique, montrent que les effets des variations des modes en fonction de la fréquence et ceux de l'interférence des différents modes normaux ne sont nullement négligeables.

НЕГАРМОНИЧЕСКИЕ ЭФФЕКТЫ И РАССЕЯНИЕ НЕЙТРОНОВ НА КРИСТАЛЛЕ. Эффекты негармонических взаимодействий между нормальными формами колебания кристалла на распределение неупруго рассеянных нейтронов рассматривались некоторыми авторами. Хорошо. известно, что в результате этих эффектов наблюдаются зависимые от температуры

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ширины и частоты у групп рассеянных нейтронов. Не так хорошо известно, что как частота, так и время жизни нормального колебания зависят не только от температуры, но также и от "применяемой" частоты, используемой для изучения нормального колебания. В результате такой частотной зависимости группы рассеянных нейтронов могут иметь более сложную структуру, чем простая форма Лоренца. Далее, если собственные векторы нормального колебания не определены полностью симметрией кристалла, то их нельзя считать независимыми. Интерференция между ними будет зависеть как от температуры, так и от применяемой частоты. В большинстве кристаллов при температуре значительно ниже точки плавления эти эффекты незначительны. Однако в некоторых кристаллах, например в ферроэлектриках, некоторые из колебаний проявляют настолько необычную зависимость от температуры, что эти эффекты мотут быть значительнее. Проведены расчеты этих эффектов с использованием модели титаната стронция. Результаты, которые довольно хорошо согласуются с температ турной зависимостью колебаний, козффициентом отражения инфракрасных лучей и тепловым расширением, говорят о том, что пренебрегать эффектами частотной зависимости колебаний и интерференцией различных нормальных колебаний ни в коем случае нельзя.

EFECTOS ANARMÓNICOS Y DISPERSIÓN NEUTRONICA EN LOS CRISTALES. Varios autores han investigado los efectos ejercidos por las interacciones anarmónicas de los modos normales de vibración de un cristal sobre la distribución de los neutrones dispersos inelásticamente. Como es bien sabido, originan en los grupos de neutrones dispersos amplitudes y frecuencias dependientes de la temperatura. Es menos conocido que tanto la frecuencia como la duración de un modo normal depende no sólo de la temperatura, sino también de la frecuencia que se «aplica» para estudiar el modo normal. Como resultado de esta dependencia, la estructura de los grupos de neutrones dispersos puede ser más compleja que una mera forma lorentziana. Además, si los vectores propios del modo normal no están completamente determinados por la simetría del cristal, no pueden considerarse independientes. La interacción de dichos vectores dependerá de la temperatura y de la frecuencia aplicada. En la mayor parte de los cristales, estos efectos son débiles a temperaturas netamente inferiores al punto de fusión. Pero en ciertos cristales, por ejemplo en los ferroeléctricos, algunos de los modos dependen de la temperatura en una medida anormal, de manera que esos efectos pueden llegar a ser más acusados. Se han calculado dichos efectos utilizando un modelo de titanato de estroncio. Los resultados, que son razonablemente compatibles con la variación de los modos en función de la temperatura, la reflectividad infrarroja y la dilatación térmica, muestran que los efectos de la frecuencia en los modos y en la interferencia de los diferentes modos normales distan mucho de ser despreciables.

#### 1. INTRODUCTION

The effects of the anharmonic interactions between the normal modes of vibration of a crystal may be studied by using the techniques of coherent inelastic scattering of slow neutrons. Several metallic [1, 2] and nonmetallic [3-5] crystals have been studied experimentally, and the results show that both the frequencies and the widths of the scattered neutron groups change with temperature.

Although ordinary perturbation theory has been used to study these effects theoretically [6, 7], more recent developments have made extensive use of the techniques of many-body perturbation theory [8-11]. In the next section, the theory is outlined using the thermodynamic time-dependent Green's functions.

Because very little is known of the nature of the anharmonic interactions, very few detailed calculations have been made. MARADUDIN and FEIN[11] have used an oversimplified model for lead and have computed the lifetimes of some of the normal modes. More recently the author [12] has calculated the shape of the one-phonon neutron groups for the long-wavelength longi-tudinal and transverse optic modes of potassium bromide and sodium iodide.

#### ANHARMONIC EFFECTS

Both of these calculations were for normal modes whose eigenvectors are entirely determined by symmetry. In this paper, we discuss the further difficulties which occur when there are several normal modes belonging to the same irreducible representation of the space group. Calculations of these effects are made by using a model of strontium titanate which is described in section 3. The results of the calculation are described in section 4 and discussed in the final section.

#### 2. THEORY

The Fourier transform of the time-ordered Green's functions for a phonon in a crystal is given by

$$G(\vec{q} j j ', \Omega) = \frac{i}{\beta h} \int_{0}^{-i\beta h} \langle PA (\vec{q} j, t) A^{*}(\vec{q} j', 0) \rangle \exp(i\Omega t) dt.$$
(1)

A( $\vec{q}$  j, t) is the sum of the destruction and creation operators for the phonon ( $\vec{q}$  j) in the Heisenberg representation, P the Dyson time-ordering operator and  $\beta$  the inverse temperature,  $\beta = 1/k_BT$ . These Green's functions are conveniently evaluated by means of diagrams [11-13], and can be shown to obey a Dyson equation,

$$\beta h \sum_{j'} \left[ \left( \omega^2 \left( \vec{q} j \right) - \Omega^2 \right) \delta_{jj'} + 2\omega \left( \vec{q} j \right) D \left( \vec{q} j j', r \right) \right] G\left( \vec{q} j'j'', \Omega \right) = \delta_{jj''} 2\omega(\vec{q}j). \quad (2)$$

 $D(\vec{q} j j', \Omega)$  is the anharmonic contribution to the self-energy of the phonon and in general depends on both temperature and the frequency  $\Omega$ .

The Dyson equation shows that the anharmonic effects couple the normal modes j and j'. Even though it is possible to choose eigenvectors which diagonalize the Hermitian part of the self-energy, there is still an anti-Hermitian part which couples the eigenvectors. It is this coupling which has a considerable effect on the physical properties, and it is both temperature and frequency dependent.

This complication does not arise if the normal modes j and j' belong to different irreducible representations of the space group of the crystal. The anharmonic effects will then alter the diagonal parts of the self-energies but will not introduce any off-diagonal contributions.

The neutron scattering from an anharmonic crystal is complicated not only because the self-energies of the phonons are altered, but also because the distinction between one-phonon and multiphonon processes becomes less sharp. This difficulty has been discussed by KOKKEDEE [9], and by AMBEGAOKAR, CONWAY and BAYM [14] who show that the one-phonon peaks interfere with the multiphonon background. This interference has two effects; firstly it alters the intensity of the one-phonon peaks, but more importantly it contributes an asymmetry to the peaks. This asymmetric contribution shifts the apparent frequency of a phonon. Fortunately, MARADUDIN and AMBEGAOKAR [15] have shown by numerical calculation that this asymmetric term is far too small to be measurable at present, and we shall neglect the interference with the multiphonon background in the remainder of this paper.

The intensity of a neutron group at frequency  $\Omega$  is then given in terms of the Green's functions as proportional to

$$\sum_{\substack{\epsilon \to 0^+ \\ j'}} h(j) h(j') \lim_{\epsilon \to 0^+} -i\beta h[G(\vec{q}jj', \Omega + i\epsilon) - G(\vec{q}jj', \Omega - i\epsilon)],$$
(3)

where the reduced structure factors are given by

$$h(j) = \sum_{k} \vec{e} (k, \vec{q}j) b_{k} \exp\left[-i(\vec{Q} - \vec{q}) \cdot \vec{R}(kk')\right].$$
(4)

 $\vec{e}(k, \vec{q} j)$  is the eigenvector of the ion k in the normal mode  $(\vec{q} j)$ ,  $b_k$  its scattering length, and  $\vec{Q}$  the wave-vector transfer to the crystal.  $(\vec{Q} - \vec{q})$  is a reciprocal lattice vector and  $\vec{R}(kk')$  the distance between the ions of types k and k' in one unit cell. The factors which have been ignored in this expression are the Debye-Waller factors, the population factors and several other numerical factors.

#### 3. THE MODEL AND THE CALCULATIONS

The anharmonic contribution to the self-energies of the long-wavelength optic modes in strontium titanate have been calculated to lowest order in perturbation theory. The contributions are shown by the diagrams given in Fig.1 and the detailed expressions are given by various authors [6-12].

$$D(\vec{q} j j', \Omega + i\epsilon) = \frac{2}{\hbar} \sum_{\alpha\beta} V_{\alpha\beta} \left( -\frac{\vec{q}}{j} - \frac{\vec{q}}{j'} \right) U_{\alpha\beta}^{T} + \frac{18}{\hbar^{2}} \sum_{\vec{q}_{1}, j_{1}, \vec{q}_{2}, j_{2}} V \left( -\vec{q} \cdot \vec{q}_{1} \cdot \vec{q}_{2} \right) V \left( \vec{q} - \vec{q}_{1} - \vec{q}_{2} \right) \left[ \frac{n(\vec{q}_{1}, j_{1}) + n(\vec{q}_{2}, j_{2}) + 1}{\omega(\vec{q}_{1}, j_{1}) + \omega(\vec{q}_{2}, j_{2}) + \Omega + i\epsilon} + \frac{n(\vec{q}_{1}, j_{1}) + n(\vec{q}_{2}, j_{2}) + 1}{\omega(\vec{q}_{1}, j_{1}) + \omega(\vec{q}_{2}, j_{2}) + \Omega - i\epsilon} + \frac{n(\vec{q}_{2}, j_{2}) - n(\vec{q}_{1}, j_{1})}{\omega(\vec{q}_{1}, j_{1}) - \omega(\vec{q}_{2}, j_{2}) + \Omega + i\epsilon} - \frac{n(\vec{q}_{2}, j_{2}) - n(\vec{q}_{1}, j_{1})}{\omega(\vec{q}_{2}, j_{2}) - \omega(\vec{q}_{1}, j_{1}) + \Omega + i\epsilon} \right] + \frac{12}{\hbar} \sum_{\vec{q}_{1}, j_{1}} V \left( \vec{q} - \vec{q} \cdot \vec{q}_{1} - \vec{q}_{1} \right) (2n(\vec{q}_{1}, j_{1}) + 1).$$
(5)

The first term arises from the thermal expansion of the crystal, and  $U_{dB}^{TB}$  is the thermal strain. The other two terms arise from the interaction with the other phonons at constant volume. The various coefficients V() describe the strength of the interaction between the phonons, and are calculated from the interatomic forces.

The model used for the eigenvectors and frequencies of strontium titanate was obtained from measurements of the dispersion curves, elastic and dielectric constants and has been described elsewhere [16]. The model chosen from those described before was Model IV at 300°K.



The anharmonic contributions to the self-energy of a phonon. Diagram (a) arises from the thermal expansion of the crystal and is due to the change in the interatomic forces which occurs when the volume alters. The other two diagrams arise from the anharmonic self-energies at constant volume.

The anharmonic interactions were introduced into the model in as simple a way as possible in order to facilitate the calculations. The effects of the electronic dipoles on the ions were neglected in treating the anharmonic effects. The electrostatic forces behave like  $1/r^3$  so that they were neglected in comparison with the short range forces which vary more strongly with distance. In the harmonic models the short range forces between the titanium and oxygen ions are an order of magnitude greater than the others. The whole of the anharmonicity was therefore taken to arise from axially symmetric forces between the titanium and the oxygen ions. Two parameters, the third and fourth derivatives, were then needed to specify the anharmonic forces.

The third derivative of the potential function was obtained by comparing with the thermal expansion measurements of LYTLE [17]. Agreement with the measurements was obtained with the third derivative -840 (in units of  $e^2/vr$ ). A check on this value can be obtained by calculating the third derivative from the pressure dependence of the Curie temperature [18]. The result is -916, in quite reasonable agreement with the result obtained from the thermal expansion.

The fourth derivative was obtained from the temperature dependence of the lowest frequency transverse optic mode [16], as 16900 (in units of  $e^2/vr^2$ ). The non-linear dielectric constants [19] can also be used to give the fourth derivative. Although the results for the different directions do not agree well, due presumably to the inadequacy of the model, they suggest a value for the fourth derivative similar to that obtained from the transverse optic mode.

The calculations of the self-energy as a function of temperature and frequency  $(\Omega)$  were then performed by evaluating Eq.(5). The frequencies and eigenvectors were evaluated at ten independent points within the unique volume of the Brillouin zone, and the expressions evaluated numerically by

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using the Edsac II computer. The limit for  $\epsilon \rightarrow 0$  in Eq.(3) was calculated by choosing  $\epsilon$  to be 0.2 (10<sup>12</sup> c/s). A larger choice of  $\epsilon$  would have smoothed the results unnecessarily, while there were insufficient points taken within the Brillouin zone to allow a smaller  $\epsilon$  to be used. Calculations have been performed of the self-energies of the three transverse optic modes, which are infrared active, for a number of temperatures and ranges of frequency.

#### 4. RESULTS

The results of the calculation of the anharmonic contributions to the self-energies are shown in Figs. 2, 3, 4 and in Table I. The first term in Eq. (5) was evaluated using the calculated thermal expansion and the results





The temperature dependence of the self-energies of the phonons arising from diagram (b) of Fig. 1; diagonal contributions

are tabulated for the diagonal components in Table I. The numbers are tabulated in terms of the differences from 300°K. The contribution of the third term in Eq.(5) is independent of the applied frequency  $\Omega$  and its temperature dependence is shown in Fig.2.

The contribution from the second term in Eq. (5) is more complicated and has both frequency-dependent real and imaginary parts. The temperature dependence of the term for the diagonal contribution to the lowest frequency transverse optic mode is shown in Fig. 3, while in Fig. 4 the frequency dependence of all the contributions is shown at  $300^{\circ}$ K.



Fig. 2(b)

The temperature dependence of the self-energies of the phonons arising from diagram (b) of Fig. 1; off-diagonal contributions

Since the harmonic model was fitted to the measurements of the dispersion curves at 300°K, the harmonic frequencies already include a large part of the anharmonicity. The strictly harmonic frequencies  $\omega(\vec{q} j)$  were therefore chosen so that the calculated frequencies for the neutron groups agreed with the measurements, and furthermore so that the normal modes at 300°K and for  $\Omega = 0$  were the same as those of the model.

As discussed in section 2, the normal modes are no longer independent of one another when the anharmonicity is included. However, if the anti-Hermitian parts of the self-energy matrix are neglected, the resulting matrix may be diagonalized to find a best set of normal modes for each frequency  $\Omega$ and for each temperature. The eigenvectors and frequencies obtained in this way are shown in Table II, as a function of frequency. The results for the lowest transverse optic mode are particularly striking in that its frequency varies between 1.65 and 8.06 (10<sup>12</sup> c/s). The temperature dependence of the eigenvectors of the normal modes, with  $\Omega$  equal to the frequency of the centres of the neutron groups, is shown in Table III.

The one-phonon inelastic scattering cross-section has been evaluated using Eqs. (3) and (4) and the self-energies deduced above. Figure 5 shows the results of the calculations for two of the transverse optic modes. The dotted lines show the effect of neglecting the off-diagonal anti-Hermitian components. The structure in the peaks arises from the frequency dependence of the real and imaginary parts of the self-energies. The shift in the fre-



Fig, 3

The temperature dependence of the diagonal part of the contribution of diagram (c) of Fig. 1 to the self-energy of the lowest frequency transverse optic mode.

|                   | 400° K         |
|-------------------|----------------|
|                   | 30 <b>0°</b> K |
| • • • • • • • • • | 200°K          |
|                   | 100° K         |

quencies when the off-diagonal parts are included arises because these parts give rise to an asymmetric contribution to the peak intensity.

In Fig. 6 the temperature dependence and the dependence upon the position in reciprocal space of the cross-section of the TO II mode are shown. The effect of the off-diagonal terms is again quite pronounced. When the diagrams showing the dependence on the position in reciprocal space are studied carefully, the centre of the peak is seen to vary from one reciprocal lattice vector to another. The reduced structure factors for the different modes vary, and so the magnitude of the interference terms varies.

The widths of the peaks are listed in Table IV, where they are compared with the measurements of SPITZER, MILLER, KLEINMAN and HOWARTH [20] by infrared spectroscopy. Unfortunately, it is not possible to compare the widths with experimental neutron groups because of uncertainties in the instrumental resolution.





The frequency dependence of the diagonal contribution from diagram (c) of Fig. 1 to the self-energy of the transverse modes at 300°K

|                         | TO I   |
|-------------------------|--------|
| · • • • • • • • • • • • | to II  |
|                         | TO III |

#### 5. CONCLUSIONS

The model described in the previous sections can hardly be considered satisfactory. Many of the assumptions made to simplify the anharmonic effects may be unjustified, while the frequencies given by the harmonic model are quite uncertain for those modes which were not measured ex-



Fig. 4(b)

The frequency dependence of the off-diagonal contribution from diagram (c) of Fig. 1 to the self-energy of the transverse modes at 300°K

perimentally. Furthermore, the calculations used only ten independent points within the Brillouin zone and more would certainly be needed to perform them accurately. However, even if the results cannot be trusted in detail, they can almost certainly be believed qualitatively. The model gives reasonable agreement with the thermal expansion, pressure dependence of the Curie temperature, non-linear dielectric constants, infrared reflectivity and lifetimes of the transverse optic modes [21].

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#### TABLE I

#### Transverse optic mode Temperature (°K) 1 Π ш 100 0.39 0.20 3.25 200 0,18 0.11 1.61 300 0 0 0 400 -0,20 -1.70-0.13

### THE TEMPERATURE DEPENDENCE OF THE SELF-ENERGIES ARISING FROM THE THERMAL EXPANSION OF THE CRYSTAL

Note: The units are  $10^{24}$  s<sup>-2</sup> and the magnitudes are expressed as differences from the values at 300°K.

The calculations have shown a number of features which are rather disturbing for neutron scattering experiments:

(a) The dependence upon the applied frequency of the lifetimes and frequencies can give rise to very anomalous shapes to the neutron peaks.

(b) The interaction between the different modes gives rise to an asymmetric contribution to the peak intensity. The magnitude of this contribution and hence the measured phonon frequency may vary from place to place in reciprocal space.

(c) The frequency dependence of the lifetimes and frequencies may alter the intensities of the peaks, even though the total one-phonon scattering must obey the longitudinal f-sum rule [8, 14].

(d) The asymmetric contribution to the peak intensity alters its intensity. Both of these last two effects would make the experimental determination of the eigenvectors, as suggested by BROCKHOUSE, BECKA, RAO and WOODS [22], more uncertain.

(e) The best set of eigenvectors are frequency dependent, so that the best eigenvectors describing two different phonons with the same wave vector may not necessarily be orthogonal.

Very similar difficulties arise from the interference between the onephonon peaks and the multiphonon background [9, 14, 15]. The intensities of the peaks are altered and their centres may be shifted by asymmetric terms. Fortunately, in some ways, at present most of these effects are smaller than can be resolved with inelastic neutron scattering techniques. However,\_ with slightly improved techniques these effects may well be detectable, and make the interpretation of the results that much more complicated.

#### TABLE II

### FREQUENCY DEPENDENCE OF THE EIGENVECTORS OF THE TRANSVERSE OPTIC MODES AT 300°K

|                          | Transverse optic mode I   |         |         |                                     |
|--------------------------|---------------------------|---------|---------|-------------------------------------|
| Applied frequency<br>(Ω) | Eigenvector               |         |         | Frequency<br>(ω <sub>T</sub> (δ j)) |
|                          | I                         | п       | III     | 1                                   |
| 0                        | 1                         | 0       | 0       | 2,83                                |
| 2.7                      | 0.9999                    | -0.0117 | 0.0020  | 2,94                                |
| 5.5                      | 0.9864                    | -0,1631 | 0.0210  | 3.73                                |
| 10.25                    | 0.9971                    | 0.0742  | -0.0143 | 1,65                                |
| 13.75                    | 0.7951                    | 0.5976  | 0,1035  | 6,92                                |
| 16.5                     | 0,9003                    | -0.4341 | 0,0322  | 4.40                                |
| 20.5                     | 0.8571                    | 0.4948  | 0.1437  | 8.06                                |
| 44                       | 0,6898                    | 0.7219  | 0.0540  | 6.25                                |
|                          | Transverse optic mode II  |         |         |                                     |
| 0                        | 0                         | 1       | 0       | 5, 18                               |
| 2.7                      | 0.0117                    | 0.9999  | 0,0009  | 5.31                                |
| 5,5                      | 0.1628                    | 0, 9865 | 0,0153  | 5.45                                |
| 10.25                    | -0,0743                   | 0.9972  | -0.0043 | 5,34                                |
| 13.75                    | -0.5984                   | 0.8007  | -0,0259 | 4.89                                |
| 16.5                     | 0,4330                    | 0.9006  | 0,0374  | 5,72                                |
| 20.5                     | -0.4958                   | 0.8672  | -0.0182 | 4,96                                |
| 44                       | -0.7220                   | 0.6915  | -0.0229 | 4.75                                |
|                          | Transverse optic mode III |         |         |                                     |
| 0                        | 0                         | 0       | 1       | 16.4                                |
| 2.7                      | -0,0020                   | -0.0008 | 1,0000  | 16.1                                |
| 5,5                      | -0.0232                   | -0.0117 | 0,9997  | 16,25                               |
| 10.25                    | 0,0139                    | 0.0054  | 0,9999  | 16.0                                |
| 13.75                    | -0.0984                   | -0.0414 | 0.9943  | 16.9                                |
| 16.5                     | -0.0452                   | -0.0197 | 0,9988  | 16.5                                |
| 20.5                     | +0.1336                   | -0,0558 | 0.9895  | 17.2                                |
| 44                       | -0.0539                   | 0.0232  | 0.9983  | 16.6                                |

Note: The results are expressed in terms of the eigenvectors for  $\Omega = 0$ . The frequency  $\omega_T(\vec{\sigma}j)$  is the frequency obtained by diagonalizing the self-energy matrix.

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# TABLE III

### THE TEMPERATURE DEPENDENCE OF THE EIGENVECTORS AND FREQUENCIES OF THE TRANSVERSE OPTIC MODES

|                     | T                         | ransverse optic mod                | e I     |      |  |
|---------------------|---------------------------|------------------------------------|---------|------|--|
| Temperature<br>(°K) |                           | Frequency $(\omega_{T}(\vec{o}j))$ |         |      |  |
|                     | I                         | п                                  | Ш       |      |  |
| 100                 | 0, 9925                   | 0,1153                             | -0.0394 | 1.05 |  |
| 200                 | 0,9962                    | 0.0841                             | -0.0219 | 2.10 |  |
| 300                 | 0.9999                    | -0.0117                            | 0.0020  | 2.94 |  |
| 400                 | 0.9988 -0.0473 0.0091     |                                    | 0,0091  | 3.09 |  |
|                     | Transverse optic mode II  |                                    |         | ]    |  |
| 100                 | 100 -0.0968               |                                    | -0,0190 | 5,23 |  |
| 200                 | -0,0258                   | 0.9996                             | -0,0068 | 5.21 |  |
| 300                 | 0.1628                    | 0.9865                             | 0.0153  | 5,45 |  |
| <b>40</b> 0         | 0.4516 0.8908 0.0497      |                                    | 5.74    |      |  |
|                     | Transverse optic mode III |                                    |         | ]    |  |
| 100                 | 0, 0247                   | 0.0206                             | 0,9995  | 15.8 |  |
| 200                 | -0.0104                   | 0.0025                             | 0, 9999 | 16.1 |  |
| 300                 | -0,0452                   | -0.0197                            | 0, 9988 | 16.5 |  |
| 400                 | -0,0849                   | -0.0396                            | 0,9956  | 16.9 |  |

Note: The frequency  $\Omega$  for each mode is chosen to be equal to the frequency of the centre of the neutron group  $\omega_T(\vec{o}j)$ .



Fig. 5

The temperature dependence of the shapes of the inelastically scattered neutron groups of the highest and lowest frequency transverse optic modes.





The shapes of the inelastically scattered neutron groups of the TO II mode, as a function of temperature and as a function of the reciprocal lattice vector at 300°K. The intensity is shown for a mode polarized along the X-direction and with no account taken of the angle between the scattering vector and the polarization vectors. The scattering at any reciprocal lattice vector is then a linear combination of the shapes shown in the figure.

#### TABLE IV

|                     | Transverse optic mode |              |       |        |       |        |
|---------------------|-----------------------|--------------|-------|--------|-------|--------|
| Temperature<br>(°K) | . 1                   | [            | II    |        | ш     |        |
| · ·                 | Calc.                 | Exptl.       | Calc. | Exptl. | Calc. | Exptl. |
| 100                 | 0,3                   |              | 0,04  |        | 0.06  |        |
| 200                 | 0.3                   |              | 0.13  |        | 0.10  | '      |
| 300                 | 0.5                   | 0.41<br>0.67 | 0,21  | 0,10   | 0.17  | 0,39   |
| 400                 | 0.8                   |              | 0.30  |        | 0.21  |        |

#### THE WIDTHS OF THE NEUTRON GROUPS AT VARIOUS TEMPERATURES

Note: The experimental values are taken from SPITZER et al. [20]

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#### DISCUSSION

R. SUBRAMANIAN: Kascheev and Krivoglaz have also applied thermodynamic Green functions to neutron scattering by anharmonic crystals. How do the results of Cowley compare with theirs?

G. DOLLING: While there is considerable common ground between the Kascheev and Krivoglaz theories and those of Cowley, this paper represents a significant advance in two respects: (i) numerical computations have been made here on the basis of a reasonable model of a real crystal; and (ii) certain effects arising from the "mixing" of normal modes in the anharmonic crystal have been allowed for - effects which have not previously been taken into account.

P. EGELSTAFF: To obtain the simplest line shape (i.e. the shape which can be most easily interpreted) what path in reciprocal space should one follow? Do you recommend constant- $\vec{Q}$ , constant- $\omega$ , or some other path?

G. DOLLING: It may be possible to adjust the observed line shape in a particular manner by alteration of the path through reciprocal space. However, I feel that the simplest interpretation of the line shapes is achieved when the method of constant- $\vec{Q}$  is utilized. The complications are already severe even when the phonon wave vector remains the same.

S. YIP: Perhaps this is a case where the theoreticians can settle the matter among themselves, and so I wonder whether Dr. Cowley can use his theory to clarify the situation to which the conflicting theories discussed by Professor Akcasu have given rise.

G. DOLLING: From my brief acquaintance with Akcasu's theory, it seems to me that there is a basic discrepancy between the two formulations, which manifests itself for example in the population factor signs in the expression for the line width. Perhaps this arises from a real difference in the <u>physical</u> bases of the theories, rather than from an "algebraic" error in one of them.
## THÉORIE MICROSCOPIQUE DES TRANSITIONS S'ACCOMPAGNANT D' UNE MODIFICATION DE LA STRUCTURE CRISTALLINE

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## Abstract — Résumé — Аннотация — Resumen

MICROSCOPIC THEORY OF TRANSITIONS ACCOMPANIED BY MODIFICATION OF CRYSTALLINE STRUC-TURE. A self-consistent microscopic theory is proposed for certain transitions where the determining factor is the influence of thermal agitation. The method is particularly applicable to displacive ferroelectric substances. A discussion of the equations derived leads to a number of general conclusions near the point of transition. The properties found in this manner are in agreement with the experimental results.

THÉORIE MICROSCOPIQUE DES TRANSITIONS S'ACCOMPAGNANT D'UNE MODIFICATION DE LA STRUCTURE CRISTALLINE. Une théorie microscopique self-consistante est proposée pour certaines transitions où l'influence de l'agitation thermique est déterminante. La méthode est en particulier applicable aux ferroélectriques de type displacif. Une discussion des équations obtenues permet d'aboutir à un certain nombre de conclusions générales au voisinage du point de transition. Les propriétés ainsi trouvées sont conformes aux résultats expérimentaux.

МИКРОСКОПИЧЕСКАЯ ТЕОРИЯ ПЕРЕХОДОВ, СОПРОВОЖДАЮЩИХСЯ ИЗМЕНЕНИЕМ В КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ. Для некоторых переходов, где воздействие теплового движения является определяющим, предлагается независимая микроскопическая теория. Метод применим, в частности, к ферроэлектрическим веществам смещенного типа. Обсуждение полученных уравнений позволяет придти к некоторым общим заключениям вблизи точки перехода. Найденные таким образом новые свойства соответствуют экспериментальным результатам.

TEORÍA MICROSCÓPICA DE LAS TRANSICIONES ASOCIADAS A UNA MODIFICACIÓN DE LA ESTRUC-TURA CRISTALINA. Se propone una teoría microscópica autoconsistente para explicar ciertas transiciones en las que la influencia de la agitación térmica es decisiva. El método es aplicable en particular a los materiales ferroeléctricos de desplazamiento. Discutiendo las ecuaciones obtenidas, se llega a un cierto número de conclusiones generales en las proximidades del punto de transición. Las propiedades halladas de esta manera concuerdan satisfactoriamente con los resultados experimentales.

### 1. INTRODUCTION

De nombreux changements de phase dans les solides s'accompagnent d'une modification de la structure cristalline. La présente théorie ne traite que de ceux où l'influence de l'agitation thermique est prépondérante. L'existence de transitions de ce type est due à certaines particularités de l'interaction interatomique qui invalident tout traitement de perturbation\*. L'expérience montre qu'au voisinage de la transition, il existe des phonons dont la durée de vie est grande, et que leurs courbes de dispersion présentent de fortes variations avec la température [1-4]. Ces faits nous ont

<sup>\*</sup> Nous nous placerons dans les conditions de validité de l'approximation adiabatique et nous supposerons les atomes ponctuels.

conduits à adopter une méthode self-consistante qui, partant d'un potentiel fortement anharmonique, lui substitue un potentiel harmonique effectif qui tient compte implicitement de l'agitation thermique.

La structure cristalline est caractérisée par des paramètres  $\eta_i$  qui varient avec la température. Un exemple simple est celui où il n'existe qu'un seul paramètre représentant un déplacement relatif de deux sousréseaux. Ce type de modification de la structure cristalline est fondamental pour une certaine classe de ferroélectriques. Dans ce cas particulier les notions évoquées plus haut se traduisent de la façon suivante. Supposons un cristal où les atomes A et les atomes B occupent les nœuds de deux réseaux de Bravais identiques. Pour qu'à basse température la structure n'ait pas de centre de symétrie, il suffit que le potentiel exercé par l'ensemble des atomes A sur un atome B soit un potentiel à plusieurs puits (fig. 1). A température finie, l'agitation thermique crée un potentiel moyen qui, compte tenu du déplacement relatif des deux sous-réseaux, est dissymétrique (fig. 2). Nous montrerons comment la connaissance de ce potentiel moyen suffit à déterminer la position moyenne des atomes et la dynamique du réseau.



Figure 1 Potentiel à plusieurs puits.



Figure 2 Potentiel dissymétrique.

## 2. LES ÉQUATIONS GÉNÉRALES ET LEUR INTERPRÉTATION

Nous écrirons les équations générales en supposant pour simplifier qu'il n'existe qu'un seul paramètre  $\eta$ , la généralisation au cas de plusieurs paramètres étant immédiate. Nous décrirons le système par un hamiltonien effectif de la forme

$$\mathcal{H} = \mathcal{H}_h + E_0,$$

$$\mathcal{H}_{h} = \mathcal{F} + \frac{1}{2} \sum_{\substack{ij \\ \mu\nu}} C_{ij}^{\mu\nu} (\mathbf{x}_{i} - \mathbf{x}_{j})^{\mu} (\mathbf{x}_{i} - \mathbf{x}_{j})^{\nu},$$
$$\mathbf{E}_{0} = \langle \mathbf{V} \rangle - \frac{1}{2} \sum_{\substack{ij \\ \nu\nu}} C_{ij}^{\mu\nu} \sigma_{ij}^{\mu\nu}.$$

 $\mathscr{T}$  est l'énergie cinétique,  $\mathbf{x}_i^{\mu}$  est le déplacement du i<sup>ème</sup> atome à partir de sa position moyenne à la température considérée, position déterminée par  $\vec{\eta}(\mathbf{T})$  (fig. 2),  $\langle \mathbf{V} \rangle$  est la moyenne thermique du potentiel calculée avec la matrice densité correspondant à l'hamiltonien effectif  $\mathscr{H}$ . Enfin  $\sigma_{ij}^{\mu\nu} = \langle (\mathbf{x}_i - \mathbf{x}_j)^{\mu} (\mathbf{x}_i - \mathbf{x}_j)^{\nu} \rangle$ . L'hamiltonien  $\mathscr{H}_h$  étant supposé bien décrire la dynamique du système, l'addition de  $\mathbf{E}_0$  assure que l'énergie a la valeur correcte.

Nous obtiendrons les équations de self-consistance en minimisant l'énergie libre F du système par rapport aux paramètres variationnels qui sont ici  $\eta$ ,  $C_{1j}^{\mu\nu}$  et  $\sigma_{1j}^{\mu\nu}$ . Notons que le nombre de paramètres indépendants  $C_{1j}^{\mu\nu}$  (ou  $\sigma_{1j}^{\mu\nu}$ ) est réduit par l'invariance par translation. L'énergie libre F est donnée par

$$\mathbf{F} = \mathbf{F}_{\mathbf{h}} + \mathbf{E}_{\mathbf{0}},$$

où F<sub>h</sub> est l'énergie libre correspondant à l'hamiltonien  $\mathscr{H}_h$ .

Les seuls paramètres variationnels qui interviennent dans l'expression de F<sub>h</sub> sont les  $C_{1j}^{\mu\nu}$  car F<sub>h</sub> n'est fonction que des fréquences du système harmonique décrit par  $\mathscr{X}_h$ .

Les coordonnées de déplacement des atomes étant repérées à partir de leurs positions moyennes,  $\langle V \rangle$ est fonction de  $\eta$ . Ainsi dans l'exemple du déplacement relatif de deux sous-réseaux,  $\langle V_{m\alpha} \rangle$  où m et  $\alpha$  désignent deux atomes d'espèces différentes, s'écrit

$$\langle V(\vec{\mathbf{R}}_{m} - \vec{\mathbf{R}}_{\alpha} - \vec{\eta} + \vec{\mathbf{x}}_{m} - \vec{\mathbf{x}}_{\alpha}) \rangle$$

(voir fig. 2). Les seuls autres paramètres qui interviennent dans l'expression de  $\langle V \rangle$  sont les  $\sigma_{1j}^{\mu\nu}$ ; ceci est une propriété des systèmes d'oscillateurs harmoniques valable pour un potentiel de paires, qui sera démontrée plus loin. La minimisation de F par rapport aux paramètres variationnels donne les équations suivantes:

$$\frac{\partial F}{\partial \eta} = \frac{\partial}{\partial \eta} \langle V \rangle = 0, \qquad (1)$$

$$\frac{\partial F}{\partial C_{ij}^{\mu\nu}} = \frac{\partial F_{h}}{\partial C_{ij}^{\mu\nu}} - \frac{N}{2} \sigma_{ij}^{\mu\nu} = 0, \qquad (2)$$

$$\frac{\partial F}{\partial \sigma_{ij}^{\mu\nu}} = \frac{\partial \langle V \rangle}{\partial \sigma_{ij}^{\mu\nu}} - \frac{N}{2} C_{ij}^{\mu\nu} = 0.$$
(3)

N est le nombre de mailles élémentaires.

Ce système contient autant d'équations que d'inconnues. L'équation (1) exprime que la position moyenne d'un atome, déterminée par  $\eta(T)$ , est à un minimum du potentiel moyen (fig. 2). L'équation (2) traduit une propriété générale des systèmes d'oscillateurs harmoniques. L'équation (3) permet d'interpréter le sens physique des paramètres self-consistants  $C_{ii}^{\mu\nu}$ . Supposons pour simplifier que le potentiel d'interaction entre deux atomes  $V_{ij}$  soit une intégrale de Fourier, bien que les propriétés qui vont être établies n'exigent nullement cette restriction\*

$$V_{ij}(\eta, \vec{x}_i - \vec{x}_j) = \int d^3 \vec{q} \exp i\vec{q} \cdot (\vec{x}_i - \vec{x}_j) V_{ij}(\vec{q}, \eta).$$

Il est bien connu que pour un système d'oscillateurs harmoniques

$$\langle \exp i \vec{q} \cdot (\vec{x}_i - \vec{x}_j) \rangle = \exp - \frac{1}{2} \langle [\vec{q} \cdot (\vec{x}_i - \vec{x}_j)]^2 \rangle = \exp - \frac{1}{2} \sum_{\mu\nu} q^{\mu} q^{\nu} \sigma_{ij}^{\mu\nu},$$

ce qui démontre déjà comme nous l'avions annoncé plus haut, qu'à l'exception de  $\eta$ , les  $\sigma_{ij}^{\mu\nu}$  sont les seuls paramètres qui apparaissent dans l'expression de  $\langle V \rangle$ . Par ailleurs

$$\frac{\partial \langle V_{ij} \rangle}{\partial \sigma_{ij}^{\mu\nu}} = \langle -\frac{1}{2} \int d^3 \vec{q} q^{\mu} q^{\nu} \exp i \vec{q} . (\vec{x}_i - \vec{x}_j) V_{ij}(\vec{q}, \eta) \rangle,$$

$$\langle V_{ij} \rangle = \frac{|M|^{1/2}}{(2\pi)^{3/2}} \int d^3 \vec{u} V_{ij}(\eta, \vec{u}) \exp{-\frac{1}{2}\vec{u} M \vec{u}}$$

où M est l'inverse de la matrice des  $\sigma_{ij}^{\mu\nu}$ .

<sup>\*</sup> En effet ces propriétés peuvent aussi s'établir comme conséquence du fait que la densité de probabilité d'un système d'oscillateurs harmoniques est gaussienne. La moyenne  $\langle V_{ij} \rangle$  peut s'écrire

d'où

$$\frac{\partial \langle V_{ij} \rangle}{\partial \sigma_{ij}^{\mu\nu}} = -\frac{1}{2} \langle \frac{\partial^2 V_{ij}}{\partial (\mathbf{x}_i - \mathbf{x}_j)^{\mu} \partial (\mathbf{x}_i - \mathbf{x}_j)^{\nu}} \rangle.$$

L'équation (3) montre ainsi que le coefficient  $C_{ij}^{\mu\nu}$  est la moyenne thermique d'une dérivée seconde du potentiel; dans l'approximation classique d'un potentiel harmonique, ce même coefficient se réduit à une constante indépendante de la température.

## 3. ANALYSE QUALITATIVE DES PROPRIÉTÉS PHYSIQUES AU VOISINAGE DE LA TRANSITION

Les équations générales que nous venons d'établir permettent d'étudier divers types de transition. Illustrons ces équations et les conséquences les plus simples qu'on peut en tirer sur l'exemple du déplacement relatif de deux sous-réseaux. Le potentiel V comprend les interactions AA, B B et A B qui sont de la forme

$$\nabla_{AA}(\vec{R}_m - \vec{R}_n + \vec{x}_m - \vec{x}_n), \quad \nabla_{BB}(\vec{R}_\alpha - \vec{R}_\beta + \vec{x}_\alpha - \vec{x}_\beta), \quad \nabla_{AB}(\vec{R}_m - \vec{R}_\alpha - \vec{\eta} + \vec{x}_m - \vec{x}_\alpha).$$

Les indices m, n désignent les atomes A et les indices  $\alpha$ ,  $\beta$  les atomes B. Les  $\vec{R}$  repèrent les nœuds des deux sous-réseaux en l'absence du déplacement relatif (fig. 2). L'équation (1) s'écrit ici

$$\nabla \eta \langle V_{AB} \rangle = 0, \tag{4}$$

et on a

$$C_{m\alpha}^{\mu\nu} = \frac{\partial^2}{\partial \eta^{\mu} \partial \eta^{\nu}} \langle V_{m\alpha} \rangle.$$
 (5)

Ces équations ne font intervenir que les dérivées premières et secondes des potentiels moyens du type  $\langle V_{m\alpha} \rangle$ .

La connaissance de F<sub>h</sub> exige celle des fréquences de phonons de l'hamiltonien  $\mathscr{H}_h$  dont les carrés sont les valeurs propres de la matrice dynamique correspondante.

L'équation aux fréquences s'écrit:

où

$$\mathbf{M} = \frac{\Gamma_{11}(\mathbf{\vec{q}}) + \mathbf{m}_1 \boldsymbol{\omega}^2 \mathbf{I}}{\mathbf{C}_{12}^*(\mathbf{\vec{q}})} \frac{\mathbf{C}_{12}(\mathbf{\vec{q}})}{\Gamma_{22}(\mathbf{\vec{q}}) + \mathbf{m}_2 \boldsymbol{\omega}^2 \mathbf{I}} \,.$$

 $\Gamma_{11}(\vec{q}),\ \Gamma_{22}(\vec{q})$  et  $C_{12}(\vec{q})$  sont des matrices  $3\times 3$  dont les éléments sont définis par

$$\begin{split} \Gamma_{11}^{\mu\nu}(\vec{\mathbf{q}}) &= C_{11}^{\mu\nu}(\vec{\mathbf{q}}) - C_{11}^{\mu\nu}(0) - C_{12}^{\mu\nu}(0), \\ \Gamma_{22}^{\mu\nu}(\vec{\mathbf{q}}) &= C_{22}^{\mu\nu}(\vec{\mathbf{q}}) - C_{22}^{\mu\nu}(0) - C_{12}^{\mu\nu}(0), \end{split}$$

où

$$\begin{split} \mathbf{C}_{11}^{\mu\nu}(\vec{\mathbf{q}}) &= \sum_{n} \mathbf{C}_{mn}^{\mu\nu} \exp \, i \vec{\mathbf{q}} \cdot (\vec{\mathbf{R}}_{m} - \vec{\mathbf{R}}_{n}), \\ \mathbf{C}_{22}^{\mu\nu}(\vec{\mathbf{q}}) &= \sum_{\beta} \mathbf{C}_{\alpha\beta} \exp \, i \vec{\mathbf{q}} \cdot (\vec{\mathbf{R}}_{\alpha} - \vec{\mathbf{R}}_{\beta}), \\ \mathbf{C}_{12}^{\mu\nu}(\vec{\mathbf{q}}) &= \sum_{\alpha} \mathbf{C}_{m\alpha}^{\mu\nu} \exp \, i \vec{\mathbf{q}} \cdot (\vec{\mathbf{R}}_{m} - \vec{\mathbf{R}}_{\alpha}). \end{split}$$

I est la matrice unité  $3 \times 3$ .

## 3. 1. Anomalies de comportement des fréquences optiques

a) Pour  $\vec{q} = 0$  la matrice M prend la forme suivante:

$$\frac{m_1\omega^2 I - C_{12}(0)}{C_{12}(0)} = \frac{C_{12}(0)}{m_2\omega^2 I - C_{12}(0)} .$$

Il est facile d'en déduire que les carrés des fréquences optiques à  $\vec{q} = 0$  sont les valeurs propres de la matrice

$$\frac{m_1 + m_2}{m_1 m_2} C_{12}(0).$$

D'après l'expression (5) des coefficients  $C_{m\alpha}^{\mu\nu}$ on voit que les carrés des fréquences optiques pour  $\vec{q} = 0$  sont proportionnels aux valeurs propres du hessien de  $\langle V_{AB} \rangle$  considéré comme fonction de  $\vec{\eta}$ .

Si la transition est du deuxième ordre,  $\vec{\eta}(T)$  tend vers zéro continûment. Supposons pour simplifier que  $\vec{\eta}(T)$  soit dirigé suivant un axe de symétrie. Le potentiel moyen  $\langle V_{AB} \rangle$  considéré comme fonction du paramètre  $\vec{\eta}$  a, suivant cette direction, l'allure représentée sur la figure 2, mais sa dissymétrie disparaît quand  $\vec{\eta}(T)$  s'annule. On voit donc,  $\vec{\eta}(T)$  étant toujours à un minimum de ce potentiel, que les trois extrema de ce dernier doivent se confondre à la transition (fig. 3). La condition pour que l'équation (4) ait une racine double (qui sera automatiquement triple) s'écrit

$$\frac{\partial^2}{\partial \eta^2} \langle V_{AB} \rangle = 0 \tag{6}$$



#### Figure 3

Potentiel dont les trois extrema sont confondus.

(il s'agit de la dérivée seconde suivant la direction de  $\vec{\eta}(T)$ ). Comme  $\vec{\eta}(T)$ . est dirigé suivant un axe de symétrie, l'équation (6) entraine que le hessien de  $\langle V_{AB} \rangle$  a une valeur propre nulle. Nous venons de démontrer qu'à la transition, au moins une fréquence optique pour  $\vec{q} = 0$  doit s'annuler. L'annulation d'une valeur propre d'un hessien est d'ailleurs un critère bien connu de limite de stabilité [5-8].

b) La dépendance en  $|\vec{q}|$  pour  $\vec{q}$  petit de la branche optique singulière tend vers une dépendence linéaire au voisinage de la transition. A la température de transition elle est rigoureusement linéaire (fig. 4). En effet les carrés des fréquences, qui sont les valeurs propres de la matrice dynamique, ont pour  $\vec{q}$  petit un développement en puissances paires de  $\vec{q}$ , de la forme



Figure 4

Branche optique singulière pour de petites valeurs de d.

Il s'ensuit que quand  $\omega_6$  s'annule,  $\omega$  dépend linéairement de  $|\vec{q}|$  dans une direction donnée.

Une pente nulle pour la branche optique singulière est donc exclue à la température de transition. Cette conclusion est conforme aux résultats expérimentaux [4]. Les calculs effectués par COCHRAN [8] donnent une pente nulle pour la branche optique singulière, à la température de transition. Ce résultat insatisfaisant est peut-être dû au caractère non selfconsistant des conditions qu'il impose à la matrice dynamique. Notons que la dépendance linéaire en  $|\vec{q}|$  de la branche optique singulière à la transition ne modifie pas son caractère de vibration d'un sousréseau à l'autre.

## 3.2. Anomalies de comportement des fréquences acoustiques

Un fait essentiel à souligner est que l'annulation d'une fréquence optique s'accompagne d'une forte décroissance de la pente d'une branche acoustique (anomalies de constantes élastiques).

Prenons le vecteur  $\vec{q}$  dirigé suivant l'axe de symétrie qui porte  $\vec{\eta}(T)$ , que nous choisirons comme axe Ox de coordonnées. Dans ce cas la matrice dynamique admet un vecteur propre de composantes

$$(u_1 0 0 u_2 0 0)$$

qui correspond à une vibration longitudinale. Pour une telle vibration on trouve deux fréquences, l'une acoustique, l'autre optique, qui sont les valeurs propres de la matrice  $2 \times 2$  suivante:

$$\begin{vmatrix} \frac{1}{m_1} \left\{ C_{11}^{11}(0) - C_{11}^{11}(\vec{q}) + C_{12}^{11}(0) \right\} & -\frac{1}{(m_1 m_2)^{\frac{1}{2}}} C_{12}^{11}(\vec{q}) \\ -\frac{1}{(m_1 m_2)^{\frac{1}{2}}} C_{12}^{11} \ast(\vec{q}) & \frac{1}{m_2} \left\{ C_{22}^{11}(0) - C_{22}^{11}(\vec{q}) + C_{12}^{11}(0) \right\} \end{vmatrix}$$

En l'absence d'interaction entre les sous-réseaux A et B, on obtiendrait les deux fréquences acoustiques des deux sous-réseaux considérés comme étant seuls, données par

$$\Omega_1^2 = \frac{1}{m_1} \left\{ C_{11}^{11}(0) - C_{11}^{11}(\vec{q}) \right\},$$
$$\Omega_2^2 = \frac{1}{m_2} \left\{ C_{22}^{11}(0) - C_{22}^{11}(\vec{q}) \right\}.$$

En présence de l'interaction, l'équation aux fréquences s'écrit

$$\left(\omega^2 - \Omega_1^2 - \frac{C_{12}^{11}(0)}{m_1}\right) \left(\omega^2 - \Omega_2^2 - \frac{C_{12}^{11}(0)}{m_2}\right) = \frac{C_{12}^{11}(\vec{q}) C_{12}^{11} \times (\vec{q})}{m_1 m_2}$$

On a vu qu'à la transition  $C_{12}^{11}(0) = 0$ ; les deux fréquences sont donc données par

$$\omega^{2} = \frac{1}{2} \left\{ \Omega_{1}^{2} + \Omega_{2}^{2} \pm \left[ (\Omega_{1}^{2} - \Omega_{2}^{2})^{2} + \frac{4}{m_{1}m_{2}} C_{12}^{11}(\vec{\mathbf{q}}) C_{12}^{11}(\vec{\mathbf{q}}) C_{12}^{11}(\vec{\mathbf{q}}) \right]^{\frac{1}{2}} \right\}.$$
(7)

Elles s'annulent bien toutes les deux pour  $\vec{s} = 0$ .

Dans le cas extrême d'une interaction AB limitée aux premiers voisins, et à la transition,  $C_{12}^{11}(\vec{q})$  est proportionnel à  $C_{12}^{11}(0)$  lorsque  $\vec{q}$  est dirigé suivant l'axe de symétrie. Les deux fréquences données par (7) se réduisent donc dans ce cas à  $\Omega_1$  et  $\Omega_2$ . Dans les conditions particulières envisagées, et pour cette direction de  $\vec{q}$ , les deux sous-réseaux A et B se comportent comme s'ils étaient parfaitement découplés.

En général  $C_{12}^{11}(\mathbf{\hat{q}})$  n'est pas proportionnel à  $C_{12}^{11}(0)$ ; donc d'après (7) l'une des fréquences  $\omega_1$  est supérieure à  $\Omega_1$  et l'autre  $\omega_2$  inférieure à  $\Omega_2$ (en appelant  $\Omega_1$  la plus grande des deux fréquences  $\Omega_1$  et  $\Omega_2$ ) (fig. 5). Lorsque  $C_{12}^{11}(0)$  tend vers zéro, on voit par continuité que  $\omega_1$  représente la branche optique singulière et  $\omega_2$  la branche acoustique. On a montré que  $\omega_2 \leq \Omega_2$ ; or  $\Omega_2$  est une fréquence anormalement basse car elle ne fait intervenir que des interactions du type AA ou BB qui sont des interactions de seconds voisins; la pente de la branche acoustique  $\omega_2$  est donc anormalement basse. La théorie permet donc de rendre compte des anomalies de constantes élastiques constatées expérimentalement [9-10, 4]. Elles ne sont pas accidentelles comme le suggère COWLEY [4].

#### 3.3 Généralisation des résultats précédents

Les conclusions de l'analyse précédente sont indépendantes de l'exemple particulier qui nous a servi d'illustration. Dans le cas général la position moyenne de l'atome i est repérée par  $\vec{R}_i + \vec{\eta}_i$ . L'équation (1) est remplacée par les équations

$$\frac{\partial F}{\partial \eta_1^{\mu}} = \frac{\partial \langle V \rangle}{\partial \eta_1^{\mu}} = 0.$$
 (8)

Au voisinage d'une transition du deuxième ordre les  $\eta_i^{\mu}$  tendent vers zéro et  $\langle V \rangle$ peut être développé en puissance de ces paramètres. Le développement limité au deuxième ordre s'écrit

$$\langle v \rangle = \langle v \rangle_0 + \frac{1}{2} \left\{ \frac{\partial^2 \langle v \rangle}{\partial (\eta_i - \eta_j)^{\mu} \partial (\eta_i - \eta_j)^{\nu}} \right\}_0 (\eta_i - \eta_j)^{\mu} (\eta_i - \eta_j)^{\nu}$$

L'indice 0 correspond à tous les  $\eta_{\mu}^{\mu}$  nuls c'est-à-dire à la transition. Or d'après ce que nous avons démontré plus haut

$$\left\{\frac{\partial^2 \langle \mathbf{v} \rangle}{\partial (\eta_i - \eta_j)^{\nu} \partial (\eta_i - \eta_j)^{\nu}}\right\}_0 = C_{ij}^{\mu\nu}(\mathbf{T}_c).$$

Etant donné la forme de l'hamiltonien  $\mathscr{H}_h$ , les équations du mouvement s'écrivent

$$\sum_{j\nu} C_{ij}^{\mu\nu} (\mathbf{x}_i - \mathbf{x}_j)^{\nu} = m_i \omega^2 \mathbf{x}_i^{\mu}, \qquad (9)$$

tandis que les équations (8) s'écrivent

$$\sum_{j\nu} C_{ij}^{\mu\nu} (\eta_i - \eta_j)^{\nu} = 0.$$
 (10)



Figure 5

Courbes  $\omega_1$ ,  $\omega_2$ ,  $\Omega_1$ ,  $\Omega_2$  en fonction de  $\vec{q}$ .

On voit donc que le système d'équations (10) est formellement identique aux équations du mouvement (9) ou la fréquence serait nulle. Cette constatation entraîne deux résultats:

1° Les déplacements  $\vec{\eta}_i$  lors d'une transition du deuxième ordre correspondent obligatoirement à un mode de vibration possible.

2° La fréquence correspondant à ce mode doit être nulle.

Les modes acoustiques à  $\vec{q} = 0$  correspondent à une translation d'ensemble du réseau. Si on veut que le réseau subisse à la transition une déformation non triviale, il faut donc qu'une fréquence non nulle tende vers zéro à la transition.

Il pourrait arriver que plusieurs fréquences tendent vers zéro à la transition. Dans ce cas, les déplacements  $\vec{\eta}_i$  peuvent être une superposition des modes correspondants.

Dans l'exemple simple que nous avons traité plus haut le déplacement relatif  $\vec{n}$  correspondait à un mode optique à  $\vec{q} = 0$  et ceci entraînait que la fréquence correspondante s'annulait. Dans le cas particulier où interviennent des interactions coulombiennes et lorsque le cristal dans la phase paraélectrique a une symétrie cubique, l'équation div  $\vec{P} = 0$  entraîne div  $\vec{\eta} = 0$ . Le mode optique dont la fréquence s'annule est donc transversal dans ce cas

Dans l'exemple des deux sous-réseaux, on peut imaginer que lorsqu'on vient de la phase paraélectrique, une fréquence en bout de zone tende vers zéro. Dans ce cas on obtient un exemple simple de structure antiferroélectrique où un des sous-réseaux est fixe et où deux atomes consécutifs, dans une direction donnée, de l'autre sous-réseau se déplacent l'un de  $\vec{\eta}$  et l'autre de  $-\vec{\eta}$  (cette déformation correspond bien à un mode de vibration en bout de zone d'un réseau biatomique).

Si la fréquence qui tend vers zéro correspond à un vecteur  $\vec{q}$  quelconque, on peut obtenir des structures où la déformation est d'un type sinusoidal. Une telle phase a été récemment mise en évidence dans NaNO<sub>2</sub> [11].

Nous poursuivons l'étude de notre méthode en vue de son application à une description plus détaillée de cas concrets.

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## DISCUSSION

K. P. SINHA: In your formulation the Hamiltonian contains only second order terms in nuclear displacements. For certain phase transitions the occurrence of linear and anharmonic terms as a result of electron lattice interaction near the transition temperature may seem essential. For ferroelectric transition in BaTiO<sub>3</sub> such effects involving electron-vibration coupling have been invoked<sup>\*</sup>.

N. BOCCARA: The essential hypothesis of the theory is that the only elementary excitations are phonons whose lifetime may be regarded as infinitely long. In this case there can be no term other than the quadratic one.

K. S. SINGWI: Have you tried to establish correspondence between various terms of your free-energy expression F and those given by the phenomenological theory of Landau?

N. BOCCARA: Yes. The two theories become identical except that our theory is microscopic while that of Landau is phenomenological. In other words we use our theory to interpret the different terms of Landau's phenomenological theory.

\* SINHA, K. P. and SINHA, A. P. B., Ind. J. pure appl. Phys. 2 3 (1964) 91.

## STRAIN DEPENDENCE OF THE FREQUENCIES AND THERMAL EXPANSION OF THE HEXAGONAL CLOSE-PACKED LATTICE

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#### Abstract — Résumé — Аннотация — Resumen

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STRAIN DEPENDENCE OF THE FREQUENCIES AND THE THERMAL EXPANSION OF THE HEXAGONAL CLOSE-PACKED LATTICE. The anisotropic thermal expansion of some hexagonal metals have been measured recently. To work out the theory of anisotropic thermal expansion of hexagonal close-packed (hcp) lattices, it is necessary to investigate the strain dependence of the frequencies of the hcp lattice. The hcp lattice with nearest-neighbour central interaction of the form  $\phi = -a/\gamma m + b/\gamma n$  has been considered. The strains employed are (1) a longitudinal expansion  $\zeta$  along the z-axis; and (2) a uniform areal expansion  $\epsilon'$  in the basal plane. These are the relevant strains in the theory of thermal expansion and they have the advantage that they do not involve interlattice displacements. The Grüneisen parameters  $\gamma'_1 = -\partial \log \omega_1/\partial \epsilon'$  and  $\gamma'_1 = -\partial \log \omega_1/\partial \xi$  have been worked out for wave-vectors lying along certain symmetry directions. These parameters for the acoustic branches are found to be strongly direction-dependent and to exhibit a wide variation.

One of the transverse acoustic branches in the basal plane has a negative value of  $\gamma''$ , whatever the values of m and n are. The dependence of the moments  $\mu_2$ ,  $\mu_4$  and  $\mu_6$  on the above strains has been worked out. The high and low temperature limits of the equivalent Grüneisen parameters  $\gamma'$  and  $\overline{\gamma}^{\circ}$  have been worked out for three pairs of values of m and n. It is found that  $\overline{\gamma}' = \overline{\gamma}''$  and the high temperature limit  $\overline{\gamma}'_{0}$  is greater than the low temperature limit  $\overline{\gamma}'_{0}$  by about 0.3. The magnitude of this difference appears to be independent of the values of m and n. Taking farther-neighbour interaction into account, one may expect to reduce this difference. These theoretical results are compared with the experimental results in magnesium,

VARIATIONS, EN FONCTION DE LA DÉFORMATION, DES FRÉQUENCES ET DE LA DILATATION THER-MIQUE DU RÉSEAU À STRUCTURE HEXAGONALE COMPACTE. Les auteurs ont mesuré récemment la dilatation thermique anisotrope de certains métaux à structure hexagonale. Pour établir la théorie de la dilatation thermique anisotrope des réseaux à structure hexagonale compacte (hc), il faut étudier les variations, en fonction de la déformation, des fréquences des réseaux hc. Les auteurs ont étudié le cas du réseau hc à interaction centrale avec le plus proche voisin de forme  $\phi = -a/y^{III} + b/y^{III}$ . Les déformations suivantes ont été utilisées: 1. une dilatation linéaire  $\zeta$  le long de l'axe  $z_i$ : 2. une dilatation surfacique uniforme  $\epsilon^i$  dans le plan principal. Ces déformations sont celles qui s'appliquent à la théorie de la dilatation thermique et elles ont l'avantage de ne pas entraîner de déplacements à l'intérieur du réseau. Les auteurs ont établi les paramètres de Grüneisen  $\gamma_1^* = -\partial \log \omega_1/\partial \epsilon^*$  et  $\gamma_j^* = -\partial \log \omega_i/\partial \zeta$  pour les vecteurs d'ondes situés le long de certaines directions de symétrie. On constate que les paramètres ainsi obtenus pour les branches acoustiques dépendent fortement de la direction et présentent des variations très étendues.

Une des branches acoustiques transversales dans le plan principal accuse une valeur négative pour  $\gamma^*$ , quelles que soient les valeurs de m et n. Les auteurs ont étudié les variations des moments  $\mu_2$ ,  $\mu_4$  et  $\mu_6$  en fonction des déformations indiquées plus haut. Ils ont déterminé pour trois paires de valeurs de m et n. les limites de température supérieure et inférieure des paramètres de Grüneisen équivalents  $\overline{\gamma}^*$  et  $\overline{\gamma}^*$ . Ils ont constaté que  $\overline{\gamma}^*$  est égal à  $\overline{\gamma}^*$  et que la limite de température supérieure  $\gamma_{\infty}^*$  dépasse de 0,3 environ la limite de température inférieure  $\overline{\gamma}_0^*$ . Il semble que la grandeur de cette différence soit indépendante des valeurs de m et n. En tenant compte d'une interaction avec des voisins plus éloignés, on peut s'attendre à une réduction de cette différence. Les auteurs comparent ces résultats théoriques aux résultats expérimentaux obtenus avec le magnésium.

ЗАВИСИМОСТЬ ЧАСТОТ И ТЕПЛОВОГО РАСШИРЕНИЯ ГЕКСАГОНАЛЬНОЙ РЕШЕТКИ С ПЛОТНОЙ УПАКОВКОЙ ОТ НАПРЯЖЕНИЯ. Недавно было измерено анизотропное тепловое расширение некоторых гексагональных металлов. Для разработки теории анизотропного теплового расширения гексагональной решетки с плотной упаковкой необходимо исследовать зависимость частот гексагональной решетки с плотной упаковкой от напряжения. Рассматривалась гексагональная решетка с плотной упаковкой с центральным взаимодействием с бли-

жайшим соседним атомом в виде  $\phi = -\frac{a}{\gamma^m} + \frac{b}{\gamma^n}$ . Используемыми напряжениями являются

 продольное расширение є' вдоль оси z; и 2) равномерное воздушное расширение ζ вдоль основной плоскости. Они являются соответствующими напряжениями в теории теплового расширения, и их преимуществом является то, что они не вызывают смещений между решетка-

ми. Были разработаны параметры Грюнайзена  $\gamma_j^i = -\frac{\delta \log \omega_j}{\delta \epsilon^i} \gamma_j^{\prime\prime} = -\frac{\delta \log \omega_j}{\delta \zeta}$  для волновых векто-

ров, идущих вдоль определенных симметричных направлений. Было установлено, что эти параметры для акустических ветвей сильно зависят от направления и сильно колеблются. Одна из поперечных акустических ветвей в основной плоскости имеет отрицательное значение  $\gamma^{"}$  для любых значений m и n. Была определена зависимость моментов  $\mu_2$ ,  $\mu_4$  и  $\mu_6$  от вышеуказанных напряжений. Были установлены верхние и нижние температурные пределы эквивалентных параметров Грюнайзена  $\overline{\gamma}^{"}$  для трех пар значений m и n. Установлено, что  $\overline{\gamma}^{"} = \overline{\gamma}^{"}$  и что верхний температурный предел  $\overline{\gamma}^{L}_{L}$  больше нижнего температурного предела  $\overline{\gamma}^{"}$  примерно в 0,3 раза. Величина этой разницы, оказывается, не зависит от значений m и n. Учитывая взаимодействие со следующим соседним членом, можно ожидать уменьшения этой разницы. Эти теоретические результаты сопоставляются с результатами экспериментов с магнием.

VARIACIÓN DE LAS FRECUENCIAS Y DE LA DILATACIÓN TÉRMICA DE LA RED HEXAGONAL COMPACTA EN FUNCIÓN DE LA DEFORMACIÓN. Recientemente se ha medido la dilatación térmica anisótropa de algunos metales de estructura hexagonal. Para desarrollar la teoría de la dilatación térmica anisótropa de las redes hexagonales compactas, es necesario estudiar la influencia de las deformaciones sobre las frecuencias de esas redes. Los autores han elegido una red hexagonal compacta con interacción central de los átomos más próximos de la forma  $\phi = -a/\gamma m + b/\gamma^n$ . Las deformaciones aplicadas son: 1) una dilatación  $\zeta$  a lo largo del eje z, y 2) una dilatación uniforme bidimensional  $\epsilon$ ' a lo largo del plano basal. Estas deformaciones son las que intervienen en la teoría de la dilatación térmica, y ofrecen la ventaja de que no entrañan desplazamientos interreticulares. Los autores determinan los parámetros de Grüneisen  $\gamma_i^* = -\partial \log \omega_i / \partial \epsilon^*$ y  $\gamma_i^* = -\partial \log \omega_i / \partial \zeta$  para vectores de onda que siguen determinadas direcciones de simetría, comprobando que para las ramas acústicas estos parámetros cambian considerablemente con la dirección y ofrecen un amplio margen de variación. Una de las ramas acústicas transversales del plano basal tiene un valor negativo de y" sean cuales fueren los valores de m y n. Se ha establecido la relación de dependencia existente entre los momentos  $\mu_2$ ,  $\mu_4$  y  $\mu_6$  y las deformaciones antes mencionadas. Se han determinado los límites superiores e inferiores de temperatura de los parámetros de Grüneisen equivalentes y y y erat tres pares de valores de m y n. Se ha comprobado que y = y y que el límite superior de temperatura y es mayor en 0,3, aproximadamente, que el límite inferior de temperatura  $\overline{y}_{h}^{*}$ . Esta diferencia cuya magnitud parece ser independiente de los valores de m y n, disminuirá probablemente al tener en cuenta la interacción de átomos vecinos más alejados. Los datos teóricos se comparan con los resultados experimentales obtenidos en el caso del magnesio.

## 1. INTRODUCTION

The lattice theory of thermal expansion has been applied with success to calculate the temperature dependence of thermal expansion of cubic crystals. Recently the thermal expansion of some hexagonal metals has been measured by WHITE [1]. As a first step in working out the theory of anisotropic thermal expansion in non-cubic crystals, we have developed in this paper the lattice theory of thermal expansion of a hexagonal closepacked (hcp) lattice with nearest-neighbour central interaction.

## 2. THEORY OF THERMAL EXPANSION OF A HEXAGONAL CRYSTAL

Assuming that the frequencies of the lattice depend on the strain parameters  $x_x \ldots z_z$ , the thermal expansion coefficients of a hexagonal lattice are given by

$$\alpha_{\mu} = \left[ (\mathbf{s}_{11} + \mathbf{s}_{12}) \sum_{j} (\gamma_{j})_{\mathbf{x}_{\mathbf{x}}} \mathbf{E}(\hbar\omega_{j}/\mathbf{kT}) + \mathbf{s}_{13} \sum_{j} (\gamma_{j})_{\mathbf{z}_{\mathbf{z}}} \mathbf{E}(\hbar\omega_{j}/\mathbf{kT}) \right]$$

$$\alpha_{\perp} = \left[ 2\mathbf{s}_{13} \sum_{j} (\gamma_{j})_{\mathbf{x}_{\mathbf{x}}} \mathbf{E}(\hbar\omega_{j}/\mathbf{kT}) + \mathbf{s}_{33} \sum_{j} (\gamma_{j})_{\mathbf{z}_{\mathbf{z}}} \mathbf{E}(\hbar\omega_{j}/\mathbf{kT}) \right].$$
(1)

Here  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  represent the linear thermal expansion coefficients, parallel and perpendicular to the unique axis, respectively.  $E(\hbar\omega_j/kT)$  is the contribution to the specific heat due to the frequency  $\omega_j$  at temperature T(°K).  $(\gamma_i)_{x_{\chi}}$  and  $(\gamma_i)_{z_{\chi}}$  are generalized Grüneisen parameters pertaining to the frequency  $\omega_i$ . They are defined by

$$(\gamma_j)_{x_x} = \frac{-\partial \log \omega_j}{\partial x_x} \text{ and } (\gamma_j)_{z_z} = \frac{-\partial \log \omega_j}{\partial z_z}$$
 (2)

 $x_x$  and  $z_z$  are the components of the strain tensor and  $s_{ij}$  are the elastic moduli. In the lattice theory of thermal expansion the parameters  $(\gamma_j)_{x_x}$  and  $(\gamma_j)_{z_z}$  are to be evaluated.

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#### 3. DYNAMICS OF THE HCP LATTICE

Referred to a Cartesian system of axes, the base vectors of the hcp lattice are

$$\vec{a}_{1} = D\left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right)$$
$$\vec{a}_{2} = D(0, 1, 0)$$
(3)
$$\vec{a}_{3} = D\left(0, 0, 2\sqrt{\frac{2}{3}}\right),$$

where D is the nearest-neighbour distance. The volume of the primitive unit cell is

$$V_z = \sqrt{2} D^3.$$
 (4)

Two non-equivalent atoms are situated in the unit cell at  $\vec{\gamma}_{\mu}$  ( $\mu$  = 1, 2)

$$\vec{r}_1 = 0; \quad \vec{r}_2 = D\left(\frac{1}{2\sqrt{3}}, \frac{1}{2}, \sqrt{\frac{2}{3}}\right).$$
 (5)

The atom at the origin has six equivalent neighbours situated at

$$\vec{R}_{1} = \vec{a}_{1}; \qquad \vec{R}_{2} = -\vec{a}_{1}$$

$$\vec{R}_{3} = \vec{a}_{2}; \qquad \vec{R}_{4} = -\vec{a}_{2} \qquad (6)$$

$$\vec{R}_{5} = (\vec{a}_{1} - \vec{a}_{2}); \qquad \vec{R}_{6} = (\vec{a}_{2} - \vec{a}_{1})$$

and six non-equivalent nearest neighbours situated at

$$\vec{R}_{7} = \frac{1}{3}(\vec{a}_{1} + \vec{a}_{2}) + \frac{1}{2}\vec{a}_{3}; \quad \vec{R}_{10} = \frac{1}{3}(\vec{a}_{1} + \vec{a}_{2}) - \frac{1}{2}\vec{a}_{3}$$

$$\vec{R}_{8} = \frac{1}{3}\vec{a}_{1} - \frac{2}{3}\vec{a}_{2} + \frac{1}{2}\vec{a}_{3}; \quad \vec{R}_{11} = \frac{1}{3}\vec{a}_{1} - \frac{2}{3}\vec{a}_{2} - \frac{1}{2}\vec{a}_{3} \quad (7)$$

$$\vec{R}_{9} = -\frac{2}{3}\vec{a}_{1} + \frac{1}{3}\vec{a}_{2} + \frac{1}{2}\vec{a}_{3}; \quad \vec{R}_{12} = -\frac{2}{3}\vec{a}_{1} + \frac{1}{3}\vec{a}_{2} - \frac{1}{2}\vec{a}_{3}.$$

The base vectors of the reciprocal lattice are

$$\vec{b}_{1} = \frac{1}{D} \left( \frac{2}{\sqrt{3}}, 0, 0 \right)$$
  
$$\vec{b}_{2} = \frac{1}{D} \left( -\frac{1}{\sqrt{3}}, 1, 0 \right)$$
  
$$\vec{b}_{3} = \frac{1}{D} \left( 0, 0, \frac{1}{2} \sqrt{\frac{3}{2}} \right).$$
 (8)

We assume a nearest-neighbour central interaction of the type

$$\phi = -\frac{a}{r^{m}} + \frac{b}{r^{n}}.$$
 (9)

The equilibrium condition yields

$$ma = nb/D^{n-m}.$$
 (10)

The lattice frequencies are obtained by solving the determinant

$$\left| \begin{bmatrix} \mu & \nu \\ \mathbf{x} & \mathbf{y} \end{bmatrix} + \lambda \delta_{\mu\nu} \delta_{\mathbf{x}\mathbf{y}} \right| = \mathbf{0}, \qquad (11)$$

where  $\lambda = \omega^2$  and the coupling coefficients

$$\begin{bmatrix} \mu & \nu \\ \mathbf{x} & \mathbf{y} \end{bmatrix} = \frac{1}{M} \sum \phi \begin{pmatrix} n \\ \mu & \nu \\ \mathbf{x} & \mathbf{y} \end{pmatrix} \exp(-i2\pi \vec{\mathbf{K}} \cdot \vec{\mathbf{R}}_n) + \frac{1}{M} (\phi_0)_{\mathbf{x}\mathbf{y}} \delta_{\mu\nu} \delta_{\mathbf{x}\mathbf{y}}, \qquad (12)$$

where the summation is over nearest neighbours n;  $(\phi_0)_{xx}$  are the components of the self-force. M is the mass of the atoms. If  $\mu = \nu$  the summation is to be carried out over the six equivalent neighbours; if  $\mu \neq \nu$  the summation is to be taken over the six non-equivalent neighbours.  $\vec{K}$  is the wave vector of the lattice wave given by

$$\vec{K} = q_1 \vec{b}_1 + q_2 \vec{b}_2 + q_3 \vec{b}_3, \qquad (13)$$

where

$$-\frac{1}{2} \le q_i < \frac{1}{2}$$
 (14)

 $(\phi_0)_{xx}$  are obtained from the condition

$$\begin{bmatrix} 11\\ xx \end{bmatrix}_{\vec{K}=0}^{+} + \begin{bmatrix} 12\\ xx \end{bmatrix}_{\vec{K}=0}^{-} = 0$$
 (15)

$$\phi \begin{pmatrix} n \\ \mu \\ \nu \\ x \\ y \end{pmatrix} = Q x_n y_n$$
 (16)

where, at equilibrium,

$$Q = \left[\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\phi}{\partial r}\right)\right] = \frac{n(n-m)b}{D^{n+4}} = \frac{2\eta M}{D^2}$$
(17)

and  $\eta = [n(n-m)]/2D^{n+2}M$ .  $x_n$  and  $y_n$  are the components of  $\vec{R}_n$ . The coupling coefficients are given below:

$$\begin{bmatrix} 11\\ xx \end{bmatrix} = \begin{bmatrix} 22\\ xx \end{bmatrix} = -\eta [8 - 3\cos 2\pi q_1 - 3\cos 2\pi (q_1 - q_2)]$$
$$\begin{bmatrix} 11\\ yy \end{bmatrix} = \begin{bmatrix} 22\\ yy \end{bmatrix} = -\eta [8 - \cos 2\pi q_1 - 4\cos 2\pi q_2 - \cos 2\pi (q_1 - q_2)]$$
$$\begin{bmatrix} 11\\ zz \end{bmatrix} = \begin{bmatrix} 22\\ zz \end{bmatrix} = -8\eta$$
$$\begin{bmatrix} 11\\ yz \end{bmatrix} = \begin{bmatrix} 22\\ yz \end{bmatrix} = 0$$
$$\begin{bmatrix} 11\\ zx \end{bmatrix} = \begin{bmatrix} 22\\ yz \end{bmatrix} = 0$$
$$\begin{bmatrix} 11\\ zx \end{bmatrix} = \begin{bmatrix} 22\\ zx \end{bmatrix} = 0$$
$$\begin{bmatrix} 11\\ xy \end{bmatrix} = \begin{bmatrix} 22\\ zx \end{bmatrix} = +\eta \sqrt{3} \left[\cos 2\pi q_1 - \cos 2\pi (q_1 - q_2)\right]$$

$$\begin{bmatrix} 12\\ xx \end{bmatrix} = \frac{\eta}{3} \left[ 1 + e^{i2\pi q_2} + 4e^{i2\pi q_1} \right] \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ yy \end{bmatrix} = \eta \left[ 1 + e^{i2\pi q_2} \right] \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ zz \end{bmatrix} = \frac{8}{3} \eta \left[ 1 + e^{i2\pi q_2} + e^{i2\pi q_1} \right] \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ yz \end{bmatrix} = -i\eta \frac{4}{\sqrt{6}} \left[ 1 - e^{i2\pi q_2} \right] \sin \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ zx \end{bmatrix} = -i\eta \frac{2\sqrt{2}}{3} \left[ 1 + e^{i2\pi q_2} - 2e^{i2\pi q_1} \right] \sin \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ zx \end{bmatrix} = -i\eta \frac{2\sqrt{2}}{3} \left[ 1 + e^{i2\pi q_2} - 2e^{i2\pi q_1} \right] \sin \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$

$$\begin{bmatrix} 12\\ xy \end{bmatrix} = \frac{\eta}{\sqrt{3}} \left( 1 - e^{i2\pi q_2} \right) \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$$
and
$$\begin{bmatrix} 12\\ xy \end{bmatrix} = \left[ \frac{12}{yx} \right] = \left[ \frac{21}{yx} \right]^*.$$

The elastic constants are given by

$$C_{x\overline{x},y\overline{y}} = \widetilde{C}_{x\overline{x},y\overline{y}} + \delta \widetilde{C}_{x\overline{x},y\overline{y}} .$$

Here

$$\widetilde{C}_{x\overline{x},y\overline{y}} = \frac{1}{v_z} \sum \phi \begin{pmatrix} n \\ x & y \end{pmatrix} \overline{x}_n \overline{y}_n.$$
(19)

The sum is to be taken over all twelve neighbours of the atom at the origin.

$$\delta \widetilde{C}_{x\overline{x},y\overline{y}} = -\sum_{z} \frac{C_{xz\overline{x}}^{1} C_{yz\overline{y}}^{1}}{C_{zz}^{12}}$$
(20)

$$C_{xz\bar{x}v}^{1} = -\frac{1}{v_{z}} \sum \phi \begin{pmatrix} n \\ x \bar{x} \end{pmatrix} z_{n}, \qquad (21)$$

where the summation is over all neighbours,

$$\mathbf{C}_{\mathbf{z}\mathbf{z}}^{\mathbf{12}} = \frac{1}{\mathbf{v}_{\mathbf{z}}} \sum \phi \begin{pmatrix} n \\ 12 \\ \mathbf{z}\mathbf{z} \end{pmatrix}.$$
(22)

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The values of the elastic constants are

$$C_{xx,xx} = C_{yy,yy} = 58 \ \eta M/12\sqrt{2} D$$

$$C_{zz,zz} = 64 \ \eta M/12\sqrt{2} D$$

$$C_{xx,yy} = 22 \ \eta M/12\sqrt{2} D$$

$$C_{xx,zz} = 16 \ \eta M/12\sqrt{2} D$$

$$C_{zy,zy} = C_{yz,zy} = C_{xz,xz} = 16 \ \eta M/12\sqrt{2} D$$

$$C_{xy,xy} = \frac{1}{2} [C_{xx,xx} - C_{xx,yy}] = C_{yx,xy}.$$
(23)

By solving the determinant for various wave vectors in the Brillouin zone the frequencies can be obtained. The moments of the frequency distribution function are

$$\mu_2 = 8 \eta$$

$$\mu_4 = 80 \eta^2$$

$$\mu_6 = 912 \eta^3.$$
(24)

# 4. STRAIN DEPENDENCE OF $\begin{bmatrix} \mu \nu \\ x v \end{bmatrix}$

To determine  $(\gamma_j)_{x_x}$  and  $(\gamma_j)_{z_z}$ , we have to find the rate of change of  $\begin{bmatrix} \mu \nu \\ x y \end{bmatrix}$  with the strain parameters. Let a macroscopic strain be imposed on the lattice. This causes a change in the position vectors of the particles. In addition to the displacement due to the macroscopic elastic strain, there will also be an interlattice displacement. According to LEIBFRIED [2], extensions in the x- or y-directions cause a relative displacement of the two sub-lattices while an extension along z does not cause such a relative displacement. An extension  $x_x$  causes a relative displacement along the y-axis and an extension  $y_y$  causes a displacement in the opposite direction. Hexagonal symmetry demands that  $(\gamma_j)_{x_x} = (\gamma_j)_{y_y}$  for every frequency and

so the complications due to interlattice displacements can be avoided by imposing a uniform areal strain  $\epsilon$ ' =  $2x_x = 2y_y$  in the basal plane. There is no interlattice displacement now as the effect of  $x_x$  is cancelled by  $y_y$ . Then

$$\gamma_{j}^{*} = \frac{-\partial \log \omega_{j}}{\partial \epsilon^{*}} = \frac{-\partial \log \omega_{j}}{\partial \mathbf{x}_{x}} = (\gamma_{j})_{\mathbf{x}_{x}}.$$
 (25)

 $(\gamma_j)_{z_z}$  is evaluated by giving a uniform extension  $\zeta$  along the z-axis. For the sake of uniformity we shall write

$$\frac{-\partial \log \omega_{j}}{\partial \zeta} = (\gamma_{j})_{z_{z}} = \gamma_{j}^{*}.$$
 (26)

Then

$$\frac{\partial}{\partial \epsilon^{\prime}} \begin{bmatrix} \mu \nu \\ x y \end{bmatrix} = \frac{1}{M} \sum_{n} \frac{\partial}{\partial \epsilon^{\prime}} \phi \begin{pmatrix} n \\ \mu \nu \\ x y \end{pmatrix} \exp(-i2\pi \vec{K} \cdot \vec{R}_{n}) + \frac{1}{M} \frac{\partial}{\partial \epsilon^{\prime}} (\phi_{0})_{xy} \delta_{\mu\nu} \delta_{xy} \quad (27)$$

 $\vec{K} \cdot \vec{R}_n$  will be a mere number and is unaffected by the strain.

$$\frac{\partial}{\partial \epsilon^{\dagger}} \phi \begin{pmatrix} n \\ \mu \nu \\ x y \end{pmatrix} = \frac{\partial P}{\partial \epsilon^{\dagger}} \delta_{xy} + \left[ \frac{\partial Q}{\partial \epsilon^{\dagger}} + \frac{Q}{2} \left( 2 - \delta_{xz} - \delta_{yz} \right) \right] x_n y_n.$$
(28)

Here  $P = \frac{1}{r} \frac{\partial \phi}{\partial r}$ . In the equilibrium position this is zero; but  $\partial P/\partial \epsilon'$  exists. Similarly

$$\frac{\partial}{\partial \zeta} \begin{bmatrix} \mu \nu \\ x y \end{bmatrix} = \frac{1}{M} \sum_{n} \frac{\partial}{\partial \zeta} \phi \begin{pmatrix} n \\ \mu \nu \\ x y \end{pmatrix} \exp(-i2\pi \vec{K} \cdot \vec{R}_{n}) + \frac{1}{M} \frac{\partial}{\partial \zeta} (\phi_{0})_{xy} \delta_{\mu\nu} \delta_{xy}.$$
(29)

Here

$$\frac{\partial}{\partial \zeta} \phi \begin{pmatrix} n \\ \mu \nu \\ x y \end{pmatrix} = \left( \frac{\partial P}{\partial \zeta} \right) \delta_{xy} + \left[ \frac{\partial Q}{\partial \zeta} + Q(\delta_{xz} + \delta_{yz}) \right] x_n y_n.$$
(30)

For the six equivalent neighbours

$$\frac{\partial P}{\partial \epsilon'} = \left(\frac{\partial P}{\partial r}\right) \left(\frac{\partial R}{\partial \epsilon'}\right) = \eta M$$

$$\frac{\partial Q}{\partial \epsilon'} = -(n+m+6)\frac{\eta M}{D^2}$$

$$\frac{\partial P}{\partial \zeta} = 0$$

$$\frac{\partial Q}{\partial \zeta} = 0.$$
(31)

For the six non-equivalent neighbours

$$\frac{\partial P}{\partial \epsilon'} = \frac{\eta M}{3}$$

$$\frac{\partial Q}{\partial \epsilon'} = -(n+m+6)\frac{\eta M}{3D^2}$$

$$\frac{\partial P}{\partial \varsigma} = \frac{4\eta M}{3}$$

$$\frac{\partial Q}{\partial \varsigma} = -\frac{4}{3}(n+m+6)\frac{\eta M}{D^2}.$$
(32)

The expressions for 
$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} \mu y \\ xy \end{bmatrix}$$
 and  $\frac{\partial}{\partial \xi} \begin{bmatrix} \mu y \\ xy \end{bmatrix}$  are given below. In the following p stands for  $(n+m)$ .  

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ 1x \end{bmatrix} = \eta \left\{ \left(\frac{10}{3} p+4\right) - \left(\frac{3p}{2}+4\right) \left[\cos 2\pi q_{1} + \cos 2\pi (q_{1}-q_{2})\right] + 2\cos 2\pi q_{2} \right\}$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ xy \end{bmatrix} = \eta \left\{ \frac{4}{3} p+4 \right\} - \frac{p}{2} \left[\cos 2\pi q_{1} + \cos 2\pi (q_{1}-q_{2})\right] + (2p+6)\cos 2\pi q_{2} \right\}$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ xz \end{bmatrix} = \eta \left\{ \frac{4}{3} p+2 \left[\cos 2\pi q_{1} + \cos 2\pi (q_{1}-q_{2})\right] + (2p+6)\cos 2\pi q_{2} \right\}$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ xy \end{bmatrix} = \eta \left\{ \frac{4}{3} p+2 \left[\cos 2\pi q_{1} + \cos 2\pi (q_{1}-q_{2})\right] \right\}$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ xy \end{bmatrix} = -\eta \left\{ \frac{4}{3} p+2 \left[\cos 2\pi q_{1} - \cos 2\pi (q_{1}-q_{2})\right] \right\}$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 11 \\ xy \end{bmatrix} = -\eta (p+4) \frac{\sqrt{3}}{2} \left[\cos 2\pi q_{1} - \cos 2\pi (q_{1}-q_{2})\right]$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \left[ \left(\frac{p}{6} - 2\right) \left(1 + e^{12\pi q_{1}}\right) + \left(\frac{2}{3} p-2\right) e^{12\pi q_{1}} \right] \cos \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{1})$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \left[ \left(\frac{p}{2} - 2\right) \left(1 + e^{12\pi q_{1}}\right) - 2e^{12\pi q_{1}} \right] \cos \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{2})$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \left(\frac{4}{3} p+6\right) \left(1 + e^{12\pi q_{1}}\right) \cos \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{2})$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = \frac{i\eta}{3} \frac{2}{\sqrt{6}} (p+3) \left(1 - e^{i2\pi q_{1}}\right) \sin \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{2})$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \frac{p}{\sqrt{3}} (1 - e^{i2\pi q_{1}}) \cos \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{2})$$

$$\frac{\partial}{\partial \epsilon^{i}} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \frac{p}{\sqrt{3}} (1 - e^{i2\pi q_{1}}) \cos \pi q_{3} e^{-i\frac{2\pi}{3}} (q_{1}+q_{2})$$

$$(34)$$

| $\frac{\partial}{\partial \zeta} \begin{bmatrix} 11\\ zz \end{bmatrix} = \left(\frac{16}{3} p + 8\right) \eta$   |                 |
|--|-----------------|
| $\frac{\partial}{\partial \xi} \begin{bmatrix} 11\\ yz \end{bmatrix} = 0$  |                 |
| $\frac{\partial}{\partial \zeta} \begin{bmatrix} 11\\ zx \end{bmatrix} = 0$  |                 |
| $\frac{\partial}{\partial \zeta} \begin{bmatrix} 11 \\ xy \end{bmatrix} = 0$   |                 |
| $\frac{\partial}{\partial \xi} \begin{bmatrix} 12\\ xx \end{bmatrix} = -\frac{\eta}{3} \left[ \left( \frac{2}{3} p - 4 \right) (1 + e^{i2\pi q_2}) + \left( \frac{8}{3} p + 8 \right) e^{i2\pi q_1} \right] \cos \pi q_3 e^{-i\frac{2\pi}{3} (q_1 + q_2)}$ |                 |
| $\frac{\partial}{\partial \xi} \left[ \begin{array}{c} 12\\ yy \end{array} \right] = -\frac{\eta}{3} \left[ (2p+4)(1+e^{i2\pi q_2}) - 8e^{i2\pi q_1} \right] \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1+q_2)}$   | (34)<br>(cont.) |
| $\frac{\partial}{\partial \zeta} \begin{bmatrix} 12\\ zz \end{bmatrix} = -\frac{\eta}{3} \left[ \left( \frac{16}{3} p + 8 \right) \left( 1 + e^{i2\pi q_1} + e^{i2\pi q_2} \right) \right] \cos \pi q_3 e^{-i\frac{2\pi}{3} (q_1 + q_2)}$                  |                 |
| $\frac{\partial}{\partial \xi} \begin{bmatrix} 12 \\ xy \end{bmatrix} = -\frac{\eta}{3} \frac{2}{\sqrt{3}} (p+6)(1-e^{i2\pi q_2}) \cos \pi q_3 e^{-i\frac{2\pi}{3}(q_1+q_2)}$  |                 |
| $\frac{\partial}{\partial \xi} \begin{bmatrix} 12 \\ yz \end{bmatrix} = \frac{i\eta}{3} \frac{2}{\sqrt{6}} (4p + 18) (1 - e^{i2\pi q_2}) \sin \pi q_3 e^{-i\frac{2\pi}{3}(q_1 + q_2)}$   |                 |
| $\frac{\partial}{\partial \xi} \begin{bmatrix} 12\\ zx \end{bmatrix} = \frac{i\eta}{3} \frac{\sqrt{2}}{3} (4p+18)(1+e^{i2\pi q_2}-2e^{i2\pi q_1}) \sin \pi q_3 e^{-i\frac{2\pi}{3}(q_1+q_2)}.$   |                 |
|  |                 |

## 5. GRÜNEISEN PARAMETERS $\gamma_{j}^{\mu}$ AND $\gamma_{j}^{\mu}$ FOR CERTAIN WAVE VECTORS

For wave vectors of the type  $(0, 0, q_3)$  and  $(q_1, 0, 0)$  the frequencies and the Grüneisen parameters  $\gamma_1^i$  and  $\gamma_j^{\mu}$  have been calculated and given in Table I. These calculations have been made for the case m = 6 and n = 12. We see from Table I that there is a wide range of variation in the  $\gamma^{i}$ - and  $\gamma^{i}$ -values for different directions. In particular the  $\gamma^{i}$ -values for the acoustic branches change rapidly as the wave-vector direction is turned through 90° from the hexagonal axis. This is more expressly seen in Table II. However the  $\gamma^{i}$  and  $\gamma^{ii}$  values do not vary so pronouncedly with magnitude of the wave vector.

#### TABLE I

## FREQUENCIES OF VIBRATION AND GRÜNEISEN PARAMETERS $\gamma'$ AND $\gamma''$ FOR WAVE VECTORS OF THE TYPE (0, 0, q<sub>3</sub>) AND (q<sub>1</sub>, 0, 0) IN A HEXAGONAL CLOSE-PACKED LATTICE FOR THE CASE m = 6 AND n = 12

| Wave vector type $(0, 0, q_3)$ $q_3 =$ | 0.1    | 0.2    | 0.3     | 0.4    | 0.5     |
|--|--------|--------|---------|--------|---------|
| Acoustic branch                        | 0.391  | 1.528  | 3, 298  | 5 528  | 8 000   |
| Acoustic Dranen                        | 1.88   | 1.020  | 1.88    | 1.88   | 1.88    |
|  | 6.50   | 6, 50  | 6, 50   | 6, 50  | 6 50    |
| Acoustic branch                        |        |        |         | 0.00   | 0.00    |
| (Doubly degenerate)                    | 0.098  | 0.382  | 0.824   | 1.382  | 2,000   |
| (Doubly degenerate)                    | 1.00   | 1.00   | 1.00    | 1.00   | 1 00    |
|  | 6.00   | 6.00   | 6.00    | 6.00   | 6 00    |
| Ontical branch                         | 15 608 | 14 472 | 12 702  | 10 472 | 8 000   |
| optical blanch                         | 1 88   | 1.88   | 1 88    | 1.88   | 1 88    |
|  | 6.50   | 6 50   | 6 50    | 6 50   | 6 50    |
| Ontical branch                         |        | 0.00   |         |        | 0.00    |
| (Doubly degenerate)                    | 3 902  | 3 618  | 3 176   | 2 618  | 2 000   |
| (Doubly degenerate)                    | 1.00   | 1 00   | 1 00    | 1.00   | 1.00    |
| ·                                      | 6.00   | 6 00   | 6:00    | 6.00   | 6.00    |
|  |        | 0.00   |         |        |         |
| Wave vector type                       |        |        |         |        |         |
| (a.0.0) a =                            | 0,1    | 0.2    | 0.3     | 0.4    | 0.5     |
|  |        |        |         |        |         |
| Acoustic branch                        | 1.233  | 4.481  | 8.561   | 11.969 | 13. 314 |
|  | 4.86   | 4.83   | 4.80    | 4.74   | 4.70    |
|  | 0.35   | 0.37   | 0.39    | 0.41   | 0.40    |
| Acoustic branch                        | 0, 382 | 1. 382 | 2.618   | 3.618  | 4.000   |
|  | 4.33   | 4.33   | 4.33    | 4.33   | 4.33    |
|  | -0.67  | -0,67  | -0.67   | -0.67  | -0.67   |
| Acoustic branch                        | 0.346  | 1.338  | - 2.826 | 4. 538 | 5. 336  |
|  | 0.78   | 0,85   | 0.95    | 1.01   | 1.12    |
|  | 6, 53  | 6, 52  | 6, 50   | 6.27   | 6. 50   |
| Optical branch                         | 15.654 | 14.662 | 13, 142 | 11.462 | 10.666  |
| · r                                    | 1.85   | 1.76   | 1.67    | 1.59   | 1.50    |
|  | 6.50   | 6, 50  | 6, 53   | 6, 59  | 6, 50   |
| Ontical branch                         | 5, 059 | 7, 811 | 11, 147 | 13.74  | 14.67   |
| option blanch                          | 1.95   | 3.22   | 3.76    | 4, 32  | 4,45    |
|  | 4.66   | 2.86   | 1.85    | 1.39   | 1.27    |
| Ontical branch                         | 4 389  | 5 382  | 6 618   | 7 618  | 8 000   |
| Sputar Mation                          | 1 29   | 1 95   | 2.45    | 2 74   | 0.000   |
|  | 5 54   | 4 63   | 3.80    | 3 47   | 2.00    |
|  | 0.01   | 7,00   | 0,00    | 0.11   | 0.00    |
|  |        |        |         |        |         |

## 6. TEMPERATURE VARIATION OF THE EFFECTIVE GRÜNEISEN PARAMETERS $\bar{\gamma}'$ AND $\bar{\gamma}''$

The effective Grüneisen parameters are defined by

$$\overline{\gamma}'' = \sum_{j} \gamma_{j}' E(\hbar\omega_{j}/kT) / \sum_{j} E(\hbar\omega_{j}/kT)$$

$$\overline{\gamma}'' = \sum_{j} \gamma_{j}'' E(\hbar\omega_{j}/kT) / \sum_{j} E(\hbar\omega_{j}/kT) .$$
(35)

 $\bar{\gamma}'$  and  $\bar{\gamma}''$  are temperature dependent. Following BARRON [3], we can define a set of parameters

$$\gamma^{\dagger}(1) = \sum_{j} \gamma_{j}^{\dagger} \omega_{j}^{\dagger} / \sum_{j} \omega_{j}^{\dagger} = -\frac{1}{1} \frac{\partial \log \mu_{1}}{\partial \epsilon^{\dagger}}$$

$$\gamma^{\dagger}(1) = \sum_{j} \gamma_{j}^{\dagger} \omega_{j}^{\dagger} / \sum_{j} \omega_{j}^{\dagger} = -\frac{1}{1} \frac{\partial \log \mu_{1}}{\partial \zeta}.$$
(36)

 $\mu_1$  is the l-th moment of the frequency distribution function. In terms of these parameters, the high-temperature limits of  $\bar{\gamma}^{\rm t}$  and  $\bar{\gamma}^{\rm m}$  are

$$\overline{\gamma}^{n}_{\infty} = \gamma^{n}(0)$$

$$\overline{\gamma}^{n}_{\infty} = \gamma^{n}(0) .$$

$$(37)$$

The low-temperature limits of these parameters are

.

$$\begin{split} \bar{\gamma}_{0}^{\dagger} &= \gamma^{\dagger}(-3) = \int \sum_{j} \gamma_{j}^{\dagger} d\Omega / v_{j}^{3} / \int \sum_{j} d\Omega / v_{j}^{3} \\ \bar{\gamma}_{0}^{\dagger} &= \gamma^{\dagger}(-3) = \int \sum_{j} \gamma_{j}^{\dagger} d\Omega / v_{j}^{3} / \int \sum_{j} d\Omega / v_{j}^{3} . \end{split}$$

$$\end{split}$$

$$(38)$$

 $v_j$  (j=1, 2, 3) represent the acoustic wave velocities and the integration is carried out over all directions in space.

## 7. CALCULATION OF THE HIGH-TEMPERATURE LIMITS OF $\overline{\gamma}$ ' AND $\overline{\gamma}$ "

The high-temperature limits  $\overline{\gamma}_{\omega}^{\dagger}$  and  $\overline{\gamma}_{\omega}^{\dagger}$  can be found by the method of BARRON [3]. The parameters  $\gamma'(2)$ ,  $\gamma'(4)$  and  $\gamma'(6)$ ;  $\gamma''(2)$ ,  $\gamma''(4)$ , and  $\gamma''(6)$  can be obtained from the expressions for  $\mu_2$ ,  $\mu_4$  and  $\mu_6$ . They are

$$\gamma'(2) = \gamma''(2) = \frac{p}{6} + \frac{1}{6}$$
  
$$\gamma'(4) = \gamma''(4) = \frac{p}{6} + \frac{7}{30}$$
 (39)

$$\gamma'(6) = \gamma''(6) = \frac{p}{6} + \frac{47}{166}$$
.

In the next section we shall see how  $\gamma'(+3)$  and  $\gamma''(-3)$  could be evaluated. If a plot is made of  $\gamma(p)$  versus p, the intercept on the axis where p=0 gives the high-temperature limits of  $\overline{\gamma}'$  and  $\overline{\gamma}''$ .

### 8. CALCULATION OF THE LOW-TEMPERATURE LIMITS OF $\overline{\gamma}$ ' AND $\overline{\gamma}$ "

The wave velocities of the acoustic waves are given by solving the Christoffel determinant

$$\left|\rho v^{2} \delta_{xy} - \Delta_{xy}\right| = 0, \qquad (40)$$

where

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$$\Delta_{\mathbf{x}\mathbf{y}} = \sum_{\overline{\mathbf{x}}, \overline{\mathbf{y}}} \mathbf{C}_{\mathbf{x}\overline{\mathbf{x}}, \mathbf{y}\overline{\mathbf{y}}} \mathbf{S}_{\overline{\mathbf{x}}} \mathbf{S}_{\overline{\mathbf{y}}}:$$
(41)

here  $S_x$ ,  $S_y$ ,  $S_z$  are the direction cosines of the wave vector  $\vec{K}$  and  $C_{x\bar{x},y\bar{y}}$  are the elastic constants. When the crystal is not strained

$$C_{x\overline{x}, y\overline{y}} = C_{y\overline{y}, x\overline{x}} = C_{\overline{x}x, y\overline{y}}.$$
(42)

When the crystal is strained

$$C_{\mathbf{x}\overline{\mathbf{x}},\,\mathbf{y}\overline{\mathbf{y}}} = C_{\mathbf{y}\overline{\mathbf{y}},\,\mathbf{x}\overline{\mathbf{x}}} \neq C_{\overline{\mathbf{x}}\mathbf{x},\,\mathbf{y}\overline{\mathbf{y}}}.$$
(43)

To calculate  $\gamma_j^{\prime}$  and  $\gamma_j^{\prime \prime}$  we need the derivatives  $(\partial/\partial \epsilon')C_{x\overline{x},y\overline{y}}$  and  $(\partial/\partial \epsilon')C_{x\overline{x},y\overline{y}}$ . They have been calculated from the expressions (19) - (22) and (29 - 32). The expressions are given below:

$$\frac{\partial}{\partial \epsilon'} C_{xx,xx} = -\left[\frac{83}{3}p + 66\right] \frac{\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \epsilon'} C_{xx,yy} = -\left[\frac{29}{3}p + 38\right] \frac{\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \epsilon'} C_{zz,zz} = -\left[\frac{32}{3}p + 112\right] \frac{\eta M}{12\sqrt{2D}}$$
(44)

| $\frac{\partial}{\partial \epsilon'}$ C <sub>xx,zz</sub> = $-\frac{8}{3}$ (p+6) $\frac{\eta M}{12\sqrt{2D}}$ |
|--|
| $\frac{\partial}{\partial \epsilon^{\dagger}} C_{xy,xy} = -(9p-6) \frac{\eta M}{12\sqrt{2D}}$                |
| $\frac{\partial}{\partial \epsilon^{\dagger}} C_{xy, yx} = -(9p+34) \frac{\eta M}{12\sqrt{2D}}$              |
| $\frac{\partial}{\partial \epsilon^{\dagger}} C_{xz, xz} = -\frac{8}{3} p \frac{\eta M}{12\sqrt{2D}}$        |
| $\frac{\partial}{\partial \epsilon}$ , $C_{zx, zx} = -\frac{8}{3}(p-9)\frac{\eta M}{12\sqrt{2D}}$            |
| $\frac{\partial}{\partial \epsilon^{\dagger}} C_{xz, zx} = -\frac{8}{3} (p+6) \frac{\eta M}{12\sqrt{2D}}$    |
|  |
| $\frac{\partial}{\partial \zeta} C_{xx, xx} = -\left[\frac{8}{3}p + 50\right] \frac{\eta M}{12\sqrt{2D}}$    |
| $\frac{\partial}{\partial \zeta} C_{xx, yy} = -\left[\frac{8}{3}p + 46\right] \frac{\eta M}{12\sqrt{2D}}$    |
| $\frac{\partial}{\partial \xi} C_{zz, zz} = -\frac{128}{3} p \frac{\eta M}{12\sqrt{2D}}$                     |
| $\frac{\partial}{\partial \zeta} C_{xx, zz} = -\left[\frac{32}{3}p + 48\right] \frac{\eta M}{12\sqrt{2D}}$   |
| $\frac{\partial}{\partial \zeta} C_{xy,xy} = + \frac{6\eta M}{12\sqrt{2D}}$                                  |
| $\frac{\partial}{\partial \xi} C_{xy, yx} = -\frac{10\eta M}{12\sqrt{2D}}$                                   |
| $\frac{\partial}{\partial \xi} C_{xz,xz} = -\left[\frac{32}{3}p - 16\right] \frac{\eta M}{12\sqrt{2D}}$      |
| $\frac{\partial}{\partial \zeta} C_{zx, zx} = -\left[\frac{32}{3}p + 32\right] \frac{\eta M}{12\sqrt{2D}}$   |
| $\frac{\partial}{\partial \zeta} C_{xz, zx} = -\left[\frac{32}{3}p + 48\right] \frac{\eta M}{12\sqrt{2D}} .$ |

.

(44) (cont.)

(45)

These relations can be checked as follows. If the stress imposed on the lattice is given by the components  $\mathrm{S}_{xy}$  , then

22\*

$$S_{xx} = [C_{yx,yx} - C_{xy,yx}],$$
 (46)

 $C_{x\overline{x},y\overline{y}}$  being the elastic constants in the strained lattice (BORN and HUANG [4]). So the coefficients in Eq. (44) should satisfy the following relations

$$\frac{\partial}{\partial \epsilon^{\dagger}} C_{zx, zx} - \frac{\partial}{\partial \epsilon^{\dagger}} C_{xz, zx} = \frac{40\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \epsilon^{\dagger}} C_{xy, xy} - \frac{\partial}{\partial \epsilon^{\dagger}} C_{xy, yx} = \frac{40\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \epsilon^{\dagger}} C_{xz, xz} - \frac{\partial}{\partial \epsilon^{\dagger}} C_{zx, xz} = \frac{16\eta M}{12\sqrt{2D}}.$$
(47)

The coefficients in Eq. (45) should satisfy the following relations.

$$\frac{\partial}{\partial \xi} C_{zx, zx} - \frac{\partial}{\partial \xi} C_{xz, zx} = \frac{16\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \xi} C_{xy, xy} - \frac{\partial}{\partial \xi} C_{xy, yx} = \frac{16\eta M}{12\sqrt{2D}}$$

$$\frac{\partial}{\partial \xi} C_{xz, xz} - \frac{\partial}{\partial \xi} C_{zx, xz} = \frac{64\eta M}{12\sqrt{2D}} .$$
(48)

In a hexagonal lattice the velocities depend only on the angle  $\theta$  between the z-axis and the direction of wave propagation. The velocities  $v_1$ ,  $v_2$  and  $v_3$  were calculated for the following angles  $\theta = 5$ , 15, 25, 35, 45, 55, 65, 75, and 85° and  $\phi = 0$ . The determinant then factorizes out to give

$$\lambda - \Delta_{yy} = 0 \qquad \lambda = \rho v_2^2 \qquad (49)$$
$$\lambda^2 - P\lambda + Q = 0 \qquad \lambda = \rho v_{1,3}^2$$
$$P = \Delta_{xx} + \Delta_{zz} \qquad (50)$$
$$Q = \Delta_{xx} \Delta_{zz} - \Delta_{xz}^2.$$

Equation (49) gives the velocity  $v_2$  of one transverse acoustic branch and Eq. (50) gives the velocities of the longitudinal acoustic branch  $v_1$  and the other transverse acoustic branch  $v_3$ . The Grüneisen parameters are given by

$$\gamma_{i}^{*} = -\frac{1}{v_{i}} \frac{\partial v_{i}}{\partial \epsilon^{*}} + \frac{1}{2} \sin^{2} \theta$$

$$\gamma_{i}^{*} = -\frac{1}{v_{i}} \frac{\partial v_{i}}{\partial \zeta} + \cos^{2} \theta.$$
(51)

#### TABLE II

## GRUNEISEN PARAMETERS FOR THE DIFFERENT ELASTIC WAVES TRAVELLING AT VARIOUS ANGLES $\theta$ WITH THE HEXAGONAL AXIS IN A HEXAGONAL CLOSE-PACKED LATTICE WITH NEAREST-NEIGHBOUR CENTRAL INTERACTION FOR m= 6, n= 12

| Angle<br>(deg.) | v <sup>2</sup> <sub>1</sub> | $\gamma_1^*$ | γ"    | V 2 2 | γ',   | γ"    | V 2<br>3 | γ'3   | γ" <sub>3</sub> |
|-----------------|-----------------------------|--------------|-------|-------|-------|-------|----------|-------|-----------------|
| 5               | 63.80                       | 1.87         | 6.50  | 16.02 | 1.03  | 5.94  | 16.16    | 1.10  | 5.83            |
| 15              | 62.26                       | 1.86         | 6.50  | 16.13 | 1.25  | 5. 51 | 17.34    | 1. 78 | 4.65            |
| 25              | 59.59                       | 1.87         | 6.45  | 16.36 | 1.65  | 4.71  | 19.34    | 2.75  | 2.98            |
| 35              | 56.64                       | 2.00         | 6.14  | 16.66 | 2.17  | 3.66  | 21.38    | 3. 53 | 1.65            |
| 45              | 54. 57                      | 2.43         | 5.24  | 17.00 | 2.75  | 2.50  | 22.43    | 3. 72 | 1.36            |
| <b>5</b> 5      | 54.25                       | 3.19         | 3. 69 | 17.34 | 3. 31 | 1.38  | 21.72    | 3.21  | 2. 31 ·         |
| 65              | 55.38                       | 3.98         | 2. 09 | 17.64 | 3.79  | 0.43  | 19.70    | 2.31  | 3, 90           |
| 75              | 56.89                       | 4.55         | 0.96  | 17.87 | 4.13  | -0.26 | 17.52    | 1.45  | 5.42            |
| 85              | 57.87                       | 4.84         | 0.41  | 17.98 | 4.31  | -0.62 | 16.18    | 0.83  | 6.37            |

Note:  $v_i^2$  are expressed in units of  $\eta D^2/24\sqrt{2}$ .

 $\gamma_i^{n}$  and  $\gamma_i^{n}$  are calculated using relations (41)-(51). The values of  $\gamma_i^{i}$  and  $\gamma_i^{n}$  calculated thus for different values of  $\theta$  are given in Table II. The calculations have been made for the case m=6 and n=12.

Table II illustrates clearly the rapid variation of  $\gamma^{1}$  and  $\gamma^{n}$  with a change in the direction of the wave propagation. In contrast, the change in the values of the velocities with direction is quite small. The range of variation of  $\gamma^{n}$  is much more than the range of variation of  $\gamma^{1}$ . The transverse acoustic branch 2 has a negative Grüneisen parameter  $\gamma^{n}$  when the wave vector lies in the basal plane. This means that the frequencies of the above branch increase with an elongation along the z-axis. The value of  $\gamma^{n}$  for this branch is independent of the values of m and n. This is therefore a peculiar feature characterizing a hcp lattice with nearest-neighbour central interaction. The values of  $\gamma^{n}(-3)$  can be obtained from Table II by numerical integration.

## 9. RESULTS AND DISCUSSION

The values of  $\gamma'(2)$ ,  $\gamma'(4)$ ,  $\gamma'(6)$  and  $\gamma'(-3)$  are given in Table III for three different values of m and n. The values of  $\gamma'(0)$  found by interpolation are also given. For all values of m and n,  $\gamma'(1) = \gamma''(1)$ . This should be expected because the hcp lattice represents one of the ways of closepacking spheres. From Table III it is seen that for a hcp lattice with nearest-

#### TABLE III

| m | n  | γ'(2) | γ'(4) | γ'(6) | γ'(-3) | γ'(0) |
|---|----|-------|-------|-------|--------|-------|
| 6 | 12 | 3. 17 | 3.23  | 3. 28 | 2.78   | 3.07  |
| 4 | 8  | 2.17  | 2.23  | 2.28  | 1.78   | 2.07  |
| 1 | 5  | 1.17  | 1.23  | 1.28  | 0.78   | 1.07  |

#### $\gamma'(1)$ FOR A HEXAGONAL CLOSE-PACKED LATTICE

neighbour central interaction, the Grüneisen constant  $\bar{\gamma} = \beta V/XC_V = \bar{\gamma}^{\dagger} = \bar{\gamma}^{\dagger}$ should decrease as the temperature is reduced and the difference between the high and low temperature limits should be 0.3 irrespective of the values of m and n. This result is similar to the results of BARRON [3], for the analogous case of a face-centred cubic lattice. Barron finds that the difference  $\bar{\gamma}_{\infty} - \bar{\gamma}_0$  is reduced when interaction with farther neighbours is taken into account. A similar behaviour is to be expected in the hcp lattice.

Magnesium is a hexagonal metal having a c/a value almost equal to the theoretical value for a hcp lattice. COLLINS [5] has determined the phonon dispersion relations in magnesium using inelastic scattering of neutrons from a single crystal of the metal. To account for the dispersion relations he finds that interactions up to fourth neighbours have to be taken into account. The interaction between the first twelve neighbours is predominantly central. The elastic constants of magnesium have been reported in HUNTINGTON's article [6] and are quoted as follows in units of 10<sup>11</sup> dyn/cm<sup>2</sup>:  $C_{11} = 5.97$ ,  $C_{12} = 2.62$ ,  $C_{33} = 6.17$ ,  $C_{44} = 1.64$  and  $C_{13} = 2.17$ . These values of the elastic constants are almost in the same ratio as the theoretical values in Eq. (23). This indicates that the conclusions of the present work may not be completely irrelevant to the case of magnesium. Since the forces are found by Collins to extend up to fourth neighbours, we should expect  $\overline{\gamma}_{\infty} - \overline{\gamma}_{0}$ to be less than 0.3. WHITE [1] has reported measurements of the thermal expansion coefficients of magnesium from 283 to 6°K. He finds that the effective Grüneisen parameter  $ar{m{\gamma}}$  decreases as the temperature is reduced and the difference  $\bar{\gamma}_{\infty}$  - $\bar{\gamma}_0$  is approximately 0.1. These results are consistent with our expectations. On the present model,  $\bar{\gamma}' = \bar{\gamma}''$  for very high and very low temperatures and so the expansion coefficients  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  must be in the ratio

$$\frac{\alpha_{11}}{\alpha_{11}} = \frac{2\mathbf{s}_{13} + \mathbf{s}_{33}}{\mathbf{s}_{11} + \mathbf{s}_{12} + \mathbf{s}_{13}}.$$
 (52)

From the measured values of the elastic constants we should expect  $\alpha_{\parallel}/\alpha_{\perp}$  for magnesium to be in the ratio 0.97/0.91 from Eq. (52). The values of  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  at 283°K are 26.8 and 25.1×10<sup>-6</sup>/°K, respectively. These values are in exactly the same ratio as is expected. However at low temperatures this relation is not satisfied,  $\alpha_{\perp}$  being more than  $\alpha_{\parallel}$ .

To extend the theory to cases where the c/a ratio differs from that for a hcp lattice, a cylindrically symmetric potential may be assumed and the departure from spherical symmetry may be related to the c/a ratio. Such theoretical calculations may have relevance to the thermal expansion of other hexagonal metals like zinc. Such work is in progress.

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## THERMAL VIBRATIONS OF BETA-BRASS AND THE ORDER-DISORDER TRANSITION

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#### Abstract — Résumé — Аннотация — Resumen

THERMAL VIBRATIONS OF BETA-BRASS AND THE ORDER-DISORDER TRANSITION. Observations of normal modes of vibration of the ordered alloy of copper and zinc, 8-brass, at 296°K have been made by means of the coherent one-phonon scattering of slow neutrons from single crystal specimens. The triple-axis crystal spectrometer at the NRU reactor has been used to measure the frequencies of modes propagating along the high-symmetry directions [00 $\zeta$ ], [ $\zeta\zeta\zeta$ ], [ $\zeta\zeta\zeta$ ] and [ $\frac{1}{2}\zeta\zeta$ ]. The dispersion curves resemble those of a simple body-centred cubic crystal such as Na, except that certain degeneracies are lifted, mainly by reason of the difference between the second nearest neighbour Cu-Cu and Zn-Zn forces. For example, we find two distinct modes of wave vector (0.5, 0.5, 0.5) (in reciprocal lattice units), whose frequencies are (4.21±0.06) and  $(4.93 \pm 0.10) \times 10^{12}$  c/s respectively. Interatomic force models which provide a satisfactory description of the 296°K results are briefly mentioned. Several normal modes have been studied at elevated temperatures, particularly in the vicinity of the order-disorder phase transition at about 727°K. There are no striking changes in the overall structure of the dispersion curves as a result of the vanishing of the long range order at this temperature, although the various "splittings" observed at 296°K are blurred out into more or less continuous "bands" of frequencies. As the temperature rises, the frequencies generally decrease, and the energy widths increase. These changes take place in a smooth manner, except for two longitudinal optic modes, observed at positions (1.27, 1.27, 0) and (1.2, 1.2, 0.2) in reciprocal space, which display sharp increases in energy width at the transition temperature. No reasonable explanation of these effects has yet been found.

VIBRATIONS THERMIQUES DANS LE LAITON BÊTA ET TRANSFORMATION ORDRE-DÉSORDRE. On a observé les modes normaux de vibration du laiton bêta, alliage ordonné de cuivre et de zinc, à une température de 296°K au moyen de la diffusion cohérente de neutrons lents à un phonon par des monocristaux. Le spectromètre triaxial à cristal du réacteur NRU a été utilisé pour mesurer les fréquences de modes se propageant le long de directions de haute symétrie [ $00\zeta$ ], [ $\zeta\zeta\zeta$ 0], [ $\zeta\zeta\zeta$ ] et [ $\frac{1}{2}\frac{1}{2}\zeta$ ]. Les courbes de dispersion ressemblent à celles d'un cristal à réseau cubique centré simple, comme Na, à l'exception près que certaines dégénérescences disparaissent, principalement du fait des différences entre les forces Cu-Cu et Zn-Zn entre un atome et le deuxième atome le plus proche. C'est ainsi que les auteurs ont trouvé deux modes de vecteurs d'onde distincts (0.5, 0.5, 0.5) (en unités de réseau réciproque), dont les fréquences sont égales respectivement à  $(4,21 \pm 0,06)$  et  $(4,93 \pm 0,10) \cdot 10^{12}$  c/s. Les auteurs mentionnent brièvement des modèles de force interatomique qui donnent une description satisfaisante des résultats obtenus à la température de 296°K. Ils ont étudié plusieurs modes normaux à des températures élevées, en particulier au voisinage de la transformation ordredésordre à environ 727°K. On n'observe pas de différence très nette dans la structure générale des courbes de dispersion du fait de la disparition de l'ordre à grande distance à cette température bien que les diverses «ramifications» («splittings») observées à 296°K se confondent en «bandes» de fréquences plus ou moins continues. L'élévation de la température s'accompagne de façon générale d'une diminution des fréquences et d'une augmentation de la largeur des énergies. Ces variations se produisent progressivement, à l'exception de deux modes optiques longitudinaux, observés aux positions (1,27, 1,27, 0) et (1,2, 1,2, 0,2) dans un espace réciproque, qui accusent une augmentation brusque de la largeur des énergies à la température de transformation. Jusqu'à présent, aucune explication logique de ces effets n'a été donnée.

ТЕПЛОВЫЕ КОЛЕБАНИЯ БЕТА – ЛАТУНИ И ПЕРЕХОД ИЗ УПОРЯДОЧЕННОГО СО-СТОЯНИЯ В РАЗУПОРЯДОЧЕННОЕ. Наблюдения за обычными формами колебания упорядоченкого сплава меди и цинка (β-латунь) при 296°К проводились с помощью когерентного одно-

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фононного рассеяния медленных нейтронов на монокристаллических образцах. Для измерения частот колебаний, распространяющихся вдоль высокосимметричных направлений (ООУ),  $[\xi \zeta 0], [\xi \zeta \zeta]$  и  $[\frac{1}{2}, \frac{1}{2}, \zeta]$  использовался трехосный кристаллический спектрометр на реакторе NRU. Кривые дисперсии напоминают кривые дисперсии простого объемно-центрированного кубического кристалла, например Na, за исключением того, что появляются некоторые вырождения, в основном ввиду различия между вторым ближайшим соседом Cu-Cu и силами Zn-Zn. Например, мы находим две различные формы волнового вектора (0.5,0.5,0.5) (в обратных единицах решетки), частоты которых соответственно составляют (4,21±0,06) и (4,93 ±10)·10<sup>12</sup> герц. Кратко упоминаются модели межатомных сил, которые представляют удовлетворительное описание результатов, полученных при 296°К. Некоторые нормальные формы колебаний изучены при повышенных температурах, особенно в области перехода из упорядоченного состояния в неупорядоченное при температуре приблизительно 727°К. В общей структуре кривых дисперсий не отмечается значительных изменений в результате исчезновения порядка дальнего расстояния при этой температуре, хотя различные "расщепления", наблюдаемые при 296°К, расплываются в более или менее постоянные "полосы" частот. При повышении температуры частоты в целом уменьшаются, а энергетические ширины увеличиваются. Эти изменения происходят плавно, за исключением двух продольных оптических форм, наблюдаемых в положениях (1,27; 1,27; 0) и (1,2; 1,2; 0,2) в обратном пространстве, в которых проявляются резкие увеличения энергетических ширин при температуре перехода. Никакого разумного объяснения для этих эффектов еще не найдено.

VIBRACIONES TERMICAS DEL LATON BETA Y TRANSICION ORDEN-DESORDEN. Los autores han estudiado los modos normales de vibración de la aleación ordenada de cobre y cinc (latón B) a 296°K por dispersión monofonónica coherente de neutrones lentos en muestras monocristalinas. Utilizan el espectrómetro triaxial de cristal del reactor NRU para medir las frecuencias de los modos que se propagan a lo largo de las direcciones de simetría elevada [005], [550], [555] y  $\left[\frac{1}{2}\frac{1}{2}5\right]$ . Las curvas de dispersión se asemejan a las de un cristal cúbico simple centrado en el cuerpo, tal como el Na, con la salvedad de que se eliminan ciertas degeneraciones, principalmente en razón de la diferencia existente entre las fuerzas que actúan entre los segundos átomos vecinos Cu-Cu y Zn-Zn. Por ejemplo, se observan dos modos distintos de vectores de onda (0,5, 0,5, 0,5) (en unidades reticulares reciprocas), cuyas frecuencias son (4,21±0,06) y (4,93±0,10) · 1012 c/s, respectivamente. Se exponen brevemente modelos de fuerzas interatômicas que explican satisfactoriamente los resultados obtenidos a 296°K. Se han estudiado varios modos normales a temperaturas elevadas, sobre todo en las proximidades de la transición de fase orden-desorden, a unos 727°K. No se observan cambios acusados en la estructura general de las curvas de dispersión como resultado de la desaparición del orden de largo alcance a esta temperatura, aunque los diferentes «desdoblamientos» observados a 296°K se unen confusamente en «bandas» de frecuencia más o menos continuas. Las frecuencias suelen disminuir al elevarse la temperatura, en tanto que las anchuras energéticas aumentan. Estas alteraciones tienen lugar gradualmente, excepto en el caso de dos modos ópticos longitudinales, observados en las posiciones (1,27, 1,27, 0) y (1,2, 1,2, 0,2) en el espacio recíproco, que presentan acusados aumentos de la anchura energética a la temperatura de transición. Estos efectos no se han podido explicar aún de manera lógica.

#### 1. INTRODUCTION

The binary alloy  $\beta$ -brass, which consists of copper and zinc in approximately equal proportions, displays several features of interest from the point of view of lattice dynamics. At room temperature,  $\beta$ -brass has an ordered CsCl structure, that is to say, it consists of two interpenetrating simple cubic lattices, with the Cu and Zn ions occupying positions (0,0,0) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  a, respectively (a is the lattice constant). Owing to the similarity between Cu and Zn, however, the system of thermal vibrations resembles that which would be appropriate to a simple body-centred cubic (bcc) crystal such as Na. Indeed, as the temperature is increased, an order-disorder transition of the second (or higher) degree to a simple bcc structure occurs. The transition temperature T<sub>c</sub> is composition-dependent, being

about 727°K for the specimen employed in the high temperature experiments described below. Although there is no long range ordering of the Cu and Zn ions at temperatures greater than  $T_c$ , a considerable degree of short range order is known [1] to persist in the "disordered" phase.

The present paper describes an investigation of the frequency-wave vector relation  $\nu(\vec{q})$  for the normal modes of vibration of  $\beta$ -brass at 296°K, and the behaviour of certain features of  $\nu(\vec{q})$  as a function of temperature, particularly near the transition temperature  $T_c$ . Preliminary reports [2, 3] of some of this work have already appeared. The measurements have been made on single-crystal specimens by means of well-known techniques of slow neutron scattering [4, 5]. Under suitable conditions, it is possible to observe coherent neutron scattering processes in which one phonon of the thermal vibrations of the crystal is created or annihilated, with consequent changes in the energy and momentum of the scattered neutrons. If the incident (scattered) neutrons have energy  $E_0(E')$  and wave vector  $\vec{K}_0(\vec{K}')$  then the conditions of conservation of energy and "crystal momentum" may be written

$$\mathbf{E}_0 - \mathbf{E}' = \pm \mathbf{h} \boldsymbol{\nu}_i \tag{1}$$

$$\vec{k}_0 - \vec{k'} = \vec{Q} = 2\pi \vec{\tau} + \vec{q}, \qquad (2)$$

where  $v_j$  is the frequency of the mode of polarization index j,  $\vec{Q}$  is the momentum transfer vector,  $\vec{q}$  the reduced wave vector of the normal mode,  $\vec{\tau}$  a vector of the reciprocal lattice, and h Planck's constant. Since coherent one-phonon scattering can take place only when v and  $\vec{q}$  satisfy the dispersion relation  $v_j(\vec{q})$  as well as Eqs.(1) and (2), an observation of the scattered neutron energy distribution will reveal one or more "peaks" from whose location the frequency and wave vector of the phonons concerned may be inferred.

Earlier experimental work on  $\beta$ -brass has been performed by COLE and WARREN [6], who determined certain normal mode frequencies from X-ray diffuse scattering measurements. Their results are in poor agreement with the present work, the frequencies being generally too low, by a factor of 2 in the worst case. Of the many possible types of spectrometer with which inelastic neutron scattering measurements may be performed, one of the most convenient is the triple-axis crystal spectrometer [5]. All the experiments described in this paper were performed on a triple-axis spectrometer installed at the NRU reactor, Chalk River.

## 2. EXPERIMENTS AT 296°K

Most of the measurements, including all those made at elevated temperatures (see section 4), were made with a cylindrical specimen (I) having the following characteristics: composition 47 at.% Zn, length 2 in, diameter 3/4 in, [1T1] axis parallel to the cylinder axis. Specimen I was oriented so that a (1T0)-type mirror plane of the crystal was parallel to the incident and scattered neutron beams of the triple-axis spectrometer. A

second cylindrical specimen (II) was employed in a small number of additional experiments at 296°K: composition 48 at.% Zn, length 2 in, diameter 3/4 in, [001] axis parallel to the cylinder axis. Specimen II was oriented so that a (001)-type mirror plane of the crystal was parallel to the incident and scattered neutron beams. The mosaic spread of both specimens was approximately 0.5°.

The experiments were carried out under conditions of either (a) constant momentum transfer of the neutron ("constant- $\vec{Q}$ " method [5]) or (b) constant energy transfer of the neutrons [5]. In all measurements, only neutron energy loss processes were employed. The complete results for specimen I at 296°K are given in Table I, and those for specimen II in Table II. Constant- $\vec{Q}$  (constant energy) measurements are tabulated with errors quoted for the phonon frequencies (wave vectors). A similar system of error indication has been used in plotting the dispersion curves in Fig.1.

Certain normal modes, e.g. all those propagating along the  $[00\zeta]$  direction, and the longitudinal (L) modes propagating along [((0)] could be observed in the experiments on both specimens and provide a test of the effect of small changes in composition. Within the experimental errors (1 to 2%), no significant discrepancies between the two crystals were observed, and hence no distinction according to specimen has been made in plotting the results in Fig.1. Other normal modes were observable only on one or other of the specimens. For example, the  $T_1[\zeta\zeta 0]$  modes (i.e. with polarization vectors parallel to [001] and all modes along  $\left[\frac{1}{22}\zeta\right]$  were measured using specimen I, while the  $T_2[\zeta\zeta 0]$  modes (i.e. with polarization vectors parallel to  $[1\overline{1}0]$ ) were observed using specimen II. The limiting slopes at zero wave vector of the acoustic mode dispersion curves correspond to the appropriate sound velocities, which may be calculated from the 296°K elastic constants determined by McMANUS [7]. The elastic constants display a significant composition dependence, but over the range 45 to 48 at .% Zn, the maximum variation is only about 2%. It is therefore not surprising that no significant differences in phonon frequencies were detected in our experiments with the two specimens.

The overall shapes of the dispersion curves in Fig.1 are rather similar to those which would be expected for a simple bcc material such as sodium, except that certain degeneracies are removed, by reason of the differences between copper and zinc. Only two of the theoretically expected "splittings" are large enough to be observable in the present experiments, namely, at  $a\vec{q}/2\pi = (0.5, 0.5, 0.5)$  and for the L modes at  $a\vec{q}/2\pi = (0, 0, 0.5)$ . Figure 2 shows two pairs of well-resolved neutron groups observed in constant- $\vec{Q}$ measurements carried out near  $a\vec{Q}/2\pi = (1.5, 1.5, 0.5)$ , i.e. near the zone boundary in the  $\Lambda$ -direction. The magnitude of this splitting depends mainly on the difference between the second nearest neighbour copper-copper and zinczinc interatomic forces (see section 3). The temperature dependence of this splitting is described in section 4.

## 3. THEORETICAL MODELS

In this section, we describe the application of the Born-von Kármán theory to the perfectly ordered  $\beta$ -brass structure, and also a calculation

## TABLE I

# FREQUENCIES (UNITS $10^{12}~c/s)$ of Normal modes observed at 296°K in $\beta\text{-}BRASS$ (specimen 1, (110) orientation)

| ζ=aq/2π           | ν               | ζ=(1/√2)(aq/2π)       | ν               | ζ=(1/√3)(aq/2π)       | ν               |  |  |
|-------------------|-----------------|-----------------------|-----------------|-----------------------|-----------------|--|--|
| LA[0              | 0 <b>g</b> ]    | LA[ 56                | LA[ 550]        |                       | LA[¿ζζ]         |  |  |
| 0.076±0.020       | 0.99            | $0.066 \pm 0.002$     | 1.50            | $0.030 \pm 0.002$     | 0.99            |  |  |
| $0.104 \pm 0.006$ | 1.50            | $0.088 \pm 0.001$     | 2.00            | $0.048 \pm 0.002$     | 1.50            |  |  |
| $0.145 \pm 0.008$ | 2.02            | 0.10                  | $2.26 \pm 0.08$ | $0.066 \pm 0.002$     | 2.02            |  |  |
| $0.193 \pm 0.012$ | 2.49            | $0.110 \pm 0.002$     | 2,50            | $0.083 \pm 0.002$     | 2.51            |  |  |
| 0.20              | $2.59 \pm 0.06$ | 0.125                 | $2.51 \pm 0.10$ | $0.103 \pm 0.002$     | 3.00            |  |  |
| $0.234 \pm 0.005$ | 3.00            | $0.135 \pm 0.002$     | 3.00            | 0,125                 | $3.51 \pm 0.10$ |  |  |
| 0.25              | $3.14 \pm 0.05$ | 0.15                  | 3.20±0.10       | $0.128 \pm 0.003$     | 3.50            |  |  |
| 0.30              | $3.66 \pm 0.07$ | $0.162 \pm 0.002$     | 3.50            | 0.13                  | 3.67±0.05       |  |  |
| 0.35              | $3.98 \pm 0.06$ | 0.18                  | $3.82 \pm 0.04$ | $0.155 \pm 0.010$     | 4.02            |  |  |
| 0.38              | $4.14 \pm 0.06$ | $0.189 \pm 0.004$     | 4.00            | 0.18 <sup>b</sup>     | 4.43±0.09       |  |  |
| 0.40              | $4.30 \pm 0.08$ | 0.20                  | $4.16 \pm 0.13$ | 0.20                  | $4.30 \pm 0.12$ |  |  |
| 0.43              | $4.56 \pm 0.08$ | 0.23 <sup>b</sup>     | $4.43 \pm 0.10$ | 0.25                  | 3.55±0.10       |  |  |
| 0.45              | $4.57 \pm 0.08$ | 0.25                  | $4.23 \pm 0.12$ | 0.26                  | $3.40 \pm 0.07$ |  |  |
| 0.47              | $4.57 \pm 0.08$ | 0.27                  | $3.86 \pm 0.07$ | 0.30                  | 2.76±0.09       |  |  |
| 0.49              | $4.69 \pm 0.11$ | 0.30                  | $3.39 \pm 0.04$ | 0.32                  | $2.65 \pm 0.06$ |  |  |
| 0.50              | $4.63 \pm 0.10$ | 0.32                  | $3.25 \pm 0.08$ | 0.35                  | $2.70 \pm 0.09$ |  |  |
|                   | 0 F 7           | 0.34                  | 2.69±0.04       | 0.375                 | 2.84±0.09       |  |  |
| LOLU              | 106]            | 0.35                  | $2.63 \pm 0.06$ | 0.38                  | $2.72 \pm 0.06$ |  |  |
| 0.00 <sup>a</sup> | $5.82 \pm 0.07$ | 0.375                 | $2.37 \pm 0.06$ | 0.40                  | $3.07 \pm 0.10$ |  |  |
| 0.05b             | $5.84 \pm 0.12$ | 0.42                  | $2.02 \pm 0.05$ | 0.42                  | $3.21 \pm 0.07$ |  |  |
| 0.10 <sup>b</sup> | 5.66±0.11       | 0.45                  | $1.69 \pm 0.04$ | 0.43                  | $3.45 \pm 0.10$ |  |  |
| 0.15 <sup>b</sup> | 5.73±0.11       | 0.50                  | $1.49 \pm 0.04$ | 0.45 <sup>b</sup>     | $3.75 \pm 0.11$ |  |  |
| 0.20 <sup>b</sup> | 5.67±0.09       | IOL                   | 01              | 0.46 <sup>b</sup>     | $3.79 \pm 0.09$ |  |  |
| 0.22 <sup>b</sup> | $5.62 \pm 0.10$ | mee                   | 0]              | 0.47b                 | 3.91±0.09       |  |  |
| 0,25 <sup>b</sup> | 5.60±0.08       | 0.00 <sup>a</sup>     | $5.82 \pm 0.07$ | 0.48 <sup>b</sup>     | 4.09±0.07       |  |  |
| 0.30              | $5.65 \pm 0.10$ | 0.05 <sup>b</sup>     | $5.84 \pm 0.20$ | 0.49 <sup>b</sup>     | 4.16±0.07       |  |  |
| 0.35              | $5.42 \pm 0.09$ | 0.10 <sup>b</sup>     | $5.57 \pm 0.13$ | 0.50 <sup>a</sup>     | 4.21±0.06       |  |  |
| 0.38              | $5.37 \pm 0.09$ | 0.125 <sup>b</sup>    | $5.51 \pm 0.15$ | LOFEE                 | r1              |  |  |
| 0.40              | $5.40 \pm 0.09$ | 0.15 <sup>D</sup>     | $5.33 \pm 0.13$ | 20[85                 |                 |  |  |
| 0.43              | $5.42 \pm 0.09$ | 0.18 <sup>b</sup>     | $5.28 \pm 0.15$ | 0.00 <sup>a</sup>     | 5.82±0.07       |  |  |
| 0.45              | $5.37 \pm 0.09$ | 0,20 <sup>b</sup>     | $4.88 \pm 0.12$ | 0.05 <sup>D</sup>     | 5.83±0.20       |  |  |
| 0.47              | $5.27 \pm 0.08$ | $0.224 \pm 0.004^{b}$ | 4.51            | 0.125                 | $5.19 \pm 0.12$ |  |  |
| 0.48              | $5.25 \pm 0.08$ | 0.25                  | $4.86 \pm 0.10$ | 0.15                  | 4.84±0.15       |  |  |
| 0.50              | $4.90 \pm 0.11$ | 0.27                  | $5.20 \pm 0.05$ | $0.172 \pm 0.020^{b}$ | 4.54            |  |  |
| TAL               | 00 <i>c</i> 1   | 0.30                  | $5.53 \pm 0.13$ | 0.20                  | 4.99±0.05       |  |  |
|                   |                 | 0.32                  | $5.69 \pm 0.10$ | 0.24                  | $5.42 \pm 0.06$ |  |  |
| $0.145 \pm 0.007$ | 1.50            | 0.33                  | $5.70 \pm 0.09$ | 0.25                  | $5.61 \pm 0.12$ |  |  |
| $0.192 \pm 0.005$ | 2.00            | 0.35                  | $5.85 \pm 0.10$ | 0.27                  | $5.64 \pm 0.11$ |  |  |
| 0.22              | $2.10 \pm 0.05$ | 0.37                  | $6.12 \pm 0.10$ | 0.30                  | 5.84±0.07       |  |  |
| 0.25              | $2.48 \pm 0.05$ | 0.375                 | $6.16 \pm 0.16$ | 0.32                  | $5.93 \pm 0.08$ |  |  |
| $0.262 \pm 0.015$ | 2.51            | 0.40                  | $6.22 \pm 0.16$ | 0.33                  | $5.97 \pm 0.08$ |  |  |
| $0.311 \pm 0.005$ | 3.00            | 0.42                  | $6.41 \pm 0.15$ | 0.35                  | 5.80±0.11       |  |  |
| 0.32              | $3.06 \pm 0.03$ | 0.43                  | $6.34 \pm 0.10$ | 0.36                  | $5.90 \pm 0.11$ |  |  |
| 0.37              | $3.44 \pm 0.04$ | 0.45                  | $6.49 \pm 0.15$ | 0,375                 | $5.94 \pm 0.12$ |  |  |
| 0.38              | $3.40 \pm 0.05$ | 0.47                  | $6.58 \pm 0.11$ | 0.40                  | $5.74 \pm 0.11$ |  |  |
| 0.40              | $3.56 \pm 0.07$ | 0.48                  | $6.56 \pm 0.13$ | 0.42                  | $5.64 \pm 0.16$ |  |  |
| 0.44              | $3.79 \pm 0.05$ | 0.50                  | $6.55 \pm 0.12$ | 0.43                  | $5.50 \pm 0.08$ |  |  |
| 0.45              | 3.88±0.07       |                       | ·               | 0.45                  | $5.33 \pm 0.15$ |  |  |

| <b>ζ</b> =aq/2π   | ν               | ζ=(1/√2)(aq/2π)                | ν                              | ζ=(1/√3)(aq/2π)   | ν                   |
|-------------------|-----------------|--------------------------------|--------------------------------|-------------------|---------------------|
| 0.47              | 4.09±0.06       | Τ <sub>ι</sub> Α[ <b>ζ</b> ζ0] |                                | 0.46 <sup>b</sup> | 5.25±0.09           |
| 0.48              | $4.24 \pm 0.06$ | 0.10                           | $1.43 \pm 0.05$                | 0.48b             | 4.94±0.08           |
| 0.49              | $4.14 \pm 0.07$ | $0.103 \pm 0.002$              | 1,50                           | 0.49b             | $4.93 \pm 0.11$     |
| 0.50              | $4.23 \pm 0.07$ | 0,125                          | $1.84 \pm 0.07$                | 0.50 <sup>a</sup> | 4.93±0.10           |
| тог               | 0021            | $0.138 \pm 0.004$              | 2.02                           |                   |                     |
| 10[               | 003]            | 0.15                           | $2.15 \pm 0.07$                | ΤΑΓΖ              | ·71                 |
| 0.00 <sup>a</sup> | $5.82 \pm 0.07$ | 0.20                           | $2.85 \pm 0.09$                | * **[ 83          | .51                 |
| 0.05 <sup>b</sup> | $5.76 \pm 0.11$ | $0.218 \pm 0.003$              | 3.00                           | $0.067 \pm 0.006$ | 0.99                |
| 0.10 <sup>D</sup> | $5.62 \pm 0.11$ | 0.25                           | $3.23 \pm 0.11$                | 0.125             | $1.53 \pm 0.05$     |
| 0.15 <sup>D</sup> | $5.62 \pm 0.11$ | 0.28                           | $3.61 \pm 0.08$                | 0.15              | $1.53 \pm 0.05$     |
| 0.17b             | $5.61 \pm 0.10$ | 0.30                           | $3.88 \pm 0.11$                | 0.25              | $2.43 \pm 0.08$     |
| 0.20 <sup>b</sup> | $5.48 \pm 0.11$ | 0.33                           | $3.98 \pm 0.08$                | 0.35              | $3.25 \pm 0.10$     |
| 0.22b             | $5.53 \pm 0.10$ | 0.35                           | $4.22 \pm 0.11$                | 0.375             | 3.49±0.11           |
| 0.25 <sup>b</sup> | $5.49 \pm 0.10$ | 0.37                           | $4.23 \pm 0.04$                | 0.40              | $3.77 \pm 0.08$     |
| 0.270             | $5.45 \pm 0.10$ | 0.375                          | $4.24 \pm 0.10$                | 0.42              | 3.90±0.18           |
| 0.30              | $5.27 \pm 0.10$ | 0.40                           | $4.45 \pm 0.10$                | 0.43              | $3.93 \pm 0.10$     |
| 0.40              | 4.75±0.09 •     | 0.42                           | $4.42 \pm 0.03$                | 0.45 <sup>D</sup> | $4.04 \pm 0.16$     |
| 0.44              | $4.51 \pm 0.08$ | 0.44                           | $4.51 \pm 0.06$                | 0.46 <sup>D</sup> | 4.12±0.07           |
| 0.45              | $4.46 \pm 0.09$ | 0.45                           | $4.47 \pm 0.06$                | 0.475             | $4.18 \pm 0.10$     |
| 0.47              | $4.43 \pm 0.07$ | 0.46                           | $4.56 \pm 0.05$                | 0.48 <sup>D</sup> | $4.20 \pm 0.08$     |
| 0.48              | $4.48 \pm 0.07$ | 0.47                           | $4.62 \pm 0.08$                | 0.490             | $4.29 \pm 0.09$     |
| 0.49              | $4.37 \pm 0.07$ | 0.48                           | $4.58 \pm 0.07$                | 0.50ª             | $4.21 \pm 0.06$     |
| Λ[ ½2             | ζ]              | 0.49                           | $4.60 \pm 0.08$                | TO[ <b>5</b> 8    | ξζ]                 |
| 0 008             | 4 60 1 0 07     | 0.50                           | 4.60±0.07                      | 0 008             | 5 82 + 0 07         |
| 0.00              | 4.51±0.06       | Τ <sub>1</sub> Ο[ζ             | ζ0]                            | 0.00              | 5 74 + 0 09         |
| 0.20              | 4.99+0.00       | 0.008                          | 5 82 + 0 07                    | 0.060             | 5 81+0 11           |
| 0.30              | 4.22 + 0.08     | 0.00<br>0.10 <sup>b</sup>      | 5 66+0 15                      | 0.12              | 5 76+0 09           |
| 0.40              | 4.21±0.12       | 0.200                          | $5.00 \pm 0.10$<br>5.94 ± 0.14 | 0,125             | $5.72 \pm 0.14$     |
| 0.50 <sup>a</sup> | $4.21 \pm 0.06$ | 0.30                           | $4.84 \pm 0.12$                | 0.20              | 5,82+0,12           |
| 0.00              |                 | 0.40                           | $4.64 \pm 0.12$                | 0.25              | 5,70+0,14           |
| πO[±              | ±€]             | 0.45                           | $4.58 \pm 0.12$                | 0.27              | $5.75 \pm 0.12$     |
| 0.00 <sup>a</sup> | $6.55 \pm 0.12$ | 0.10                           |                                | 0.30              | $5.55 \pm 0.10$     |
| 0.10              | $6.34 \pm 0.25$ |                                |                                | 0.37              | $5.39 \pm 0.11$     |
| 0.15              | $6.42 \pm 0.20$ |                                |                                | 0.375             | $5.37 \pm 0.12$     |
| 0.20              | $6.19 \pm 0.15$ |                                |                                | 0.40              | $5.34 \pm 0.12$     |
| 0.25              | $6.09 \pm 0.07$ |                                |                                | 0.42              | $5.10 \pm 0.10$     |
| 0.30              | $5.88 \pm 0.06$ |                                |                                | 0.45              | $4.98 \pm 0.16$     |
| 0.35              | $5.64 \pm 0.08$ |                                |                                | 0.46 <sup>b</sup> | $5.16 \pm 0.07$     |
| 0.40              | $5.37 \pm 0.10$ |                                |                                | 0.47b             | 5.00±0.07           |
| 0.50ª             | $4.93 \pm 0.10$ |                                |                                | 0.48 <sup>b</sup> | $4.94 \pm 0.11^{2}$ |
| - 4 5 1           | 1.17            |                                |                                | 0.49 <sup>b</sup> | 4.92±0.08           |
| πΑι               | 226]            |                                |                                | 0.50 <b>a</b>     | 4.93±0.10           |
| 0.00 <sup>a</sup> | $1.49 \pm 0.04$ |                                |                                |                   |                     |
| 0.30              | $2.77 \pm 0.06$ |                                |                                |                   |                     |
| 0.35              | $3.14 \pm 0.08$ |                                |                                |                   | ļ                   |
| 0.40              | $3.60 \pm 0.10$ |                                |                                |                   |                     |
| 0.50ª             | $4.21 \pm 0.06$ |                                |                                |                   |                     |

TABLE I (cont.)

a Frequency listed elsewhere in the table.
 b Polarization undetermined, but probably as shown.
# TABLE II

# FREQUENCIES (UNITS $10^{12}$ c/s) OF NORMAL MODES OBSERVED AT 296°K IN $\beta$ -BRASS (SPECIMEN II, (001) ORIENTATION)

| $\zeta = aq/2\pi$ | ν               | $\zeta = (1/\sqrt{2})(aq/2\pi)$ | ν               |
|-------------------|-----------------|---------------------------------|-----------------|
| LA                | [005]           | LA[\$\$0]                       |                 |
| 0.25              | 3.13±0.10       | 0.15                            | $3.32 \pm 0.05$ |
|                   | F00 #3          | 0.23 <sup>b</sup>               | $4.42 \pm 0.07$ |
| , D               | [006]           | 0.24                            | $4.25 \pm 0.05$ |
| 0.00 <sup>a</sup> | $5.84 \pm 0.12$ | 0.30                            | $3.39 \pm 0.04$ |
| 0.25              | $5.52 \pm 0.25$ | 0.40                            | $2.16 \pm 0.05$ |
| 0.30              | $5.45 \pm 0.25$ | 0.50 <sup>a</sup>               | $1.44 \pm 0.03$ |
| ТА                | .[005].         | LO[\$\$0]                       |                 |
| 0.32              | $3.08 \pm 0.03$ | 0.00 <sup>a</sup>               | $5.84 \pm 0.12$ |
| 0.40              | $3.66 \pm 0.05$ | 0.10 <sup>b</sup>               | $5.57 \pm 0.10$ |
| 0.45              | $3.98 \pm 0.04$ | 0.18 <sup>b</sup>               | $5.04 \pm 0.10$ |
| <b>m</b> a        | F0.0 +=         | 0.20                            | $4.86 \pm 0.07$ |
| TC                | ξουζ]           | 0.21 <sup>b</sup>               | $4.68 \pm 0.08$ |
| 0.00 <sup>a</sup> | $5.84 \pm 0.12$ | 0.27                            | $5.21 \pm 0.07$ |
| 0.30              | $5.26 \pm 0.08$ | 0.35                            | $6.07 \pm 0.09$ |
| 0.35              | $5.05 \pm 0.09$ | 0.50 <sup>a</sup>               | $6.55 \pm 0.15$ |
| 0.40              | $4.78 \pm 0.06$ |                                 |                 |
|                   |                 | Τ <mark>2</mark> Α[ζζ0]         |                 |
|                   |                 | 0.20                            | 0.96±0.02       |
|                   |                 | 0.30                            | $1.23 \pm 0.02$ |
|                   |                 | 0.40                            | $1.40 \pm 0.03$ |
| x                 |                 | 0.50a                           | $1.44 \pm 0.03$ |
|                   |                 | Τ₂Ο[ζζ0]                        |                 |
|                   |                 | 0.00 <sup>a</sup>               | 5.84±0.12       |
|                   |                 | 0.10                            | $5.94 \pm 0.08$ |
|                   |                 | 0.20                            | $6.06 \pm 0.15$ |
|                   |                 | 0.30                            | $6.22 \pm 0.10$ |
|                   |                 | 0.40                            | $6.53 \pm 0.10$ |
|                   |                 | 0.50 <sup>a</sup>               | $6.55 \pm 0.15$ |

<sup>a</sup> Frequency listed elsewhere in the table.

b Polarization undetermined, but probably as shown.

of the frequency distribution function  $g(\nu)$  for the normal modes. An alternative description of the long range part of the effective interatomic potential in  $\beta$ -brass is also discussed. A more comprehensive and detailed exposition of these matters will be given elsewhere [8].





Dispersion curves of β-brass 296°K for four high-symmetry directions. Triangular points denote L and A modes and circles indicate T and π modes. Solid points denote uncertain polarization. The dashed curve is the best fit to the results on the basis of a Born-von Kármán model involving general first and second nearest-neighbour interatomic forces. The solid curve represents the Born-von Kármán fourth nearest-neighbour model (4E) best fit.



Fig.2

Neutron groups for B-brass at constant-Q associated with modes (a) L[555] and (b) T[555], near the Brillouin zone boundary. A splitting into optic and acoustic branches is observed in both cases.

Since there are two atoms in the primitive unit cell of perfectly ordered  $\beta$ -brass (of stoichiometric composition), and since equilibrium positions of both atoms are at centres of inversion symmetry, the thermal vibrations may be expressed by means of a real, symmetric  $(6 \times 6)$  matrix whose eigenvalues are proportional to the squares of the normal mode frequencies. For normal modes propagating along certain special directions in the crystal, namely  $[00\xi]$ ,  $[\xi\xi 0]$ ,  $[\xi\xi\xi]$  and  $(\frac{1}{2}\frac{1}{2}\xi)$ , the dynamical matrix factorizes into  $(2 \times 2)$  matrices; this fact greatly facilitates the interpretation and analysis of experimental results for these directions. In the  $\left[\frac{1}{2}\frac{1}{2}\zeta\right]$  direction, one of the  $(2 \times 2)$  matrices factorizes further into two linear expressions for the squared frequencies of normal modes (denoted by  $\Lambda_0$ ,  $\Lambda_1$ ) which involve the vibration of the two types of atom independently; thus the  $\Lambda_0$  modes involve the vibration only of atoms of type 0. The 1st, 4th, 7th .... nearest neighbours of an origin atom of type 0 are of type 1, whereas the remaining neighbours (2nd, 3rd, 5th, 6th ....) are of the same type 0. Thus force constants representing interactions between identical atoms are of two kinds, Cu-Cu and Zn-Zn. Extension of the Born-von Kármán theory to distant neighbours therefore involves a substantial number of disposable parameters. For example, a 1st-through-5th nearest-neighbour model (general forces) for perfectly ordered  $\beta$ -brass involves 20 force constants (cf. 13 constants for the simple bcc structure). Preliminary attempts to fit the experimental dispersion curves with such general force models (by means of a non-linear least squares fitting programme) showed (i) that forces only out to 3rd or 4th nearest neighbours were important and (ii) that "tangential" or "shearingtype" force constants were always small or zero except for the 1st nearest neighbour. A simple Fourier analysis may also be performed on the sums of the squared frequencies of various pairs of branches of the dispersion relation, e.g. the  $LA[\zeta \zeta 0]$  and  $LO[\zeta \zeta 0]$  branches. The Fourier coefficients are linear combinations of interatomic force constants, and the number of such coefficients required to obtain a fit to the observed sums of squared frequencies gives an indication of the range of the interatomic forces. Analysis of the results for  $\beta$ -brass in this way shows that significant forces exist at least out to 5th, and very probably at least out to 7th, nearest neighbours. The 5th-through-7th neighbour force constants are, however. relatively small, as indicated by the above-mentioned Born-von Kármán analysis.

To facilitate the description of Born-von Kármán force models, we define a force constant matrix

$$\begin{aligned} &\alpha_{1\sigma}^{s} \quad \beta_{3\sigma}^{s} \quad \beta_{2\sigma}^{s} \\ &\beta_{3\sigma}^{s} \quad \alpha_{2\sigma}^{s} \quad \beta_{1\sigma}^{s} \\ &\beta_{2\sigma}^{s} \quad \beta_{1\sigma}^{s} \quad \alpha_{3\sigma}^{s} \end{aligned}$$

where s refers to the order of the neighbour (e.g. first nearest neighbours are denoted by s = 1) and  $\sigma$  to the two kinds of atom ( $\sigma$  = 0, 1) which may be involved when s = 2, 3, 5, 6, etc. The number of independent force constants for any neighbour s may be reduced by symmetry considerations. Thus, for s = 2,  $\alpha_{2\sigma}^2 = \alpha_{3\sigma}^2$  and  $\beta_{1\sigma}^2 = \beta_{2\sigma}^2 = \beta_{3\sigma}^2 = 0$ . The most general model involving

#### TABLE III

# BEST-FIT VALUES OF INTERATOMIC FORCE CONSTANTS INCLUDING FOURTH NEAREST NEIGHBOURS (MODEL 4E) (Only non-zero coefficients are listed)

| Neighbour | Force constants<br>(dyn/cm) |                        |  |
|-----------|-----------------------------|------------------------|--|
| 1         | $\alpha_1^1 = 8420$         | $\beta_1^1 = 11340$    |  |
| · 2       | $\alpha_{10}^2 = 7110$      | $\alpha_{11}^2 = 730$  |  |
| 3         | $\alpha_{10}^{3} = 1070$    | $\alpha_{11}^3 = 1190$ |  |
| 4         | $\alpha_1^4 = 280$          | $B_3^4 = 370$          |  |

forces extending to 1st and 2nd nearest neighbours only is not capable of providing a satisfactory fit to the experimental results, as is shown by the dashed curves in Fig.1. A good fit can be obtained, however, by means of a restricted 4th-neighbour model (denoted by 4E) having eight disposable parameters, as listed (with their best-fit values) in Table III. All tangential type force constants except for 1st nearest neighbours have been arbitrarily set to zero in this model, which is represented by the solid lines in Fig.1. A general feature of all the Born-von Kármán models used to fit the results was that almost identical fits could be achieved for any model merely by interchanging the masses  $M_0$  and  $M_1$ , or alternatively, by labelling all the Cu-Cu force constants as Zn-Zn type, and vice versa. Reference to Table III shows that, for example,  $\alpha_{10}^2 \gg \alpha_{11}^2$ ; however, it is impossible to determine unambiguously from these best-fit computations which constant refers to Cu and which to Zn. Although it is probable that this question may be settled only by means of a theoretical calculation of these force constants from first principles, some experimental indication of the correct labelling is given by the neutron group intensities observed for the  $\Lambda[\frac{1}{2}\xi]$  modes which correspond to independent vibrations of Cu and Zn atoms. In experiments designed to study these modes, scattered neutron energy distributions at appropriate values of  $\vec{Q}$  should in principle consist of two peaks, associated with independent vibrations of the Cu and Zn sub-lattices respectively. The former peak should be more intense, and its identification would permit the correct assignment of the 0-0 and 1-1 type force constants. The frequencies of the two modes are, however, very similar for all  $\zeta$  (see Fig.1), and no well-resolved neutron groups were obtained in experiments designed to observe them. The shapes of the peaks observed did suggest that the lower frequency mode is probably associated with the copper atom vibrations, i.e. that the copper-copper second-neighbour constant is  $\alpha_{11}^2 = 730 \, \text{dyn/cm}$ , substantially less than the analogous zinc-zinc constant. However, this conclusion is largely tentative at the present time.

Although model 4E is of course purely phenomenological and involves several arbitrary assumptions, it is probably adequate as an interpolation formula for computing frequencies of normal modes not observed experimentally, and hence for computing the frequency distribution function  $g(\nu)$ . This computation may easily and accurately be performed by means of an extrapolation method developed by the present authors [9]\*. Full details of this computation will be given elsewhere [8], together with calculations of thermodynamic functions of  $\beta$ -brass based on it. Here we merely present the result of the calculation (Fig. 3) in the form of a histogram. (The individual points and their fluctuations are too small to be plotted separately.)



Fig.3

The frequency distribution function for  $\beta$ -brass at 296°K obtained from model 4E by means of an extrapolation method [9]. In this histogram the frequencies of 96, 018, 048 normal vibrations are sorted into over 300 channels of width  $\Delta \nu = 0.02 \times 10^{12}$  c/s.

The long-range character of the effective interatomic potential in  $\beta$ -brass, as shown by the Fourier analysis mentioned earlier, has so far been described by rather arbitrary Born-von Kármán force constants of little physical significance. This long range potential may be regarded as the sum of two parts (i) the Coulomb potential V<sub>c</sub> between the bare ions and (ii) a potential V<sub>E</sub> arising from the interaction through the conduction electrons, including the electron-electron interaction. The latter contribution may under certain assumptions (see, for example references [10-12]) be expressed in terms of a "form factor" and "dielectric function" for the metal. At long range (say, for 3rd nearest neighbours and beyond) V<sub>C</sub> and V<sub>E</sub> tend to cancel each other. There remains, however, an interaction of long range oscillatory form arising from the mild singularity in the dielectric function at the Fermi level. In the case of a simple metal such as Na, it seems

<sup>\*</sup> The g(v) for  $\beta$ -brass mentioned in [9] is based on an earlier force model, fitted to a smaller number of experimental results than are utilized in the present calculations.

plausible that the effective interatomic potential (beyond 2nd nearestneighbour atoms) may be described to a first approximation by such an oscillatory term:

$$V_{\rm P}(r_{\rm ij}) = (A/r_{\rm ij}^{3}) \cos (2K_{\rm F}r_{\rm ij} + \phi), \qquad (3)$$

where  $r_{ij}$  is the distance between ions i, j and  $K_F$  is the Fermi radius (the Fermi surface is assumed to be spherical). The coefficient A and phase factor  $\phi$  might possibly be calculated from basic principles but this has not yet been successfully carried out.

An oscillatory term of the same form may also be derived from a treatment of the scattering of free electrons (described by plane waves) from a charged impurity ion embedded in a host metal crystal [13-15]. A model containing such an oscillatory potential function has been proposed [16,17] to calculate the order-disorder energy in  $\beta$ -brass, and this kind of term has also been obtained [18] from a study of the scattering of free electrons (in the Born approximation) by a dipole (or plane of dipoles) in a metal crystal, the dipole being produced when the metal is perturbed by a normal mode of vibration.

The term  $V_P$  is complicated in the case of  $\beta$ -brass by the existence of two different ions in the unit cell. It may no longer be adequate to treat the conduction electrons in terms of the single plane wave approximation utilized in the derivation of Eq. (3), and the dielectric function may well have appreciable off-diagonal elements [19]. We have attempted to fit the observed dispersion curves for  $\beta$ -brass by means of a model in which the 1st and 2nd nearest-neighbour forces are described by empirical Born-vonKármán force constants, and in which the 3rd and more distant neighbour interactions are calculated from the potential  $V_P$  (Eq. (3)). The quality of fit obtained was rather poor, scarcely better than that obtained when  $V_P$  was neglected. A very good fit (slightly better than model 4E) has, however, been obtained with a semi-empirical expression of the form

$$V_{p}(r_{ii}) = (A \pm B)(1/r_{ii}^{3}) \cos (2K_{F}r_{ii} + \phi), \qquad (4)$$

where B depends (presumably) on the off-diagonal components of the dielectric function and the +(-) sign refers to Cu-Cu or Zn-Zn (Cu-Zn) interactions respectively. In spite of the successful description of the experimental results given by this modified potential, it cannot be regarded as satisfactory in the absence of a rigorous derivation from a basic formalism such as is described in [19].

# 4. MEASUREMENTS AT HIGH TEMPERATURES

Two series of measurements have been made, in which the energies and energy widths of selected normal modes of vibration have been measured at several temperatures, both above and below the order-disorder transition temperature  $T_c$ . A general result of these measurements is that the normal mode energies decrease and the widths increase as the temperature T rises. It is of particular interest to compare and correlate the behaviour of various normal modes and to attempt to detect any anomalous temperature effects as T passes through  $T_c$ . An account of the first series of measurements has already been given [3], in which no definite conclusions were drawn concerning either correlations between modes or anomalous energy shifts or widths near  $T_c$ . For certain longitudinal modes, however, there were indications of possible anomalous increases in width of the observed scattered neutron groups, and a second series of more precise measurements was carried out to investigate these possibilities in further detail. An apparently significant correlation was then observed between the character of certain normal modes and the behaviour, as a function of temperature, of the energy width of the associated neutron groups. The results of both sets of measurements are mutually consistent and are discussed together below.

The energies and energy widths of seven normal modes specially selected for the sharpness and high intensity of the associated scattered neutron groups, were measured at several temperatures both above and below the transition temperature  $T_c$ , and the results are listed in Table IV. The system for labelling the normal modes in Table IV differs from that used in the earlier account [3] where the modes were assigned labels "optic" (O) or "acoustic" (A) according to the kind of atomic motions involved (i.e. according to the eigenvectors). This convention is experimentally convenient but leads to ambiguities in the regions of "splitting" between longitudinal (L) modes near  $a\vec{q}/2\pi = (0.22, 0.22, 0)$  and (0.17, 0.17, 0.17). For future discussion, we refer to these wave vectors as  $\vec{q}_{S1}$  and  $\vec{q}_{S2}$ . We now define the optic mode in each case to be that with the <u>higher</u> frequency and disregard the change in <u>character</u> (i.e. the phase relation between the Cu and Zn atoms) of the L modes which occurs near the wave vectors  $\vec{q}_{S1}$  and  $\vec{q}_{S2}$ .

For most normal modes studied, the energy and energy width vary smoothly with temperature even through the transition point. All the energies' decrease and widths increase with increasing temperature. Thus, although the scattered neutron groups associated with the mode  $LA\Sigma(1.30,$ 1.30, 1.0) are at each temperature much wider than those of LA $\Sigma$ (1.18, 1.18, 0.0), a smooth variation of width is observed in both cases. The behaviour of the mode  $LO\Sigma(1.27, 1.27, 0.0)$  is, on the other hand, significantly different; a sharp increase in width is observed when the temperature is raised through  $T_c$ . The observed neutron groups for two of these modes at two temperatures are illustrated in Fig. 4. A similar effect is observed for the mode LOA(1.20, 1.20, 0.20). Only these two normal modes, of all those studied, display other than smooth monotonic behaviour as a function of temperature. In both cases, the wave vector is somewhat greater than that of the closest approach of the LO and LA branches ( $\vec{q}_{s1}$  and  $\vec{q}_{s2}$ ). The observed frequency widths for these modes are illustrated in Fig.5, together with sketches of the relevant parts of reciprocal space and the wave vector values. A typical transverse acoustic mode is included for comparison. It shows no anomalous behaviour near T<sub>c</sub>. The normal mode frequencies in all cases show a smooth decrease with temperature, within the accuracy of the present measurements. In this connection, it is interesting to note

## TABLE IV

#### Wave vector Temperature Frequency Line-width<sup>a</sup> (aQ/2π) (°K) (10<sup>12</sup> c/s) (10<sup>12</sup> c/s) mode $3.39 \pm 0.04$ 0.50 (1.30, 1.30, 1.0) 296 . $3.27 \pm 0.05$ 0.44 499 0.70 LA **D** 693 $3.23 \pm 0.05$ $3.22 \pm 0.06$ 0.80 714 725 $3.21 \pm 0.08$ 0.80 739 $3.22 \pm 0.10$ 0.85 751 $3.17 \pm 0.09$ 0.70 $3.12 \pm 0.15$ 1.00 774 (1.0, 1.0, 0.37)296 $3.44 \pm 0.04$ 0.25 693 $3.16 \pm 0.04$ 0.40 $3.15 \pm 0.05$ 0.50 τα Δ 714 $3.11 \pm 0.05$ 0.50 739 0.55 774 $3.07 \pm 0.55$ $3.06 \pm 0.03$ 0.20 (1.0, 1.0, 0.32)296 0.30 499 $2.96 \pm 0.04$ 693 $2.81 \pm 0.03$ 0.38 τα Δ 0.40 $2.77 \pm 0.03$ 714 0.40 $2.76 \pm 0.04$ 739 751 $2.73 \pm 0.04$ 0.50 0.45 774 $2.71 \pm 0.04$ 0.24 $4.99 \pm 0.05$ (1.20, 1.20, 0.20) 296 $4.90 \pm 0.07$ 0.42 499 693 $4.80 \pm 0.06$ 0.65 LO A $4.73 \pm 0.05$ 0.55 714 0.90 739 $4.73 \pm 0.08$ 0.90 751 $4.68 \pm 0.10$ $4.71 \pm 0.07$ 0.90 774

# TEMPERATURE DEPENDENCE OF FREQUENCY AND LINE-WIDTH FOR SEVEN NORMAL MODES IN $\beta\text{-}BRASS$

a Errors are in most cases of the order of 20%.

| Wave vector<br>(aQ/2π)<br>mode | Temperature<br>(°K) | Frequency<br>(10 <sup>12</sup> c/s) | Line-width <sup>a</sup><br>(10 <sup>12</sup> c/s) |
|--------------------------------|---------------------|-------------------------------------|---|
| (1.18, 1.18, 0.0)              | 296                 | 3.82±0.04                           | 0.24  |
|                                | 693                 | $3.65 \pm 0.04$                     | 0.40  |
| LA Σ                           | 714                 | $3.63 \pm 0.04$                     | 0.45  |
|                                | 739                 | $3.62 \pm 0.04$                     | 0.40  |
|                                | 774                 | $3.59 \pm 0.05$                     | 0.40  |
| (1.27, 1.27, 0.0)              | 296                 | 5.20±0.05                           | 0.35  |
|                                | 499                 | $5.09 \pm 0.07$                     | 0.50  |
| LO Σ                           | 693                 | 5.00±0.06                           | 0.55  |
|                                | 714                 | $5.01 \pm 0.06$                     | 0.55  |
|                                | 739 <sup>-</sup>    | $4.90 \pm 0.08$                     | 0.85  |
|                                | 751                 | $4.91 \pm 0.12$                     | 0.80  |
|                                | 774                 | $4.94 \pm 0.06$                     | 0.90  |
| (1.13, 1.13, 0.13)             | 360                 | 3.65±0.04                           | 0.30  |
|                                | 714                 | $3.42 \pm 0.04$                     | 0.45  |
| LA A                           | 739                 | $3.41 \pm 0.05$                     | 0.55  |

TABLE IV (cont.)

<sup>a</sup> Errors are in most cases of the order of 20%.

the anomalous temperature dependence [7] of the elastic constant  $\rm C_{44}$  in the vicinity of  $\rm T_c$  .

It would perhaps be too daring to draw any definite conclusions concerning the anomalous behaviour of L-modes on the basis of these two examples. It would be highly desirable to obtain more experimental data before such conclusions can be drawn. However, the experimental conditions under which such observations may be made at all are quite restrictive, and so we cannot readily produce further independent examples of similar anomalies. Assuming, nevertheless, that these energy width anomalies are indeed real, it seems plausible that they are closely associated with the type of mode involved, and perhaps also with its wave vector and/or frequency. It is interesting to point out (though this may be purely coincidental) that the magnitudes of  $2\pi/\vec{q}_{S1}$  and  $2\pi/\vec{q}_{S2}$  are similar, and are of the order of the extent of the short range order (~10 Å) which is known [1] to exist in $\beta$ -brass at temperatures just above T<sub>c</sub>. We also notice that the anomalous modes have similar frequencies (about  $5 \times 10^{12} \text{ c/s}$ ) which are somewhat higher than those of all the other modes listed in Table IV. As yet, however, no reason-



Fig.4

Observed neutron groups associated with two different modes of the same polarization  $L[\zeta\zeta 0]$ , each at two different temperatures (below and above  $T_c$ ). The frequency shifts as well as the changes in width are clearly shown. The change in the width is noticeably larger for the  $\zeta = 0.27$  mode.

> o 296°K x 774°K

able framework has been established within which these anomalies may be completely understood.

It is perhaps of interest to mention the behaviour of the "splitting" of the normal modes for wave vectors near (0.5, 0.5, 0.5) as a function of temperature. The two neutron groups are fairly well resolved at 296°K (see Fig.2), but considerable blurring together has occurred even for  $T = 499^{\circ}K$ . Above this temperature, it was no longer possible to resolve the two peaks. One would expect to observe such a single wide peak for  $T > T_c$ ; its appearance for  $T < T_c$  may well be due to the poor instrument-focussing conditions obtaining in these particular experiments.

A few remarks should be made about the intensities of the observed neutron groups as a function of temperature. No attempt has been made to compare in detail the intensities at different temperatures. Such an analysis would be very inaccurate, particularly at the higher temperatures, owing to the large increase in "background" intensity and to the relatively poor statistics in the wings of the distributions. These facts also contribute to the error in the measurement of the widths of the neutron groups. The precision of the width measurements (about 20% in most cases) is however substantially better than that of the intensities. In any event, no significant changes in the intensity of any of the neutron groups were observed in the vicinity of  $T_c$ .

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Fig.5

The observed frequency width as a function of temperature is plotted for several phonons. The location of these phonons on the dispersion curves is schematically shown. For the TA mode,  $\zeta = 0.32$ . The variation of line width in the vicinity of T<sub>c</sub> for the LO mode (triangles) differs qualitatively from that of the other modes studied.

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#### DISCUSSION

I. WALLER: In connection with your investigations of a disordered alloy I should like to remark that it would be of great interest to study the inelastic neutron scattering from a disordered alloy for a wide range of compositions.

G. DOLLING: As a matter of fact Dr. Woods is shortly going to study a series of molybdenum-niobium alloys.

M.G. ZEMLYANOV: In the disordered state of beta-brass the translational symmetry is not maintained. In view of this, how are the dispersion curves interpreted?

G. DOLLING: This is a rather interesting point. In general, phonons appear to be much more resilient excitations than one might expect. However, in beta-brass, Cu and Zn are really quite similar and so the disordered material is not very different from a monatomic bcc metal. The situation would be less favourable for an alloy of very dissimilar metals. Furthermore, we know that a considerable amount of short range order, extending for 10 Å or so, exists in the "disordered" phase just above  $T_c$ , which is perhaps sufficient for the establishment of the phonon spectrum. Thus we see that the conditions in beta-brass are quite favourable for the continued existence of well-defined phonons over most of the zone, even at temperatures above  $T_c$ .

# DISPERSION CURVES FOR PHONONS IN DIAMOND\*

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# Abstract — Résumé — Аннотация — Resumen

DISPERSION CURVES FOR PHONONS IN DIAMOND. A three-axis neutron diffraction spectrometer at the Los Alamos Omega West Reactor has been used to measure the dispersion curves for phonons propagating in the [100] and [111] directions in diamond. All measurements were made at room temperature. The sample was a type IIa brown industrial diamond weighing 242.8 carats (48.56 g). A neutron diffraction study showed it to consist of a large single crystal with a mosaic spread of  $-1^{\circ}$  full width at half maximum, plus two small regions misoriented by 3 and 5°. The spectrometer was programmed for "constant- $\vec{O}^{\circ}$  operation. In all cases, the energy of the incident neutrons was fixed and the scattered neutrons lost energy. Sufficient intensity at an incident energy high enough to excite the optical modes of diamond was obtained by the use of the (1122) reflection of a beryllium monochromator. Uncertainties in the measured frequencies are estimated to be of the order of 2-3%.

The most striking result of these measurements is the verification of the predictions, based on infrared absorption and specific heat data, that diamond is not homologous to silicon and germanium. The lack of homology is manifested principally in the behaviour of the transverse branches. The transverse acoustic branches are relatively much higher in diamond than in silicon and germanium. The transverse optical branches are relatively lower, so that in diamond the highest branch is the longitudinal optical rather than the transverse optical. Frequencies at the zone boundaries are in reasonable agreement with those predicted from infrared absorption data, although the identification of the polarizations is different.

COURBES DE DISPERSION DES PHONONS DANS LE DIAMANT. Les auteurs ont utilisé un spectromètre triaxial pour la diffraction des neutrons produits par le réacteur Omega West de Los Alamos en vue de déterminer plusieurs courbes de dispersion des phonons se déplaçant dans des directions de symétrie à l'intérieur du diamant. Toutes les mesures ont été effectuées à la température ambiante. Il s'agissait d'un diamant industriel brun du type IIa, de 242.8 carats (48,56 grammes). D'après une étude par diffraction des neutrons, cet échantillon était constitué par un grand monocristal à dispersion mosaïque atteignant une largeur maximum d'environ 1° à mi-hauteur du pic, plus deux petites régions déviées de 3 à 5°. Le programme du spectromètre était établi pour « $\vec{Q}$  constant». Dans tous les cas, l'énergie des neutrons incidents était fixe et les neutrons diffusés ont perdu de l'énergie. Pour une énergie des neutrons incidents assez élevée pour exciter les modes optiques du diamant, on a obtenu une intensité suffisante grâce à la réflexion (11 $\overline{22}$ ) d'un système mono-chromateur de béryllium. Parmi les difficultés soulevées par l'expérience, indépendamment de celles qui résultent des fréquences très élevées des phonons dans le diamant, il faut citer l'existence de pics anormaux qui a rendu difficile l'identification des polarisations. On estime que l'imprécision des mesures des fréquences es de l'ordre de 2 à 3%.

Le résultat le plus frappant de ces mesures a été la confirmation des prévisions, fondées sur les données relatives à l'absorption dans l'infrarouge et à la chaleur spécifique, que le diamant n'est pas homologue du silicium et du germanium. Ce manque d'homologie se manifeste principalement dans le comportement des branches acoustiques transversales, dont la fréquence exprimée en unités convenablement réduites est près de deux fois plus élevée dans le diamant que dans le silicium ou le germanium. Les autres courbes de dispersion pour le diamant sont assez semblables à celles que l'on observe pour le silicium et le germanium. Ces résultats indiquent peut-être que les effets de la «polarisabilité»atomique, qui ont une grande importance dans le cas du silicium et du germanium, en ont moins dans le cas du diamant.

<sup>\*</sup> Work performed under the auspices of the United States Atomic Energy Commission.

КРИВЫЕ ДИСПЕРСИИ ДЛЯ ФОНОНОВ В АЛМАЗЕ. Трехосный дифракционный спектрометр нейтронов на Лосаламосском реакторе "Омега Вест" использовался для измерения некоторых кривых дисперсии для распространения фононов в направлениях [100]и [111] в алмазе. Все из мерения проводились при комнатной температуре. Образец представлял собой коричневый промышленный алмаз типа II а весом 242,8 карат (48,56 граммов). Изучение явлений дифракции нейтронов показало, что алмаз состоит из большого единичного кристалла с мозаичным разбросом в размере ~1° полной ширины при полумаксимуме, плюс двумя небольшими областями, разориентированными на 3-5°. Спектрометр программировался для операции "постоянная Q". Во всех случаях энергия падающих нейтронов была постоянной, и рассеянные нейтроны теряли энергию. Достаточная интенсивность при энергии бомбардировки, достаточно большой для возбуждения оптических форм алмаза, была достигнута в результате использования отражения (1122) бериллиевого монохроматора. К трудностям проведения экспериментов, помимо трудностей, возникающих в связи с наличием очень высоких частот фононов в алмазе, относится возникновение аномальных пиков, что затрудняет распознавание точек поляризации. Считается, что неопределенности в измеренных частотах составляют величину порядка 2-3 процентов.

Наиболее разительным результатом этих измерений является подтверждение предположений, основанных на данных относительно поглошения инфракрасной области спектра и относительно удельного тепла, что алмаз не является гомологом с кремнием и германием. Отсутствие соответствия проявляется в основном в поведении поперечных акустических ветвей, которые в случаях выражения их в соответствующих приведенных единицах по своей частоте почти в два раза выше в алмазе, чем в кремнии и германии. Остальные наблюдаемые кривые дисперсии для алмаза довольно похожи на кривые дисперсии для кремния и германия. Эти результаты, по-видимому, свидетельствуют о том, что эффекты атомной поляризуемости, которые имеют довольно большое значение для кремния и германия, являются менее важными для алмаза.

CURVAS DE DISPERSIÓN DE LOS FONONES EN EL DIAMANTE. Los autores han utilizado un espectrómetro triaxial de difracción neutrónica en el reactor Omega West de Los Alamos para medir varias curvas de dispersión de los fonones que se propagan en el diamante siguiendo direcciones de simetría. Todas las mediciones se realizaron a la temperatura ambiente. La muestra consistió en un diamante industrial pardo del tipo IIa, de 242,8 quilates (48,56 g). Su estudio por difracción neutrónica reveló que estaba constituido por un monocristal de gran tamaño con una dispersión mosaica de un ancho total a la semialtura de  $-1^{\circ}$ , más dos pequeñas zonas desviadas en  $3-5^{\circ}$ . La utilización del espectrómetro se programó para el método de « $\vec{Q}$ constante». En todos los casos se fijó la energía de los neutrones incidentes y los neutrones dispersos perdieron energía. Por empleo de la reflexión (1122) de un monocromador de berilio se obtuvo una intensidad suficiente a una energía incidente bastante elevada como para excitar los modos ópticos del diamante. Entre las dificultades experimentales, además de las debidas a las frecuencias muy altas de los fonones en el diamante, figuró la aparición de picos anómalos, lo que obstaculizó la identificación de las polarizaciones. Se calculó que el margen de error en la medición de las frecuencias era del orden de 2-3%.

El resultado más notable de estas mediciones lo constituye la confirmación de las previsiones, basadas en la absorción infrarroja y en datos acerca del calor específico, de que el diamante no es un homólogo del silicio ni del germanio. Esa falta de homología se manifiesta principalmente en el comportamiento de las ramas acústicas transversales, las cuales, cuando se expresan en unidades debidamente reducidas, presentan una frecuencia que es casi doble en el diamante que en el silicio o el germanio. El resto de las curvas de dispersión observadas para el diamante se asemeja bastante a las del silicio y germanio. Estos resultados parecen indicar que los efectos de la polarizabilidad atómica, que tanta importancia revisten en los dos elementos recién mencionados, la tienen menos en el caso del diamante.

# I. INTRODUCTION

Recently, attempts have been made to deduce the phonon dispersion curves in diamond, following two basically different approaches. In one, phonon frequencies at critical points have been obtained from an analysis of the two-phonon infrared lattice absorption spectrum of diamond. These have been combined with information obtained from measurements of elastic constants, Raman frequency, and specific heat to construct a set of dispersion curves [1]. A measurement of the high end of the phonon frequency distribution spectrum has been made by studying the inelastic scattering of neutrons from a diamond powder sample. The results were consistent with the critical point frequencies obtained from the infrared absorption experiments [2].

In the other approach, use is made of the fact that dispersion curves have been measured by neutron spectroscopy for silicon [3] and germanium [4]. The results for these two substances, which both have the diamond structure, are very similar when an appropriate scaling factor is applied. Moreover, the dispersion curves for both silicon and germanium can be fitted by a theory which takes into account the polarization of the atoms which occurs during their vibrations [5, 6]. It has been suggested that the dispersion curves for diamond might be obtained by properly scaling those measured in silicon and germanium [7]. It turned out that these two approaches predicted rather different dispersion curves for diamond. This experiment was undertaken in an effort to establish the dispersion curves in diamond by a direct measurement, using the methods of neutron spectroscopy.

Preliminary results, including data for the transverse acoustic branches only, have been given in a previous report [8].

#### II. THE DIAMOND SAMPLE

Since lattice vibrations are relatively insensitive to the degree of perfection of the crystal, it was felt that an industrial grade diamond might prove to be an adequate sample. Such a stone was obtained on loan from Industrial Distributors (Sales) Limited. It was light brown in colour and weighed 242.80 carats (48.56 g). (See Fig. 1).

Diamonds have been classified as type I and type II on the basis of their absorption of ultraviolet and infrared radiation [9]. Type II diamonds absorb strongly in the ultraviolet below about 2270 Å, and have infrared lattice absorption bands between 2.5 and 6  $\mu$ m. Type I diamonds show strong absorption below about 3000 Å, and possess an infrared absorption band in the neighbourhood of 8  $\mu$ m, in addition to those bands seen in type II. The additional absorption in type I has been attributed to nitrogen present as a substitutional impurity [10]. Some type II diamonds are semiconductors; these have been designated type II b, and the non-conducting variety are called type II a [11]. In order to classify the diamond sample and to determine its crystallographic quality, the following measurements were made.

1. Infrared absorption. The absorption spectrum was measured in the range from 2.5 to 16  $\mu$ m with a Perkin Elmer Model 421 Grating Spectrometer. The spectrum was characteristic of a type II diamond, with negligible absorption in the neighbourhood of 8  $\mu$ m.

2. Ultraviolet absorption. The absorption spectrum in the range from 6000 to 2330 Å was measured with a Cary Spectrometer Model 14. The absorption increased monotonically with decreasing wavelength. It increased sharply at 2350 Å, and by 2320 Å had exceeded the range of the instrument.





The diamond sample

3. Electrical resistance. The resistance of the diamond was measured across the shortest dimension (about 5/8 in) between electrodes formed of conducting paint, using a Keithley Model 415 micromicroammeter and a 45-V impressed potential. The resistivity was calculated to be greater than  $10^{12} \ \Omega \text{cm}$ .

4. Birefringence. The diamond exhibited birefringence when placed between crossed polaroids.

5. Mosaic structure. The crystal was placed in a neutron diffractometer and a scan made over the surface of a reciprocal space sphere corresponding to (111) reflections. This scan revealed that there were actually three distinct mosaic groups. The most intense reflections, which may be considered as due to the main body of the crystal, were approximately 40 times as strong as the next most intense, and 60 times as strong as the least intense. The centres of these latter groups were displaced by five and three degrees, respectively, from the centre of the main group. Reciprocal lattice points due to the misoriented regions were about two degrees below the (110) plane in the quadrant in which the phonon dispersion curves were measured, which reduced their effect on the measurements. The mosaic spread of the main body of the crystal was approximately Gaussian in shape, with a full width at half maximum of ~1°.

6. Lattice space. The crystal was aligned with a (110) plane horizontal, and an intensity contour map of the reciprocal lattice sites (008), (444), (660), (444), (008), (444), (660) and (444) was made. The contours were roughly elliptical in shape, with major axes directed approximately along radial lines through (000). The centroids of the half-height contours were used to calculate the lattice space of the crystal. Values computed from individual reciprocal lattice points ranged from 3.5577 to 3.5750 Å. The average value obtained from the eight symmetrically placed reciprocal lattice points was  $3.5680 \pm 0.0037$  Å, which is in good agreement with the value 3.5672 Å given in [12]. The spread in values obtained from individual reciprocal lattice points is felt to be real and indicative of the presence of internal strain in the crystal. This is consistent with the observed birefringence of the crystal.

The above measurements indicate that the diamond sample was type II a, had a relatively large mosaic distribution, and was subject to internal strain. To investigate whether these properties of the sample affected the lattice vibrations, a measurement of the first order Raman line was made using a Cary Model 81 Raman Spectrometer. A value of  $1331 \pm 1 \text{ cm}^{-1}$  was obtained for the frequency shift. This is in close agreement with the published value of  $1332 \text{ cm}^{-1}$ .

## III. EXPERIMENTAL DETAILS

Phonon dispersion curves in the diamond sample were measured with a three-axis neutron diffraction spectrometer located at the Los Alamos Omega West Reactor. A schematic diagram of the apparatus is shown in Fig. 2. Neutrons from the reactor core passed through 3 in of beryllium and entered a beam tube, 3 in in diameter at the inner end tapering to a 2-in square cross-section. At the reactor operating power of 5 MW, the thermal neutron flux was  $2.5 \times 10^{13}$ /cm<sup>2</sup> s at the inner end of the beam tube and  $1.2 \times 10^{9}$ /cm<sup>2</sup> s at the monochromator position. The monochromator Bragg angle  $\theta$  was fixed at 18.9°. The incident neutron collimator employed Soller slits and had an angular divergence of 0.60° full width at half maximum.

The (220) planes of an aluminium crystal and the  $(11\overline{2}2)$  planes of a beryllium crystal were used as monochromators. Both monochromator crystals had a mosaic structure approximately 0.4° full width at half maximum. The aluminium monochromator gave a neutron wavelength of 0.925 Å (0.096 eV) and the beryllium 0.627 Å (0.208 eV). The use of these rather high incident neutron energies was necessitated by the phonon energy spectrum in diamond, which extends up to 0.165 eV. The monochromatic flux incident on the sample, as measured by a fission counter containing 3 mg of U<sup>235</sup>, was  $6.4 \times 10^5/\text{cm}^2$  s at 0.925 Å and  $6.7 \times 10^4/\text{cm}^2$  s at 0.625 Å.

The diamond was aligned in place by neutron diffraction. All measurements were made in the  $(1\overline{10})$  plane of the sample at room temperature. Scattered neutron collimators having angular divergences of 0.67° and 0.90° full width at half maximum were used at various times. These collimators were also of Soller slit construction. The (111) planes of an aluminium crystal were used to analyse the wavelength distribution of the scattered neutrons. A ceramic end window  $B^{10}F_3$  proportional counter, Reuter-Stokes Model RSN-108 S, was used as the neutron detector. Extensive shielding surrounded the monochromator, analyser and detector. The detector counting rate, with the reactor on and the beam tube open and with the sample removed, was less than 1 cpm and was essentially independent of the scattering angle and analyser setting. No filters or other special devices were used to reduce the fast neutron background.



Schematic diagram of the three-axis spectrometer.

The analyser Bragg angle A, the scattering angle B and the crystal orientation angle C were automatically set to values which were read from a punched paper tape. Angle A could be set to the nearest 0.001°, and angles B and C to the nearest 0.01°. Data were recorded on an electric typewriter, and could be punched on paper tape if desired. The constant- $\vec{Q}$  method of operation [13], with neutron energy loss, was used exclusively. Programme tapes were prepared directly on the Los Alamos MANIAC II digital computer. Scans of a single-phonon peak required from 3.5- to 32-h running time. Because of the long running times involved and the known constancy of the back-ground, no background counts were taken during the scans.

Care was taken to avoid satisfying the conditions for Bragg scattering of the incident neutrons when the analyser was set to reflect neutrons of twice or three times the incident wavelength. Under these conditions, elastically scattered neutrons could reach the detector via second or third order reflection at the analyser and interfere with the observation of true one-phonon neutron groups.

#### TABLE I

# FREQUENCY $\omega$ (IN UNITS OF 10<sup>14</sup> rad/s) versus REDUCED WAVE VECTOR q/q<sub>max</sub> (DIMENSIONLESS) FOR PHONONS PROPAGATING IN THE [100] DIRECTION IN DIAMOND

| q/q <sub>max</sub> | $\omega_{\mathrm{TA}}$ | ٣το  | ωLA  | ωLO  |
|--------------------|------------------------|------|------|------|
| 0.30               | 0.645                  | 2.42 |      |      |
| 0.35               | 0.743                  |      |      |      |
| 0.40               | 0.858                  | 2,37 |      |      |
| 0.45               | 0.946                  |      |      |      |
| 0.50               | 1.025                  | 2.29 | 1.39 |      |
| 0.55               | 1.091                  |      |      |      |
| 0,60               | 1.156                  | 2.25 | 1.68 |      |
| 0.65               | 1.215                  |      |      |      |
| 0.70               | 1.274                  | 2.18 | 1.87 | _    |
| 0.75               | 1.322                  |      |      |      |
| 0.80               | 1.370                  | 2.12 | 2,00 | 2.42 |
| 0,85               | 1.418                  |      |      |      |
| 0 <b>.</b> aó      | 1.459                  | 2.07 | 2.14 |      |
| 0,95               | 1.492                  |      |      |      |
| 1.00               | 1.513                  | 2.03 | 2.25 | 2.25 |

Note: Errors are estimated to be in the range 2-3%.

Polarizations were identified by selecting regions in the reciprocal lattice where the desired phonon was the only one which would be expected to have appreciable intensity.

## IV. RESULTS

The experimental data are given in Tables I and II. Some of the data are averages of frequencies obtained from two or more individual scans. In general, the transverse phonons were more intense and better focused than the longitudinal ones, and are therefore considered to be the more accurate. Errors in the individual frequencies are estimated to be of the order of 2-3%.

In Fig. 3 we show the experimental dispersion curves together with the critical point frequencies deduced from infrared absorption by HARDY and SMITH [1]. The agreement may be seen to be reasonably good. One discrepancy exists, however. Hardy and Smith assumed that the highest fre-

#### TABLE II

# FREQUENCY $\omega$ (IN UNITS OF 10<sup>14</sup> rad/s) versus REDUCED WAVE VECTOR q/q<sub>max</sub> (DIMENSIONLESS) FOR PHONONS PROPAGATING IN THE [111] DIRECTION IN DIAMOND

| q/q <sub>max</sub> | ω <sub>TA</sub> | ωτο    | ωLA  | ωLO   |
|--------------------|-----------------|--------|------|-------|
| 0.30               | 0.531           |        |      |       |
| 0.35               | 0.606           |        |      |       |
| 0.40               | 0.671           |        | 1.06 |       |
| 0.45               | 0.734           | •      |      |       |
| 0.50               | 0.791           | 2.37   | 1,25 |       |
| 0.55               | 0.839           |        |      |       |
| 0.60               | 0.877           | 2.29   |      | 2.40  |
| 0.65               | 0.921           | :      |      |       |
| 0.70               | 0.948           | 2.27   | 1.63 |       |
| 0.75               | 0.981           |        |      |       |
| 0.80               | 1.008           | 2.26   | 1.83 | *2,38 |
| 0.85               | 1.014           |        |      |       |
| 0.90               | 1.028           | 2.26   | 1.87 |       |
| 0.95               | 1.036           |        |      |       |
| 1.00               | 1.040           | . 2.28 | 1.95 | 2,34  |
| 1                  | 1               | 1      |      |       |

Note: Errors are estimated to be in the range 2-3%.

quency at each critical point is the transverse optical, whereas we find that the longitudinal optical branch has the highest frequency.

In order to make a comparison between silicon and diamond we have put the frequencies into dimensionless form by dividing by the corresponding Raman frequency. This is not the only way to make a dimensionless comparison but should at least be independent of any theoretical model. The comparison is given in Fig. 4.

It is immediately evident that the two substances are not homologous. In diamond the LO branch is highest and in silicon the TO branch is highest. The TA branches are much flatter in silicon than they are in diamond. The longitudinal branches are in general somewhat higher in diamond than in silicon. The most striking differences may be expressed by saying that the splitting of the TA and TO branches at the zone boundaries is much larger in silicon than it is for diamond.

For phonons which propagate in symmetry directions, the atomic motions correspond to whole planes of atoms moving in phase. The equations of motion are formally equivalent to those for a linear chain and can be



Fig. 3

Experimental dispersion curves for diamond. The point indicated by the square symbol is the Raman frequency determined from optical measurements. The solid lines through the origin indicate initial slopes calculated from the elastic constants of McSKIMIN and BOND [14]. The dashed lines suggest the trend of the curves but have no theoretical significance. The points with error bars plotted at the sides of the figure are the critical point frequencies obtained from infrared absorption measurements by HARDY and SMITH [1]. They are to be compared with the zone boundary values of the observed dispersion curves.

solved exactly in terms of parameters which represent the force on a given atom due to the displacement of an entire plane of neighbours. As a first step in the analysis of the dispersion curves, we have fitted the data with theoretical curves derived from linear chain models to obtain interplanar force constants for each measured polarization and direction of propagation. We have not yet obtained atomic parameters from the interplanar force constants. We have, however, obtained estimates of the elastic constants by going to the long wavelength limit of the linear chain models. Although this method of determining elastic constants is not particularly accurate, the values obtained were much closer to those of McSKIMIN and BOND [14] than they were to any of the other reported values [15, 16, 17].

# V. SUMMARY

Dispersion curves for the [100] and [111] directions in diamond have been obtained with 2-3% accuracy by neutron spectroscopy. Frequencies



Fig. 4

Comparison of the experimental dispersion curves of diamond and silicon. The curves for silicon were plotted from the data of DOLLING [6]. Both sets of curves have been normalized by dividing by the Raman frequency.

at the zone boundary critical points are in reasonable agreement with those deduced from infrared lattice absorption measurements, although the identification of the polarizations is different. Diamond is definitely not homologous to silicon and germanium. Of the various elastic constants which have been reported for diamond, those of McSkimin and Bond are the most compatible with the neutron data.

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# DISCUSSION

G. DOLLING: You mention that you tried a Fourier analysis, in terms of "interplanar" force constants, for the TA and TO modes along the [111] direction. Did you try a simple Fourier analysis of the L [100] modes, which are continuous in the extended zone scheme and, if so, how many Fourier coefficients (and hence interatomic forces) were required?

J. WARREN: The data required only three interplanar force constants in the L [100] direction. This implies only three atomic neighbours. However, the data for the transverse branches in the [111] direction, which is more accurate, indicate that five or perhaps even six atomic neighbours will be necessary as in the case of germanium.

# THE CRYSTAL DYNAMICS OF URANIUM DIOXIDE

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#### Abstract — Résumé — Аннотация — Resumen

THE CRYSTAL DYNAMICS OF URANIUM DIOXIDE. The normal modes of vibration of uranium dioxide have been studied by means of coherent one-phonon scattering of slow neutrons from a single crystal specimen of stoichiometric composition. The measurements, which were performed at room temperature, were made using the triple-axis crystal spectrometer at the NRU reactor at Chalk River, mainly by means of the "constant- $\vec{\sigma}$ " technique. Since the crystal structure of uranium dioxide is of the calcium fluoride type, it is possible to measure six distinct branches of the dispersion relation propagating along the highly symmetric directions  $[00\zeta]$ ,  $[\zeta\zeta\zeta]$  and  $[\zeta\zeta\zeta]$ , with the crystal oriented in the  $(1\overline{10})$  mirror plane. ( $\zeta$  is a wave vector co-ordinate expressed in reciprocal lattice units). There are three frequencies for the long wavelength optic modes of the calcium fluoride structure. In uranium dioxide the triply-degenerate mode has a frequency of 13.42 ± 0.16 (units  $10^{12}$  c/s), the transverse optic mode a frequency of  $8.52 \pm 0.11$ , and the longitudinal mode a frequency of  $16.7 \pm 0.6$ . These results may be used together with the measured refractive index, and the relation connecting the frequencies of the optic modes and the dielectric constants derived by Lyddane, Sachs and Teller, to predict a static dielectric constant of  $20.4 \pm 1.5$ . The frequencies of the acoustic modes with wave vector (0, 0, 1) are for the transverse branch 3.27 ± 0.08, and for the longitudinal branch, 5.27 ± 0.08. For the wave vector (0.5, 0.5, 0.5), the corresponding frequencies are 2.75±0.04 and 5.24±0.10. The slopes of the acoustic dispersion curves at long wavelengths enable the elastic constants to be predicted as follows:  $C_{11}$ ,  $4.2 \pm 0.2$ ;  $C_{12}$ ,  $1.3 \pm 0.2$ ;  $C_{44}$ ,  $0.75 \pm 0.06$  (units  $10^{12}$  dyn/cm<sup>2</sup>).

DYNAMIQUE DES CRISTAUX DE BIOXYDE D'URANIUM. Les auteurs ont étudié les modes normaux de vibration du bioxyde d'uranium au moyen de la diffusion cohérente, à un phonon, des neutrons lents provoquée par un monocristal de composition stoéchiométrique. Les mesures ont été effectuées, à la température ambiante, au moyen du spectromètre à cristal triaxial du réacteur NRU, à Chalk River, en général à l'aide de la technique de «Q constant». Etant donné que la structure cristalline du bioxyde d'uranium est du type fluorure de calcium, il est possible de mesurer les six branches distinctes de la relation de dispersion qui se propagent dans les directions fortement symétriques [00g] et [ggg], le cristal étant orienté dans le plan miroir (110). (5 est une coordonnée du vecteur d'onde exprimée en inverses d'unités du réseau.) Les modes optiques de grande longueur d'onde de la structure fluorure de calcium comportent trois fréquences. Dans le bioxyde d'uranium, le mode triplement dégénéré a une fréquence de  $13.42 \pm 0.16$  (unités de  $10^{12}$  c/s), le mode optique transversal, une fréquence de  $8,52\pm0.11$  et le mode longitudinal, une fréquence de  $16.7\pm0.6$ . Ces résultats utilisés en conjonction avec la mesure de l'indice de réfraction et la relation entre fréquences des modes optiques et constantes diélectriques établie par Lyddane, Sachs et Teller, permettent de prévoir une constante diélectrique statique de 20,4±1,5. Les fréquences des modes acoustiques à vecteur d'onde (0, 0, 1) sont, pour la branche transversale, 3,27 ± 0,08 et pour la branche longitudinale, 5,27 ± 0,08. Pour le vecteur d'onde (0,5, 0,5, 0,5), les fréquences correspondantes sont 2,75 ± 0,04 et 5,24 ± 0,10. Les pentes des branches acoustiques de la courbe de dispersion pour les grandes longueurs d'onde permettent de prévoir les constantes d'élasticité suivantes: C11, 4,2±0,2; C12, 1.3±0,2; C44, 0,75±0,06 (en unités de 10<sup>12</sup> dyn/cm<sup>3</sup>).

ДИНАМИКА КРИСТАЛЛА ДВУОКИСИ УРАНА. Нормальные формы колебания двуокиси урана были изучены с помощью когенентного однофононного рассеяния медленных нейтронов на монокристаллических образцах стехиометрической структуры. Измерения, которые осуществлялись при комнатной температуре с помощью трехосного кристаллического спектрометра на реакторе NRU в Чок-Ривер, проводились главным образом с применением методики "постоянного Q". Поскольку кристаллическая структура двуокиси урана подобна структуре фторида кальция, можно измерить шесть отдельных ветвей связей дисперсии, распространяющихся вдоль высокосимметричных направлений [005], [550] и [555], если кристалл ориенти-

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рован в плоскости зеркала (110). ( $\xi$ -координат волнового вектора, выраженный в обратных единицах решетки). Имеются три частоты для длинноволновых оптических колебаний структуры фторида кальция. В двуокиси урана трижды вырожденное колебание имеет частоту 13,42±0,16 (единиц 10<sup>12</sup> герц), поперечное оптическое колебание -частоту 8,52±0,11 и продольное колебание-16,7±0,6. Эти результаты можно использовать вместе с измеренным показателем преломления и соотношением, связывающим частоты оптических колебаний и диэлектрические постоянные, выведенным Лидданом, Захсом и Теллером для определения статической диэлектрической постоянной порядка 20,4±1,5. Частоты акустических колебаний с волновым вектором (0,0,1) составляют для поперечной ветви 3,27±0,08, а для продольной-5,27±0,08. При волновом векторе (0,5,0,5,0,5) соответствующие частоты составляют 2,75±0,04 и 5,24±0,10. Наклоны кривых акустической дисперсии при больших длинах воли позволяют предсказать следующие размеры постоянных упругости: С<sub>11</sub>, 4,2±0,2; С<sub>12</sub>, 1,3±0,2; С44, 0,75±0,06 (единиц 10<sup>12</sup> дин/см<sup>2</sup>).

DINAMICA DE LA RED CRISTALINA DEL DIOXIDO DE URANIO. Los autores han estudiado los modos normales de vibración del dióxido de uranio por dispersión coherente monofonónica de neutrones lentos en un monocristal de composición estequiométrica. Efectuaron las mediciones a temperatura ambiente con el espectrómetro de cristal triaxial instalado en el reactor NRU de Chalk River, aplicando principalmente la técnica de « constante». Dado que la estructura cristalina del dióxido de uranio es del mismo tipo que la del fluoruro cálcico, las seis ramas separadas de la relación de dispersión que se propagan en las direcciones de elevado grado de simetria  $[00\zeta]$ ,  $[\zeta\zeta\zeta]$  y  $[\zeta\zeta\zeta]$  pueden medirse con el cristal orientado según el plano especular (110). ( $\zeta$  es una coordenada del vector de ondas, expresada en unidades del reticulado recíproco.) Los modos ópticos de onda larga de la estructura del fluoruro cálcico presentan tres frecuencias. En el dióxido de uranio, la frecuencia del modo de degeneración triple es  $13.42 \pm 0.16$  (unidad:  $10^{12}$  c/s), la del modo óptico transversal  $8.52 \pm 0.11$ , y la del longitudinal  $16.7 \pm 0.6$ . Estos resultados se pueden emplear en combinación con el índice de refracción medido y con la fórmula de Lyddane, Sachs y Teller, que vincula las frecuencias de los modos ópticos con las constantes dieléctricas, para predecir una constante dieléctrica estática de 20,4±1,5. Las frecuencias de los modos acústicos con un vector ondulatorio (0,0,1) ascienden a  $3,27 \pm 0,08$  para la rama transversal y a  $5,27 \pm 0,08$  para la longitudinal. Las frecuencias correspondientes al vector de ondas (0.5, 0.5, 0.5) son 2.75±0.04 y 5.24±0.10. La pendiente de las curvas de dispersión acústica para grandes longitudes de onda permite evaluar las constantes de elasticidad siguientes:  $C_{11} = 4.2 \pm 0.2$ ;  $C_{12} = 1.3 \pm 0.2$ ;  $C_{44} = 0.75 \pm 0.06$ . (unidad;  $10^{12} \text{ dinas/cm}^2$ ).

# 1. INTRODUCTION

The physical properties of uranium dioxide  $(UO_2)$  have been the subject of considerable study, particularly those properties of the bulk material which are required for engineering applications [1, 2]. In spite of this, information concerning the crystal dynamics (including measurements of the elastic and dielectric constants) is very sparse, and while it is known to become antiferromagnetic [3, 4] at about 28%, the details of the magnetic structure are still uncertain.

Accordingly, a series of experiments utilizing inelastic neutron scattering from a single crystal specimen has been initiated to study the dynamical properties of UO<sub>2</sub>; this paper reports measurements of the frequency-wave vector ( $\nu(\vec{q})$ ) dispersion relation for the normal modes of vibration propagating in the [005], [550], and [555] directions.

Previous experiments [5] using a powdered specimen have measured the energy distribution of neutrons at several angles of scattering. Features of this distribution can be correlated with the measurements of  $\nu(\vec{q})$  described below.

Uranium dioxide has the calcium fluoride structure, i.e. three interpenetrating face-centred cubic lattices, a uranium ion being at the origin and oxygen ions at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$  and  $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})a$ , where a is the cubic unit cell side. Measurements of  $\nu(\vec{q})$  for calcium fluoride have been carried out using X-ray [6] and inelastic neutron scattering [7] techniques.

#### 2. EXPERIMENT

The measurements were made at a temperature of 296 K using a singlecrystal specimen about 1 cm in diameter and 3 cm in length. The specimen was oriented with its (110) plane parallel to the plane containing the incident and scattered neutron beams. The experiments were carried out using the triple-axis crystal spectrometer at Chalk River, generally in its constant- $\vec{Q}$  mode of operation [8]. Neutron energy loss processes were observed and the energy of the incident neutrons was varied. Analyser angles corresponding to scattered neutron energies of 0.0217 and 0.0320 eV were used for the majority of the measurements. Measurements were made along the [00 $\zeta$ ], [ $\zeta \zeta 0$ ] and [ $\zeta \zeta \zeta$ ] symmetry directions, and structure factor calculations, based on a rigid ion model for UO<sub>2</sub>, were used as a guide in determining the most suitable points in reciprocal space at which to conduct the experiments.

The determination of the dispersion curves yielded to straightforward techniques quite readily in most cases. The longitudinal acoustic  $(\Delta_1(A))$  branch in the [00\$] direction near  $\$ \approx 0.7$ , proved difficult to observe and no position in reciprocal space could be found which simultaneously had a favourable structure factor and a good focussing arrangement. The highest frequency optic branches,  $\Delta_1(0)$ ,  $\Sigma_1(01)$  and  $\Lambda(01)$ , were also difficult to determine but this was mainly due to the high frequencies involved.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the measured dispersion curves for the  $[00\zeta]$ ,  $[\zeta\zeta 0]$  and  $[\zeta\zeta\zeta]$  directions and Table I lists the frequencies of some selected modes. The errors are generally 2 to 3% in frequency but are considerably larger for the branches of highest frequency.

These curves show several unexpected features. The longitudinal acoustic and transverse optic branches are accidentally degenerate, within the limits of the experiment, at the point (0, 0, 1). The ratio of the mass of uranium to that of oxygen is very large, 14.9, and it might be expected that there would be a considerable gap in the frequency distribution function between the optic and acoustic branches. The curves show quite clearly that there is no band gap between the optic and acoustic branches. For example, the  $\Delta_2^1$  branch in the [005] direction falls steeply from a frequency of  $13.42 \times 10^{12}$  c/s at q = 0 to a frequency of  $5.27 \times 10^{12}$  c/s at the zone boundary.

Table II lists some of the properties of  $UO_2$  compared with values derived from the experimental results. Agreement with limited data on the elastic constants is reasonably good. The high frequency dielectric constant is known, but a literature search failed to disclose a value for the static

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### TABLE I

| Wave vector co-ordinates $(\zeta_1, \zeta_2, \zeta_3)$ | Mode               | Frequency<br>(units 10 <sup>12</sup> c/s) |
|--|--------------------|---|
| (0, 0, 0)  | (Longitudinal)     | 16.7 ± 0.6                                |
|  | . Γ25              | 13.42±0.16                                |
|  | (Transverse)       | 8.52±0.11                                 |
| (0, 0, 1,0)  | Mı                 | 18.6 ±1.0                                 |
|  | M'5                | 13.68 ± 0.21                              |
|  | Ms                 | 6.98 ± 0.12                               |
|  | M*2                |   |
|  | M*3                | 5.27 ± 0.08                               |
|  | M*5                | 3.27±0.08                                 |
| (0.6, 0.6, 0)  | Σ1(01)             | 16.8 ±0.7                                 |
|  | Σ1(02)             | 14.0 ±0.5                                 |
|  | Σ3(01)             | 9.85±0.20                                 |
|  | Σ3(02)             | 6.49±0.11                                 |
|  | Σ <sub>1</sub> (A) | 4.64 ± 0.07                               |
|  | Σ <sub>3</sub> (A) | 4.25 ± 0.06                               |
| (0.5, 0.5, 0.5)  | L'1                | (17.5 ±1.3)                               |
|  | L <sub>1</sub>     | 12.6 ±0.4.                                |
| · · · ·  | L'3                | 12.2 ±0.4                                 |
|  | L <sub>3</sub>     | $10.57 \pm 0.25$                          |
|  | L'i                | $5.24 \pm 0.10$                           |
|  | L'3                | 2.75±0.04                                 |

# FREQUENCIES OF SELECTED NORMAL MODES OF VIBRATION IN URANIUM DIOXIDE AT 296%

Note: No space group symbol is shown for the  $\Gamma_{15}$  modes at q=0 which are split by the macroscopic electric field.

dielectric constant. This may be calculated from the LYDDANE, SACHS and TELLER relation [9], namely

$$(\nu_{\rm LO}^2 / \nu_{\rm TO}^2)_{\rm q=0} = \epsilon_0 / \epsilon_\infty.$$

In this equation  $(\nu_{LO})_{q=0}$  and  $(\nu_{TO})_{q=0}$  are the frequencies of the non-degenerate longitudinal and transverse optic modes at q=0, and  $\epsilon_0$  and  $\epsilon_{\infty}$  the static



# Fig. 1

The dispersion curves of uranium dioxide at 296°K Open circles and triangles indicate the polarization index assigned to each mode, Solid points denote uncertain polarization. No space group symbol is shown for the  $\Gamma_{15}$  modes at q=0which are split by the macroscopic electric field. The solid lines represent the best least-squares fit to the results on the basis of a rigid ion model.

# TABLE II

# SOME PROPERTIES OF URANIUM DIOXIDE AT 296%

| _   | Values      |                  |  |
|---|-------------|------------------|--|
| Property  | This paper  | Other references |  |
| Lattice constant (Å)  |             | 5.469 [1]        |  |
| Elastic constants; C11  | 4.2 ±0.2    |                  |  |
| (10 <sup>12</sup> dyn/cm) C <sub>12</sub>                             | 1.3 ± 0.2   |                  |  |
| C <sub>44</sub>   | 0.75 ± 0.06 |                  |  |
| (0.61 C <sub>11</sub> + 0.39 C <sub>12</sub> + 0.78 C <sub>44</sub> ) | 3.65±0.2    | 3.4±0.2[2]       |  |
| Dielectric constants: $\epsilon_{\infty}$                             | -           | 5.3 [1]          |  |
| ε <sub>0</sub>  | 20.4 ± 1.5  |                  |  |

and high frequency dielectric constants, the resulting  $\epsilon_0$  is included in Table II.

The solid curves shown in Fig. 1 were calculated on the basis of a rigid ion model for the interionic forces in uranium dioxide. Six parameters were employed to describe axially symmetric short range forces between the uranium and the oxygen ions, between nearest-neighbour oxygen ions, and between neighbouring uranium ions. The ionic charge was described by a seventh parameter. Best-fit values for the seven parameters were obtained from a least-squares analysis of the experimental results along the  $[00\zeta]$  and  $[\zeta\zeta\zeta]$  directions. The agreement obtained with experiment is not good, but could presumably be improved by taking account of the polarizability of the ions by means of a shell model. We hope to complete an analysis of this kind in the near future.

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## DISCUSSION

W. GLÄSER: Have you tried to calculate a frequency distribution from the force constants of your fit and, if so, how does this compare with the directly measured distribution of Thorson and Haywood?

G. DOLLING: No, we have not done this, since we are not yet fully satisfied with the dipole approximation models we have recently constructed. However, there are a few kinks in the scattering distribution observed by Thorson and Haywood, and these correspond quite well with certain flat regions  $(d\nu/dq = 0)$  of our measured dispersion curves.

# INTERFERENCE EFFECTS IN SLOW NEUTRON INELASTIC SCATTERING FROM POLYCRYSTALLINE SOLIDS\*

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#### Abstract — Résumé — Аннотация — Resumen

INTERFERENCE EFFECTS IN SLOW NEUTRON INELASTIC SCATTERING FROM POLYCRYSTALLINE SOLIDS. Slow neutron inelastic scattering measurements have been made at the MTR on polycrystalline samples of beryllium and aluminium, both coherent scatterers. The inelastic scattering for both samples displays considerable structure which is directly related to the interference conditions for coherent scattering. Energy transfers observed in both experiments extend beyond the range for single-phonon scattering, and the observed wave-vector changes span the region where interference effects are important. Details in the observed structure are correlated with (1) the periodic nature of the reciprocal lattice, (2) the polarization factor  $(\vec{x} \cdot \vec{\xi})^2$ , (3) the so-called "dynamic structure factor"  $g_1^2$  ( $\vec{d}$ ), and (4) the frequency distribution of the lattice vibrations. An attempt was made to obtain the frequency distribution from the data by applying the incoherent approximation, and it is concluded that this approximation can be relied on only to give the approximate locations of strong maxima and the approximate cut-off frequency of the distribution.

EFFETS D'INTERFÉRENCE DANS LA DIFFUSION INÉLASTIQUE DES NEUTRONS LENTS PAR DES SOLIDES POLYCRISTALLINS. Au réacteur d'essai de matériaux exploité par la Phillips Petroleum Company à Idaho Falls (Idaho, Etats-Unis), les auteurs ont procédé à des mesures de la diffusion inélastique des neutrons lents par des polycristaux de béryllium et d'aluminium, agents de diffusion cohérente l'un et l'autre. La diffusion inélastique par ces deux polycristaux présente une structure dont une grande partie est en relation directe avec les conditions d'interférence pour la diffusion cohérente. Les transferts d'énergie observés dans l'une et l'autre expérience ont une portée plus grande que pour la diffusion à un phonon, et les variations du vecteur d'onde observées couvrent la région où les effets d'interférence sont importants. Des aspects particuliers de la structure observée sont en correlation avec les caractéristiques suivantes: 1. le caractère périodique du réseau réciproque; 2. le facteur de polarisation ( $\vec{k} \cdot \vec{\xi}$ )<sup>2</sup>. 3. le « facteur de structure dynamique»  $g_1^2$  ( $\vec{q}$ ); 4. la distribution de fréquence des vibrations du réseau. A partir des données établies, les auteurs se sont efforcés la conclusion que cette approximation permet seulement de determiner d'une manière approximative les emplacements des maxima élevés et la fréquence de coupure de la distribution.

ЭффЕКТЫ ИНТЕРФЕРЕНЦИИ ПРИ НЕУПРУГОМ РАССЕЯНИИ МЕДЛЕННЫХ НЕЙ-ТРОНОВ НА ПОЛИКРИСТАЛЛИЧЕСКИХ ТВЕРДЫХ ТЕЛАХ. Измерения неупругого рассеяния медленных нейтронов проведены на реакторе МТВ в поликристаллических образцах бериллия и альминия, оба-когерентные рассеятели. При неупругом рассеянии у обоих образцов обнаруживается сложная структура, которая непосредственно связана с условиями интерференции при когерентном рассеянии. Передача энергии, наблюдаемая в обоих экспериментах, выходит за рамки диапазона рассеяния единичного фонона, и наблюдаемые изменения волнового вектора охватывают область, в которой эффекты интерференции играют важное значение. Подробности в наблюдаемой структуре уточняются с учетом 1) периодичности обратной решетки, 2) коэффициента поляризации  $(\vec{x}, \vec{\xi})^2$ , 3) так называемого "коэффициента динамической структуры"  $g_i^2$  (d) и 4) частотного распределения колебаний решетки. Была предпринята попытка вывести частотное распределение из данных путем применения некогерентного приближения. Делается вывод, что такое приближение может служить основанием только при определении приблизительных местоположений основных максимумов и приблизительной пороговой частоты распределения.

<sup>\*</sup> Work performed under the auspices of the United States Atomic Energy Commission.

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EFECTOS DE INTERFERENCIA EN LA DISPERSIÓN INELASTICA DE NEUTRONES LENTOS EN SOLIDOS POLICRISTALINOS. Los autores han efectuado en el reactor MTR mediciones de la dispersión inelástica de neutrones lentos en muestras policristalinas de los dispersores coherentes berilio y aluminio. La dispersión inelástica en estos elementos presenta una estructuración considerable, que guarda una relación directa con las condiciones de interferencia para la dispersión coherente. Las transferencias de energía observadas en los dos experimentos abarcan un intervalo más extenso que el que corresponde a la dispersión monofonónica, y los cambios del vector de onda observados llegan hasta la región en que los efectos de interferencia adquieren importancia. Se establece una correlación entre los detalles estructurales observados y 1) el carácter periódico del reticulado recíproco, 2) el factor de polarización  $(\vec{x} \cdot \vec{\xi})^2$ , 3) el denominado «factor dinámico de estructura»  $g_1^2(\vec{q})$ , y 4) la distribución de las frecuencias de las vibraciones reticulares. Los autores procuran establecer la distribución de las frecuencias a partir de los datos obtenidos, utilizando la aproximación incoherente, y llegaron a la conclusión de que sólo es válida para determinar la localización aproximada de los máximos acusados y hallar la frecuencia aproximada de corte de la distribución.

# 1. INTRODUCTION

Inelastic scattering studies of polycrystalline solids have been focused primarily on incoherent or partially incoherent scatterers [1] for which one can extract the phonon frequency distribution from the scattering data. By way of contrast, in this paper we are concerned with scattering from polycrystalline materials which are purely coherent scatterers. Previous work in this area includes measurements on graphite [2] and beryllium [3].Beryllium powder was studied at the Materials Testing Reactor (MTR) [4] as a supplement to the previous measurements of the dispersion relations for single-crystal beryllium [5], and because of the structure observed in the beryllium powder data, measurements on aluminium were undertaken.

The choice of aluminium was made because of its simpler crystal structure, face-centred cubic, compared to the hexagonal close-packed structure of beryllium. Aluminium has one atom per primitive unit cell compared to two for beryllium and, hence, three branches to its dispersion relation compared to six for beryllium. The phonon dispersion relations [5,6] have been measured for both materials and their frequency distributions [7,8] have been calculated. Both materials are coherent scatterers with low absorption cross-sections.

In the neutron scattering process the energy and momentum transfer are given by hw and hk respectively where  $\vec{k} = \vec{k}_0 - \vec{k}$  and  $h\omega = E - E_0$ . The energy and wave vector of the neutron before and after scattering are given respectively by  $E_0$ ,  $\vec{k}_0$  and  $\vec{E}$ ,  $\vec{k}$ . For the case of coherent scattering by a solid, the wave vector equation is modified to  $\vec{k} = \vec{k}_0 - \vec{k} = 2\pi \vec{\tau} - \vec{q}$ , where  $\vec{\tau}$  is a translation vector of the reciprocal lattice,  $\vec{q}$  is the phonon wave vector, and the phonon dispersion relation is given by  $\omega = \omega(\vec{q})$ . The differential cross-section for coherent single-phonon scattering by a solid has been worked out by others [9, 10] and will be referred to in the analysis of the aluminium and beryllium data. In addition, EGELSTAFF [11] has discussed the interpretation of data for coherent scattering from polycrystalline solids.

Slow neutron scattering measurements were made on polycrystalline samples of aluminium and beryllium using the MTR phased-chopper velocity selector [12], and the results are presented in the form of reduced partial differential cross-sections  $S(\kappa, \hbar\omega)$ . Structure is observed in the data for both samples and is due in part to the modified form of the wave vector equation which applies here. The shift in the structure on the  $\kappa$ -scale for aluminium as the energy transfer increases is related to the polarization factor  $(\vec{\kappa} \cdot \vec{\xi})^2$  where  $\vec{\xi}$  is a unit vector in the direction of the phonon polarization. The effect of the polarization factor appears to be obscured in the beryllium data; however, a shift of the structure for energy transfers in the range of the optical frequencies is observed and is attributed to the structure factor  $g^2(\vec{q})$ .

An attempt was made to obtain a frequency distribution from the aluminium data by assuming the sample to be an incoherent scatterer. The results of this calculation indicate that the approximation, at best, can give only an approximate description of the frequency distribution.

#### 2. EXPERIMENTAL DETAILS

#### 2.1. Apparatus

The scattering data of these experiments were obtained using the MTR phased-chopper velocity selector [12]. A plan view of the experiment is shown in Fig. 1. The rotor system as it now exists consists of a pair of Fermi-type choppers, designated A and D, and two rotating collimators, designated B and C, the latter of which are 12 in in diameter. Rotor speeds of 12 000 rpm and 6000 rpm are now used for choppers and collimators, respectively. At the time that measurements on beryllium powder were started, all rotors were spun at 6000 rpm. Subsequent data were obtained with all rotors at 7500 rpm and finally with the choppers at 12 000 rpm. All aluminium data were obtained with the highest chopper speed. A factor of two has been gained in the time resolution of the neutron burstingoing from 6000 rpm to 12 000 rpm.

The angular resolution of the experiment has also been improved, particularly at forward scattering angles, by using a smaller number of  $BF_3$  detectors to define each scattering angle. The angle subtended in the horizontal plane by each detector bank increased from 3.64° at the most forward angle of 16° to 7.28° at a scattering angle of 144°. A total of fifteen scattering angles were used in these experiments.

The mode of operation in these experiments has followed the pattern established in other MTR experiments [13]. The sample and an identical empty sample holder were cycled into the beam alternately for 10-min intervals, the data for each scattering angle being stored in a 256-channel segment of the time-of-flight analyser. Ten microsecond channels were used in obtaining all data. Incident energies between 0.04 and 0.10 eV were used in the beryllium experiment and between 0.02 and 0.06 eV for the aluminium.

# 2.2. Samples

The beryllium sample consisted of a layer of powder held between 10-mil aluminium sheets, being clamped around the edges. Principal contaminant in the beryllium sample was oxygen which, because of its small amount and scattering properties, had a negligible effect on the results.



Plan view of the MTR slow-neutron velocity selector

The aluminium sample was composed of a set of blocks, each 2 in  $\times$  0.25 in  $\times$  0.46 in. These blocks were made by pressing aluminium powder and then heating each to 500°C in a vacuum to remove the uniwax lubricant which was used in pressing. To assess the effects of multiple neutron scattering in the sample, data were obtained in the aluminium experiment with and without the aluminium blocks separated by a layer of cadmium.

Both samples had a transmission of 0.87 with the sample oriented at  $45^\circ$  to the incident beam.

### 3. RESULTS

The data from both experiments were converted to partial differential cross-sections  $d^2\sigma/d\epsilon d\Omega$  and reduced partial differential cross-sections  $S(\kappa, \hbar\omega)$ , the latter being presented here in the form S versus  $\kappa$  for constant  $\hbar\omega$ . Reference to the energy transfer is in terms of the dimensionless variable  $\epsilon = \hbar\omega/k_BT$ . With data having been obtained at fifteen different scattering angles and a number of incident energies the data are overdetermined, and for this reason the data have been averaged [4]. A comparison of the averaged data and the unaveraged data is made in Fig. 2 for beryllium data at an energy transfer  $\epsilon = \hbar\omega/k_BT = 1.75$ . Through the averaging process the number of data points in this figure is reduced from 183 to 20. Errors have been evaluated for the averaged points by two methods, first from counting statis-



Fig. 2

Reduced partial differential cross-section data for beryllium comparing the averaged (open points) and unaveraged (solid points) data

tics and second from the standard deviation of the data points from the average value  $\bar{S}$ , and the larger error is displayed in the figure. In Fig.3 a composite of the reduced partial differential cross-sections for beryllium is shown and Fig.4 displays the corresponding data for aluminium.

In these measurements the elastic portion of the scattering in the crosssection profiles is easily distinguishable from the inelastic scattering because of its magnitude and the fact that it matches closely the resolution of the incident neutron burst. For these reasons it has been possible to separate out the reduced partial differential cross-sections for elastic scattering which are displayed for beryllium and aluminium in Figs. 5 and 6, respectively. For the aluminium data of Fig. 6, a comparison is made of the data obtained with and without cadmium spacers in the sample.

#### 4. DISCUSSION

The elastic scattering data of Figs. 5 and 6 display very prominent structures which are due to Bragg scattering. Scattering from a given set of crystalline planes (hkl) is restricted such that  $|\vec{k}_{Bragg}| = 2\pi/d_{hkl}$  which makes it easy to identify contributions from different planes. At  $\kappa$ -values below the minimum allowed for single Bragg scattering the data are due primarily to multiple elastic scattering. The effect of the cadmium spacers in the aluminium sample is shown in Fig.6. These spacers reduced the amount of multiple scattering which was a result of primary scattering in the vertical direction, i.e. in a direction normal to the cadmium spacers and the scattering plane of the experiment. Multiple scattering was also evident in the inelastic scattering data but need not be considered in discussing the structure in the data.

In discussing the inelastic scattering data of Figs. 3 and 4, reference to a given reciprocal lattice point should be interpreted as reference to a





A composite of the reduced partial differential cross-sections for inelastic scattering from polycrystalline beryllium at a temperature of 25°C  $d^2o/d\Omega dE = (E/E_p)^{\frac{1}{2}} e^{-\epsilon/2} \Im(\vec{\kappa}|, \hbar\omega)$ , where

$$\epsilon = \hbar \omega / k_{\rm B} T$$
 and  $|\vec{\kappa}| = |\vec{k} - \vec{k_0}|$


Fig.4

A composite of the reduced partial differential cross-sections for inelastic scattering from polycrystalline aluminium The curves were hand-drawn through the data to illustrate the structure.

 $d^{2}\sigma/d\Omega dE = (E/E_{0})^{\frac{1}{2}} e^{-\varepsilon/2} S(|\kappa|, \hbar\omega).$ 

where  $\epsilon = \hbar \omega / 0.0254 \text{ eV}$  and T = 22°C



Fig. 5

Reduced partial differential cross-sections for elastic scattering from polycrystalline beryllium Slash marks have been added to the  $\kappa$ -scale at values for which the various crystallographic planes contribute Bragg scattering.

$$d^2\sigma/d\Omega dE = (E/E_n)^{\frac{1}{2}} e^{-\epsilon/2} S([R], \hbar\omega),$$

where  $\epsilon = \hbar \omega / 0.02567$  eV and T = 25°C and E<sub>0</sub> has the following values:

| <b>▲</b> = 0.040 | = 0.0547   |
|------------------|------------|
| Δ = 0.0419       | O = 0.0578 |
| <b>=</b> 0,0427  | ♦ = 0,07   |
| 🗀 = 0,0525       | ♦ = 0,10   |

set of points which are equivalent by symmetry. Further, consider frequency contours mapped about each lattice point for the different branches of the dispersion relation for either aluminium or beryllium. A cut taken through the data of Fig. 3 or 4 is equivalent to circumscribing a sphere of radius  $\kappa$  about the origin in wave-vector space, and at points where this sphere intersects the frequency contours, contributions to the inelastic scattering with a given energy transfer h $\omega$  are recorded. Because of the nature of the dispersion relations for the acoustical vibrations, low frequencies necessarily correspond to frequency contours which are restricted to a small region surrounding each lattice point. This is equivalent to saying that for low energy transfers  $\kappa$  is restricted to  $\kappa = \kappa_{\text{Bragg}} \cong 2\pi/d_{\text{hkl}}$ , and that in the limit of the lowest frequencies the structure should approach that observed in the elastic scattering data. This is confirmed by comparing the data of Figs. 3 and 5 or 4 and 6.





Reduced partial differential cross-sections for elastic scattering from polycrystalline aluminium

 $d^{2}\sigma/d \Omega dE = (E/E_{0})^{\frac{1}{2}} e^{-\epsilon/2} S(\kappa, \hbar\omega)$  where

 $\epsilon = \hbar \omega / 0.0254 \text{ eV}$  and T = 22°C

with Cd spacers
 without Cd spacers



Fig.7

Idealized Brillouin zones and vector diagrams depicting two different scattering events where the polarization factor  $(\vec{\kappa} \cdot \vec{\xi})^2$  favours interaction with transverse vibrations  $(\vec{\kappa_1})$ and longitudinal vibrations  $(\vec{\kappa_2})$ 

To discuss the interpretation of the data further we consider aluminium and then beryllium separately. From the measured dispersion relations for aluminium it is known that most of the transverse vibrations are restricted to frequencies where  $\epsilon = \hbar \omega / k_{\rm B} T < 0.9$  and the higher frequencies in the distribution are accounted for primarily by the longitudinal vibrations. Another important consideration in the following discussion is the point that the onephonon differential cross-section is proportional to a polarization factor  $(\vec{\kappa}\cdot\vec{\xi})^2$  where  $\vec{\xi}$  is a unit vector in the direction of the phonon polarization [14]. In Fig. 7 are depicted wave vector plots which demonstrate the effect of the polarization factor. The vector  $\vec{\kappa} = 2\pi \vec{\tau}$  connects the origin with some specific lattice point (hkl), and the large circles which are drawn about both the origin and the point (hkl) portray Brillouin zone boundaries, while the small circle about the lattice point (hkl) we consider to be a particular frequency contour. For the scattering process corresponding to  $\vec{k}_1$  in the figure the interaction would be favourable for a vibration with transverse polarization since  $\vec{\xi}_{\tau}$  is nearly parallel to  $\vec{k}_1$  and with  $\vec{q}$  perpendicular to  $\vec{k}_1$ , we have  $\kappa_1 \cong \kappa_{Bragg}$ . If on the other hand  $\vec{k}$  is nearly parallel to  $\vec{k}_{Bragg}$  as depicted by  $\vec{k}_2$ , then the polarization factor favours neutron interactions with the longitudinal vibrations and  $\kappa \simeq 2\pi\tau \pm q$ .

Because of the effect of the polarization factor and the restriction of the transverse vibrations to  $\epsilon < 0.9$  one would expect the structure to appear at approximately the same  $\kappa$ -values as for Bragg scattering for low energy transfers. Slash marks have been added to the  $\kappa$ -scale of Fig.4 at values corresponding to  $2\pi\tau$  for the various lattice points and the peaks in the data for  $\epsilon < 0.9$  agree with the position of these marks. For the higher frequencies ( $\epsilon > 0.9$ ) which are primarily longitudinal the cross-section does not peak at  $\kappa = 2\pi\tau$  but is shifted to  $\kappa$ -values which approximate more nearly vectors drawn to the Brillouin zone boundaries  $\kappa_{\min} = 2\pi\tau$ -q and  $\kappa_{\max} = 2\pi\tau$  + q due to the effect of the polarization factor. This shift in the structure is readily apparent for  $\epsilon = 1.3$  and 1.4 which correspond to a maximum in the frequency distribution of aluminium.

In the case of scattering from beryllium it is necessary to consider, in addition, the dynamical structure factor  $g_1^2(\vec{q})$  [10] because of the more complex crystal structure. This factor indicates that the cross-section for interaction with a given phonon polarization is not a constant throughout wave-vector space but varies from one Brillouin zone to another. In a given zone  $g_i^2(\vec{q})$  generally tends to favour either acoustical or optical transitions, and therefore functions as a selection rule. At low frequencies ( $\epsilon < 1.75$ ) all interactions are with acoustical vibrations for those Brillouin zones which are favoured by the structure factor [5]. At high frequencies ( $\epsilon \sim 3.0$ ) the vibrations are all optical, and the cross-section is high in different Brillouin zones. Slash marks have been added to the  $\kappa$ -scale of Fig. 3 above the data points for  $\epsilon = 1.25$  and  $\epsilon = 3.0$  at values given by  $\kappa = 2\pi\tau$  according to whether interactions with acoustical or optical vibrations were favoured. Effects due to the polarization factor are not so obvious in the beryllium data because of the overlapping of the acoustical and optical frequencies in the frequency distribution.

The frequency distribution in the incoherent approximation [15] is given by

$$g(\epsilon) = [(\hbar^2/2MkT) e^{-2W}]^{-1} (2\epsilon/\kappa^2) \sinh(\epsilon/2)S(\kappa,\epsilon) - (multiphonon corrections)$$



The frequency distribution of aluminium obtained from the data at several values of  $\kappa$  compared with the calculation of the distribution by PHILLIPS [8]

κ(Å<sup>-1</sup>)

● = 2, 88 ○ = 3, 85 ■ = 4, 82 □ = 5, 75 PHILLIPS [8]

which has been applied to the  $S(\kappa, \epsilon)$  data for aluminium. This relation has been tested at several values of  $\kappa$  using PHILLIPS' [8] frequency distribution to obtain a two-phonon correction, and the results are displayed in Fig.8. No particular value of  $\kappa$  appears to give any better distribution than the others, and none of the distributions agrees with the theoretical distribution of Phillips. The results of these calculations show that the use of the incoherent approximation is not valid in the case of a strong coherent scatterer. At best, the approximation can be expected to give the locations of strong maxima in the frequency distribution.

## 5. SUMMARY

This paper describes some of the work being done at the MTR on polycrystalline solids, some of the interesting structure effects which have been observed and how these structure effects are related to the various factors which are important in coherent scattering.

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## ACKNOWLEDGEMENTS

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## DISCUSSION

W. WHITTEMORE: Can you explain why your Fig.2 gives values of  $S(|\vec{\kappa}|,\hbar\omega)$  versus  $\vec{\kappa}$  which vary by factors of two for nearly every value of  $\vec{\kappa}$ ?

R.E. SCHMUNK: This variation is primarily the statistical fluctuation in the data. Measurements were made at several different energy and angular resolutions, and no clear trend due to resolution effects was observed in the data.

## ВЛИЯНИЕ АНГАРМОНИЗМА НА СПЕКТР ФОНОНОВ ВБЛИЗИ ТОЧКИ ВЫРОЖДЕНИЯ

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#### (Доклад представлен Ф.Л. Шапиром)

#### Abstract — Résumé — Аннотация — Resumen

EFFECT OF ANHARMONICITY ON THE PHONON SPECTRUM NEAR ITS DISCONTINUITY. The method based on Green's function is used in investigating the effect of anharmonicity on the phonon spectrum near its discontinuity. In contrast to the usual case, the effect that phonon branches, which are independent in the harmonic approximation, have on one another requires the solution of the Dyson system of equations.

The authors consider cases of significant and irregular discontinuity and show that for irregular discontinuity the excitations which arise can have a widely varying lifetime and frequency renormalization with respect to both value and temperature dependence. In particular, the one-phonon coherent neutron scattering crosssection near the spectrum discontinuity is analysed.

INFLUENCE DE L'ANHARMONICITÉ SUR LE SPECTRE DES PHONONS AU VOISINAGE DU POINT DE DÉGÉNÉRESCENCE. La méthode fondée sur les fonctions de Green est employée pour étudier l'influence de l'anharmonicité sur le spectre des phonons au voisinage du point de dégénérescence. Contrairement au cas habituel, l'effet que les branches de phonons indépendantes dans l'approximation harmonique exercent les unes sur les autres conduit à la nécessité de résoudre le système d'équations de Dyson,

Dans le mémoire, on examine des cas de dégénérescence essentielle et fortuite. On montre que, lors d'une dégénérescence fortuite, l'excitation qui en résulte peut varier sensiblement quant à la durée et à la renormalisation de la fréquence, tant du point de vue de la grandeur que de la dépendance thermique. On étudie plus spécialement la section efficace de diffusion cohérente monophononique des neutrons au voisinage du point de dégénérescence.

ВЛИЯНИЕ АНГАРМОНИЗМА НА СПЕКТР ФОНОНОВ ВБЛИЗИ ТОЧКИ ВЫРОЖДЕНИЯ. Метод функции Грина используется для анализа вопроса о влиянии ангармонизма на спектр фононов вблизи точки вырождения. Влияние независимых в гармоническом приближении фононных ветвей друг на друга, в отличие от обычного случая, приводит к необходимости решения системы уравнений Дайсона.

Рассматриваются случаи существенного и случайного вырождения. Показано, что при случайном вырождении возникающие возбуждения могут иметь сильно различающееся время жизни и перенормировку частоты как по величине, так и по температурной зависимости. Специально анализируется сечение однофононного когерентного рассеяния нейтронов вблизи точки вырождения.

INFLUENCIA DE LA ANARMONICIDAD SOBRE EL ESPECTRO FONÓNICO EN LA PROXIMIDAD DEL PUNTO DE DEGENERACIÓN. Se utiliza el método basado en las funciones de Green para analizar el problema de la influencia de la anarmonicidad sobre el espectro fonónico en la proximidad del punto de degeneración. A diferencia del caso habitual, la influencia que las ramas de fonones independientes en la aproximación armónica ejercen unas sobre otras obliga a resolver el sistema de ecuaciones de Dyson.

En la memoria se estudia la degeneración esencial y la fortuita. Se demuestra que en este último caso la excitación resultante puede variar sensiblemente en cuanto a duración y a renormalización de la frecuencia (magnitud e influencia de la temperatura). Se estudia en particular la sección eficaz de dispersión monofonónica coherente de los neutrones cerca del punto de degeneración.

1. В последнее время в целом ряде работ [1], [2], [3] исследовалось влияние ангармонизма на спектр фононов и одновременно на сечение когерентного рассеяния медленных нейтронов. При этом молчаливо предполагалось, что все фононные ветви строго изолированы друг от друга. Как следствие, ангармонизм приводил к независимой перенормировке частоты и появлению затухания для каждого отдельного фонона. С другой стороны, ширина пика когерентного рассеяния, отвечающего фиксированной передаче импульса  $\vec{k}$  и энергии  $\Delta E$ , оказывалась однозначно определенной через величину затухания (мнимую часть соответствующего поляризационного оператора) фонона отдельной ветви (с квазиимпульсом  $\vec{f} = \vec{k}$  и частотой  $\omega_{\vec{f},\alpha}^* \simeq \Delta E$ ).

Однако задача существенно меняется, если ветви фононного спектра пересекаются или просто подходят друг к другу. В этом случае ангармонизм приводит к смешению независимых в гармоническом приближении ветвей, и для анализа возникающего закона дисперсии и затухания фононов, а также характера рассеяния нейтронов, необходимо эти фононные ветви учитывать одновременно. Формально это соответствует тому, что теперь вместо одного уравнения Дайсона появляется система уравнений. Решение этой задачи и рассматривается в настоящем докладе.

2. Для нахождения спектра фононов будем искать запаздывающую (опережающую) гриновскую функцию G<sub>λλ</sub> (ω), полюса аналитического продолжения которой определяют закон дисперсии и затухания.

По определению G<sub>λλ'</sub> (ω) - фурье-компонента функции

$$G_{\lambda\lambda}, (t-t^{\dagger}) = -i\theta(t-t^{\dagger}) \langle [A_{\lambda}(t), A_{-\lambda}, (t^{\dagger})] \rangle.$$
(1)

Здесь  $A_{\lambda} = a_{\lambda} + a_{-\lambda}^{+}$ , а буквой  $\lambda$  обозначена совокупность индексов  $\vec{f}, \alpha(-\lambda = -\vec{f}, \alpha)$ , где  $\vec{f}$  — квазиимпульс и  $\alpha$  — номер ветви. Индексы  $\lambda$  и  $\lambda'$  в (1) имеют одно и то же значение  $\vec{f}$  и отличаются только номерами ветвей.

Для функции Грина G<sub>λλ</sub> (1) можно записать уравнения Дайсона в следующей форме:

....

$$G_{\lambda\lambda'}(\omega) = G_{\lambda\lambda}^{(c)}(\omega)\delta_{\lambda\lambda'} + G_{\lambda\lambda}^{(c)}(\omega)P_{\lambda\lambda''}(\omega)G_{\lambda''\lambda'}(\omega) ,$$

$$G_{\lambda\lambda}^{0}(\omega) = \frac{2\omega_{\lambda}}{\omega^{2} - \omega_{\lambda^{2}}} .$$
(2)

#### В (2) поляризационный оператор определяется выражением:

 $\langle \alpha \rangle$ 

$$\begin{split} \mathbf{P}_{\lambda\lambda^{*}}\left(\omega\right) &= \frac{1}{2\hbar^{2}}\sum_{\lambda_{1}\lambda_{2}}\mathbf{B}_{-\lambda\lambda_{1}\lambda_{2}} \quad \mathbf{B}_{-\lambda^{*}\lambda_{1}\lambda_{2}}^{*} \quad \left\{\frac{1+n\lambda_{1}+n\lambda_{2}}{\omega-\omega_{\lambda_{1}}-\omega_{\lambda_{2}}}-\frac{1+n\lambda_{1}+n\lambda_{2}}{\omega+\omega_{\lambda_{1}}+\omega_{\lambda_{2}}}+2\frac{n\lambda_{1}-n\lambda_{2}}{\omega+\omega_{\lambda_{1}}-\omega_{\lambda_{2}}}\right\} \\ &+ \frac{1}{\hbar}\sum_{\lambda_{1}}\mathbf{B}_{-\lambda\lambda^{*}\lambda_{1}-\lambda_{1}}\left(n\lambda_{1}+\frac{1}{2}\right), \end{split}$$

где все обозначения общепринятые.

Поляризационный оператор при самом общем виде ангармонического взаимодействия диагонален по индексу f. Поэтому в общем случае (2) представляет собой систему 3q алгебраических уравнений, где q – число атомов в элементарной ячейке. Обычно анализируется одно уравнение с λ = λ' (и λ" = λ). Однако, рассматривая задачу вблизи точки пересечения ветвей фононного спектра, мы должны рассматривать систему уравнений(2).

Ограничимся для простоты случаем одноатомной решетки (обобщение на более общий случай — тривиально). Тогда решение системы (2) может быть записано в виде:

$$G_{\alpha\alpha'}(\omega) = \frac{(-1)^{\alpha+\alpha'} M_{\alpha'\alpha}}{\Delta(\omega)}, \quad G_{\alpha\alpha'}(\omega) = G_{\alpha'\alpha}(\omega)$$
(3)  
$$\Delta(\omega) = \begin{vmatrix} G_{11}^{(0)-1}(\omega) & -P_{11}(\omega) & -P_{12}(\omega) & -P_{13}(\omega) \\ -P_{21}(\omega) & G_{22}^{(0)-1}(\omega) & -P_{22}(\omega) & -P_{23}(\omega) \\ -P_{31}(\omega) & -P_{32}(\omega) & G_{33}^{(0)-1}(\omega) & -P_{33}(\omega) \end{vmatrix}$$
(4)

 $(M_{\alpha'\alpha} - соответствующий минор, индекс <math>\vec{f}$  для простоты опущен). Заметим, что в той области  $\omega$ , где определены функции  $G_{\alpha\alpha'}$ , определитель системы (2) нигде в нуль не обращается. Поэтому однородная система уравнений имеет только тривиальное решение.

Найдем теперь полюса аналитического продолжения функций (3), определяя соответственно решение уравнения

$$\Delta(\omega) = 0 . \tag{5}$$

Пусть при некотором значении f перескаются две фононные ветви, так что  $\omega_{\vec{f},1} = \omega_{\vec{f},2} = \omega_0$  и пусть  $|\omega_{\vec{f},3} - \omega_0| \gg P_{23}$ . Тогда, введя обозначения  $Z = \omega^2 - \omega_1^2$ ,  $\delta = \omega_2^2 - \omega_1^2$ ,  $\Pi_{\alpha\alpha'}(\omega) = 2 \sqrt{\omega_\alpha \omega_{\alpha'}} P_{\alpha\alpha'}(\omega)$ , запишем приближенное решение (5) вблизи точки вырождения, как

$$Z = \frac{1}{2} (\Pi_{11}(\omega_0) + \Pi_{22}(\omega_0) + \delta) \pm \\ \pm \sqrt{\frac{1}{4}(\Pi_{11}(\omega_0) + \Pi_{22}(\omega_0) + \delta)^2 - (\Pi_{11}(\omega_0)\Pi_{22}(\omega_0) - \Pi_{12}(\omega_0)\Pi_{21}(\omega_0) - \delta)}.$$
 (6)

Из анализа этого выражения непосредственно следует, что в общем случае и переномировка и затухание обоих возбуждений зависят как о мнимых, так и действительных частот поляризационных операторов, относящихся к обеим ветвям и соответствующих фиксированному f.

Рассмотрим сначала картину в самой точке вырождения, т.е. когда  $\delta = 0$ . При существенном вырождении (обусловленным симметрией)  $\Pi_{11} = \Pi_{22}$  и, кроме того,  $\Pi_{12} = 0$ . Последний результат является прямым следствием того, что есть групповой элемент симметрии, совмещающий вектор поляризации одного фонона с вектором поляризации другого. При этом вырождение не снимается, хотя наличие ангармонизма приводит как к сдвигу, так и затуханию

$$\omega'^2 = \omega''^2 = \omega_0^2 + \Pi_{11} . \tag{7}$$

Гораздо интереснее, когда имеет место случайное вырождение. (Заметим, что этот случай встречается весьма часто. См., например, недавнюю работу по анализу фононного спектра ниобия [4]). При этом  $\Pi_{12} \neq 0$ и, вообще говоря, одного порядка с  $\Pi_{11}$ ,  $\Pi_{22}$ . Как следствие, ангармоническое взаимодействие снимает вырождение. Предполагая, что  $\Pi_{12}$  близко по величине к  $\Pi_{11}$ ,  $\Pi_{22}$ , приближенно имеем:

$$\omega^{12} = \omega_0^2 + \Pi_{11} + \Pi_{22} - \frac{\Pi_{11}\Pi_{22} - \Pi_{12}\Pi_{21}}{\Pi_{11} + \Pi_{22}},$$

$$\omega^{12} = \omega_0^2 + \frac{\Pi_{11}\Pi_{22} - \Pi_{12}\Pi_{21}}{\Pi_{11} + \Pi_{22}}.$$
(8)

Если допустить, что  $\Pi_{11} = \Pi_{22}$ , то из (6) получаем просто

$$\omega^{12} = \omega_0^2 + \Pi_{11} + \Pi_{12} ,$$

$$\omega^{n2} = \omega_0^2 + \Pi_{11} - \Pi_{12} .$$
(8<sup>1</sup>)

Таким образом, при снятии вырождения оба возбуждения ведут себя совершенно по-разному. Может оказаться, что одно из возбуждений имеет слабую переномировку с температурой и слабое затухание, тогда как другое возбуждение, наоборот, будет иметь большую перенормировку и заметное затухание.

Интересно проанализировать влияние третьей фононной ветви на полученный результат. Рассматривая для простоты частый случай, соответствующий (8<sup>1</sup>), из уравнения (5), находим:

$$\begin{split} \omega^{12} &= \omega_0^2 + \Pi_{11} + \Pi_{12} + \frac{(\Pi_{13} + \Pi_{23})^2}{\omega_3^2 - \omega_0^2}, \\ \omega^{12} &= \omega_0^2 + \Pi_{11} - \Pi_{12} + \frac{(\Pi_{13} - \Pi_{23})^2}{\omega_3^2 - \omega_0^2} \end{split}$$

Отсюда видно, что на аномальный второй корень рассматриваемое влияние оказывается в общем случае резко ослабленным.

Вблизи точки вырождения ( $\delta \neq 0$ ) конкретный анализ (5) или (6) становится громоздким, однако качественная картина целиком диктуется характером поведения в точке вырождения.

Рассмотрим теперь случай, когда две ветви, хотя и не пересекаются, но сравнительно близко подходят друг к другу. Из (5), (6) имеем при этом

$$\omega'^{2} = \omega_{1}^{2} + \Pi_{11} - \frac{\Pi_{12} \Pi_{21}}{\delta},$$

$$\omega''^{2} = \omega_{2}^{2} + \Pi_{22} + \frac{\Pi_{12} \Pi_{21}}{\delta}.$$
(8<sup>2</sup>)

#### ВЛИЯНИЕ АНГАРМОНИЗМА НА СПЕКТР ФОНОНОВ

Из этих выражений следует, что подходящая близко ветвь может заметно изменить перенормировку и затухание фонона, принадлежащего другой ветви, и, главное, изменить температурную зависимость. Действительно, если значение  $|\Pi_{12}|$  сравнимо по величине с  $\delta$  (хотя и меньше), то в классической температурной области сдвиг и затухание будут наряду с обычным линейным по T членом содержать и заметный квадратичный член.

3. Определим сечение когерентного рассеяния медленных нейтронов при значении переданного импульса  $\vec{f} = \vec{k}$ , близкому к квазиимпульсу фононов в точке вырождения. В обычном приближении

$$\frac{\mathrm{d}^{2}\tau(\Delta \mathbf{E},\vec{\kappa})}{\mathrm{d}\mathbf{E}\,\mathrm{d}\Omega} = \frac{\mathrm{m}^{2}\kappa^{2}\,\kappa^{\prime}}{8\pi^{2}\mathrm{h}^{2}\kappa_{0}} \cdot \frac{1}{\mathrm{M}}\,\mathrm{A}^{2}\,\mathrm{e}^{-\mathrm{W}} \sum_{\alpha,\alpha'} \frac{(\vec{\kappa}\,\vec{\upsilon}(\vec{\kappa},\alpha))(\vec{\kappa}\,\vec{\upsilon}(\vec{\kappa},\alpha'))}{[\omega(\vec{\kappa},\alpha)\omega(\vec{\kappa},\alpha')]^{\frac{1}{2}}} \times \frac{1}{\mathrm{e}^{-\beta\Delta \mathbf{E}}-1}\,\mathrm{Im}\,\mathrm{G}_{\alpha\alpha'}\,(\Delta \mathbf{E}).\,(9)$$

 $G_{\alpha\alpha'}(\Delta E) = G_{\alpha'\alpha}(\Delta E)$ 

Здесь все обозначения общепринятые. (Функции Грина  $G_{\alpha\alpha}$  содержат индекс  $\vec{\kappa}$ , который мы для упрощения записи снова опускаем).

В соответствии с (3) при пересечении двух ветвей, когда третья ветвь расположена достаточно далеко, имеем:

$$G_{11} = \frac{2\omega_1 [(\Delta E)^2 - \omega_2^2 - \Pi_{22}]}{[(\Delta E)^2 - \omega'^2][(\Delta E)^2 - \omega''^2]} ,$$

$$G_{12} = \frac{2\sqrt{\omega_1 \omega_2 \Pi_{12}}}{[(\Delta E)^2 - \omega'^2][(\Delta E)^2 - \omega''^2]} .$$
(10)

В точке существенного вырождения G<sub>12</sub> = 0, и сечение когерентного рассеяния, если принять во внимание (10) и (7), будет иметь точно такой же пик, как и в случае изолированной фононной ветви.

Вблизи точки случайного вырождения сечение будет иметь аномальный вид. Действительно, теперь при суммировании в (9) по  $\alpha, \alpha'$  необходимо принимать во внимание и недиагональные элементы G<sub>12</sub> = G<sub>21</sub>; которые в общем случае одного порядка с диагональными. Если мнимая часть элементов поляризационной матрицы  $\Pi_{\alpha\alpha'}$  будет мала по сравнению с действительной частью, то сечение будет иметь два близких пика разной интенсивности и, главное, разной ширины. Если же  $Im\Pi_{\alpha\alpha'} \sim Re\Pi_{\alpha\alpha'}$ , то появится один неразрешенный пик с резкой асимметрией, причем эта асимметрия будет заметно меняться с температурой. (Заметим, что при малой константе ангармонизма все другие причины асимметрии оказываются слабыми [1], [3]).

Эти результаты особенно наглядно можно проследить на частном случае, которому соответствует  $\Pi_{11} = \Pi_{22}$ . Используя (8<sup>1</sup>), легко найти соответствующие выражения для функций (10) в точке вырождения

$$G_{11}(\Delta E) = \frac{\omega_0}{(\Delta E)^2 - \omega_0^2 - \Pi_{11} - \Pi_{12}} + \frac{\omega_0}{(\Delta E)^2 - \omega_0^2 - \Pi_{11} + \Pi_{12}}$$

$$\mathbf{G}_{22}\left(\Delta \mathbf{E}\right) = \frac{\omega_0}{\left(\Delta \mathbf{E}\right)^2 - \omega_0^2 - \Pi_{11} - \Pi_{12}} - \frac{\omega_0}{\left(\Delta \mathbf{E}\right)^2 - \omega_0^2 - \Pi_{11} + \Pi_{12}}.$$

Подставляя эти выражения в (9), мы непосредственно получаем приведенную выше картину.

## DISCUSSION

H. HAHN: If you calculate the anharmonicity effects on the dispersion curves by a Pauli-Weisskopf type of simple perturbation approach, you would, in the case of the degenerate point, have to use the perturbation theory for degenerate states. This corresponds to Kagan's use of two Dyson equations in the Green's function approach.

G. CAGLIOTI: In our [001] longitudinal branches of white tin we find that the two branches are very nearly along the wave vector transfers for  $\mathbf{Q}$ , the phonon wave vector, less than 0.3 in terms of  $\mathbf{Q}_{max}$ . It was much more difficult to find those branches in white tin than it was, for instance, in zinc. In the case of the latter metal it was very easy to make the measurements because the frequencies were much higher. There is another point: when one can measure an acoustic branch, one cannot measure an optic branch in the same range because of the structure factor. I do not know whether the difficulty of measuring these branches is an intrinsic difficulty or is connected with the neutron method.

# MAGNETIC SYSTEMS

## DYNAMICS OF MAGNETIC SYSTEMS INVESTIGATED BY MOSSBAUER AND NEUTRON SCATTERING EXPERIMENTS

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#### (Presented by R.J. Elliott)

#### Abstract — Résumé — Аннотация — Resumen

DYNAMICS OF MAGNETIC SYSTEMS INVESTIGATED BY MÖSSBAUER AND NEUTRON SCATTERING EXPERIMENTS. A general discussion is given of Lamb-Mössbauer and neutron scattering experiments which can be used to investigate magnetic systems. It is shown that only in very special circumstances can the Mössbauer effect be used to examine directly the fluctuations of the magnetic spins with time. Therefore the Mössbauer effect is usually used to measure time-averaged quantities. It follows that Mössbauer experiments are closely related, in principle, to strictly elastic neutron scattering experiments. Both techniques and also the nuclear magnetic resonance technique are useful in studies of ferromagnetic alloys. Recent studies of this kind are reviewed and the difficulties of interpreting the experiments are described.

DYNAMIQUE DES SYSTÈMES MAGNÉTIQUES ÉTUDIÉS AU MOYEN DE L'EFFET MÖSSBAUER ET DE LA DIFFUSION DES NEUTRONS. L'auteur procède à une discussion générale des expériences que l'on peut faire pour étudier les systèmes magnétiques au moyen de l'effet Lamb-Mössbauer et de la diffusion des neutrons. 11 montre que l'effet Mössbauer ne permet d'étudier directement les fluctuations des spins magnétiques en fonction du temps que dans des cas très particuliers. C'est pourquoi on l'utilise généralement pour mesurer les moyennes dans le temps de diverses grandeurs. Il s'ensuit que les expériences fondées sur cet effet sont en principe étroitement liées aux expériences au moyen de la diffusion strictement élastique des neutrons. Ces deux méthodes ainsi que celle de la résonance magnétique nucléaire donnent de bons résultats dans des études sur les alliages ferromagnétiques. L'auteur fait un examen critique des études de ce genre et décrit les difficultés auxquelles donne lieu l'interprétation des expériences.

ДИНАМИКА МАГНИТНЫХ СИСТЕМ, ИССЛЕДОВАННАЯ ПО МЕТОДУ МЕССБАУЭРА И С ПОМОЩЬЮ ЭКСПЕРИМЕНТОВ ПО РАССЕЯНИЮ НЕЙТРОНОВ. Рассматриваются в общих чертах эксперименты Лэмба-Мессбауэра и эксперименты по рассеянию нейтронов, которые могут быть использованы для исследования магнитных систем. Показано, что эффект Мессбауэра может применяться для непосредственного изучения флуктуаций магнитных спинов во времени только в сугубо определенных условиях. Следовательно, эксперименты Мессбауэра, в принципе, тесно связаны с экспериментами по действительно упругому рассеянию нейтронов. Оба эти метода, а также метод ядерного магнитного резонанса могут применяться для исследования ферромагнитных сплавов. Рассматриваются последние исследования этого вида, описываются трудности интерпретации результатов экспериментов.

ESTUDIO DE LA DINÁMICA DE SISTEMAS MAGNÉTICOS MEDIANTE EXPERIMENTOS DE MÖSSBAUER Y DE DISPERSIÓN NEUTRÓNICA. Se examinan en términos generales los experimentos de Lamb-Mössbauer y de dispersión neutrónica que pueden utilizarse para estudiar la estructura de los sistemas magnéticos. Se demuestra que sólo en circunstancias muy particulares puede recurrirse al efecto Mössbauer para examinar directamente las fluctuaciones temporales de los spins magnéticos. En consecuencia, el efecto Mössbauer se suele utilizar para medir cantidades ponderadas con respecto al tiempo. Los experimentos de Mössbauer están por tanto estrechamente relaciónados, en principio, con los experimentos de dispersión estrictamente elástica de neutrones. Estas dos técnicas y la de resonancia magnética nuclear son útiles para el estudio de las aleaciones ferromagnéticas. En la memoria se examinan los recientes estudios de esta índole y se exponen las dificultades que entraña la interpretación de los resultados experimentales.

### W. MARSHALL

## 1. INTRODUCTION

This paper reviews the dynamics of magnetic spin systems as revealed by Mössbauer experiments and by neutron scattering techniques. The subject is too wide to cover completely but fortunately there is no necessity to do so because most neutron-scattering techniques are now widely known and a recent review article [1] has summarized the use of the Mössbauer effects. Therefore I mention only a few points of special interest so as to highlight the developing parts of the subject.

In section 2 we write down the neutron scattering cross-section in terms of the spin correlation functions and in section 3 we derive a similar formula for the Mössbauer absorption cross-section. This latter formula is discussed in general terms in section 4 and it is shown that in one subject, that of ferromagnetic alloys, there is a potential influence of neutron and Mössbauer experiments upon one another. Section 5 summarizes the conclusions of this review.

## 2. NEUTRON SCATTERING CROSS-SECTIONS

Following Van Hove's work [2,3] the relation connecting the neutron cross-sections to correlation functions has become well known. For the sake of completeness it is worth writing down the full expression allowing for polarization of the neutron beam. The coherent scattering is then given by:

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega^{1}\mathrm{d}E^{1}} = \frac{\mathrm{k}!}{2\pi \,\mathrm{fik}} \int \mathrm{d}t \,\exp(-\mathrm{i}\omega t) \sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'} \langle \exp(-\mathrm{i}\vec{\mathrm{K}}\cdot\vec{\mathrm{R}}!(0)) \exp(\mathrm{i}\vec{\mathrm{K}}\cdot\vec{\mathrm{R}}(t)) \rangle \Gamma_{\vec{\mathrm{R}}'\vec{\mathrm{R}}} \,(t), \quad (2.1)$$

where

$$\Gamma_{\vec{R}'\vec{R}}(t) = a_{\vec{R}'} a_{\vec{R}} + \left(\frac{\gamma e^2}{2mc^2}\right) [\vec{p} - (\vec{p} \cdot \vec{K})\vec{K}] \cdot [\langle \vec{S}_{\vec{R}'} \rangle g_{\vec{R}'} f_{\vec{R}'}(\vec{K}) a_{\vec{R}} + \langle \vec{S}_{\vec{R}} \rangle g_{\vec{R}} f_{\vec{R}'}(\vec{K}) a_{\vec{R}'}]$$

$$+ \left(\frac{\gamma e^2}{2mc^2}\right)^2 g_{\vec{R}} f_{\vec{R}}(\vec{K}) g_{\vec{R}'} f_{\vec{R}'}(\vec{K}) [\delta_{\beta \phi} - \hat{K}_{\beta} \hat{K}_{\phi}] \langle S_{\vec{R}'}^{\beta}(0) S_{\vec{R}}^{\phi}(t) \rangle$$

$$+ \left(\frac{\gamma e^2}{2mc^2}\right)^2 g_{\vec{R}} f_{\vec{R}}(\vec{K}) g_{\vec{R}'} f_{\vec{R}'}(\vec{K}) g_{\vec{R}'} f_{\vec{R}'}(\vec{K}) i p_{\psi}$$

$$\times [\epsilon_{\psi\beta\phi} - \epsilon_{\psi\beta\alpha} \hat{K}_{\alpha} \hat{K}_{\phi} + \epsilon_{\psi\phi\alpha} \hat{K}_{\alpha} \hat{K}_{\beta}] \langle S_{\vec{R}'}^{\beta}(0) S_{\vec{R}'}^{\phi}(t) \rangle .$$

$$(2.2)$$

In this expression the neutron is scattered from k to k' with  $\vec{K} = \vec{k} - \vec{k'}$ ,  $\vec{K} = \vec{K} / |\vec{K}|$  and  $\hbar\omega = E - E'$ .  $a_{\vec{R}}$  is the coherent nuclear scattering amplitude of the nucleus at  $\vec{R}$ ,  $g_{\vec{R}}$  is the g-value,  $f_{\vec{R}}(\vec{K})$  the form factor and  $\vec{p}$  the polarization.

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For zero polarization and purely magnetic scattering, only the third term of Eq. (2.2) survives. Specializing to the case of strictly elastic scattering we find

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega^{\dagger}} = \left(\frac{\gamma \mathrm{e}^{2}}{2\mathrm{m}\mathrm{c}^{2}}\right)^{2} \left[1 - \hat{\mathrm{K}}_{z}^{2}\right] \mathrm{e}^{-2\mathrm{W}} \sum_{\vec{n},\vec{m}} \exp\left(\mathrm{i}\vec{\mathrm{K}}\cdot(\vec{n}-\vec{\mathrm{m}})\right) \left\langle \mu_{\vec{\mathrm{m}}}\,\mu_{\vec{\mathrm{n}}} \right\rangle f_{\vec{\mathrm{m}}}(\vec{\mathrm{K}}) f_{\vec{\mathrm{n}}}(\vec{\mathrm{K}}), \quad (2.3)$$

where  $\vec{n}$  and  $\vec{m}$  refer to lattice points and we have introduced the timeaveraged magnetic moments  $\mu_{\vec{n}} = g_{\vec{n}} \langle S_{\vec{n}} \rangle$ . This strictly elastic magnetic scattering is most useful in the study of ferromagnetic alloys where the moments  $\mu_{\vec{n}}$  and  $\mu_{\vec{m}}$  are correlated in space. In many cases it is satisfactory to assume the same form factor for all atoms and to subtract off the Bragg scattering from Eq. (2.3) to give the diffuse scattering as:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'_{\mathrm{Diffuse}}} = \left(\frac{\gamma e^2}{2\mathrm{m}c^2}\right)^2 \left[1 - \hat{\mathrm{K}}_{z}^{2}\right] e^{-2W} f(\vec{\mathrm{K}}) \Big|_{\vec{\mathrm{n}},\vec{\mathrm{m}}}^2 \exp\left(\mathrm{i}\vec{\mathrm{K}}\cdot(\vec{\mathrm{n}}-\vec{\mathrm{m}})\right) \left[\langle \mu_{\vec{\mathrm{m}}}\mu_{\vec{\mathrm{n}}}\rangle - \langle \mu \rangle^2\right].$$
(2.4)

We shall return to Eq. (2.4) in section 4.

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#### 3. MÖSSBAUER ABSORPTION CROSS-SECTION

Suppose that a photon of frequency  $\omega$  and polarization p(p=1, 0 or -1 relative to the quantization axis) is incident on an absorber containing a suitable Mössbauer nucleus. We suppose that the Hamiltonian of the absorber, excluding the interaction with the Mössbauer nucleus, is  $\mathscr{H}_0$ , so that with the nucleus in the ground state with nuclear spin I, the full Hamiltonian is:

$$\mathscr{H} = \mathscr{H}_0 + A\vec{S} \cdot \vec{I} + I^{\alpha} Q_{\alpha\beta} I^{\beta} , \qquad (3.1)$$

where the second term represents the hyperfine interaction between the nuclear spin  $\vec{I}$  and the electron spin  $\vec{S}$  on that atom. The third term written in general form represents the quadrupole interaction, if any, between the nucleus and its surroundings. In the excited state the nucleus has spin  $\vec{J}$  and the total Hamiltonian becomes

 $\mathcal{H} = \mathcal{H}_0 + \mathbf{A}^{\mathbf{i}} \mathbf{\vec{S}} \cdot \mathbf{\vec{J}} + \mathbf{J}^{\alpha} \mathbf{Q}^{\mathbf{i}}_{\alpha\beta} \mathbf{J}^{\beta} , \qquad (3.2)$ 

where, to an excellent approximation, the ratio between A<sup>†</sup> and A is that of the nuclear magnetic moments.

The transition amplitude of the  $\gamma$ -ray converting the nucleus from Im to JM involves a Wigner coefficient. Therefore it is convenient to define an operator U acting solely on the nucleus with non-zero matrix elements given by:

$$(JM | U | Im) = (-1)^{J-M} \begin{pmatrix} J & 1 & I \\ M & p & m \end{pmatrix},$$
 (3.3)

where we have chosen to use the 3j symbols. We now define states  $|q\rangle$  as eigenstates of  $\mathcal{H}$  and in terms of them the probability of absorption of a photon of frequency  $\omega$  is

$$P(\omega) \sim \sum_{Q} W_{q} \sum_{q'} (\mathbf{q} | \mathbf{U} | \mathbf{q'}) (\mathbf{q'} | \mathbf{U} | \mathbf{q}) \frac{(\Gamma_{a}/2\pi)}{(E_{q'} - E_{q} - \omega)^{2} + \Gamma_{a}^{2}/4} .$$
(3.4)

In this formula we have put n=1,  $\Gamma_a$  is the width of the excited states in the absorber, all final states q' have been summed over and the initial states q have been averaged with the Boltzmann probability  $W_a$ .

We now notice that

$$\frac{\Gamma_{a}}{\omega^{2} + \Gamma_{a}^{2}/4} = \int_{-\infty}^{\infty} dt \exp\left(-i\omega t - \Gamma_{a} \left| t \right| / 2\right)$$
(3.5)

and we substitute this expression into Eq. (3.4) to give:

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left(-i\omega t - \Gamma_{a} |t|/2\right) \sum_{q} W_{q} \sum_{q'} (q |U|q')(q'|U|q) \exp\left(it(E_{q'} - E_{q})\right)$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left(-i\omega t - \Gamma_{a} |t|/2\right) \sum_{q} W_{q} \sum_{q'} (q |U(0)|q')(q'|U(t)|q)$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left(-i\omega t - \Gamma_{a} |t|/2\right) \langle U(0)|U(t) \rangle, \qquad (3.6)$$

where we have introduced the Heisenberg representation and in the usual way the symbol  $\langle 0 \rangle$  denotes the thermal expectation value of 0.

In practice the result shown in Eq. (3.6) is not exactly what is required because the incident  $\gamma$ -ray frequency is not precisely defined. If the incident spectrum has central frequency  $\omega$  and width  $\Gamma_s$ , where  $\omega$  is determined by the nature of the source and the Doppler shift given to it by the Mössbauer apparatus, then the quantity actually observed is:

$$A(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{\Gamma_{s}/2\pi}{(\omega - \omega')^{2} + \Gamma_{s}^{2}/4} P(\omega')$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega' \exp(-it'(\omega - \omega') - \tilde{\Gamma}_{s} |t'|/2) P(\omega')$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t - |t| (\Gamma_{s} + \Gamma_{a})/2) \langle U(0) U(t) \rangle.$$
(3.7)

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The last formula, (Eq. (3.7)), suitably multiplied by the Debye-Waller factor and other terms, represents the actual absorption spectrum from a thin absorber.

We notice the similarity between Eqs. (3.7) and (2.1); both involve time integrals over correlation functions; but beyond that statement the similarity ends. In the approximation where the fluctuations in the electronic system are ignored, i.e.  $\vec{S}$  replaced by  $\langle \vec{S} \rangle$  and  $\mathscr{H}_0$  by  $\langle \mathscr{H}_0 \rangle$ , then we have:

$$\langle U(0) U(t) \rangle = \langle U(0) \exp(itA \cdot \langle \vec{S} \rangle \cdot \vec{J}) U(0) \exp(-itA \langle \vec{S} \rangle \cdot \vec{I}) \rangle.$$
 (3.8)

(For simplicity we also ignore quadrupole effects.) Assuming a quantization axis along z, this is:

$$\langle U(0) U(t) \rangle = \sum_{m,M} P_m U_{mM} U_{Mm} \exp(it \langle S_z \rangle (A^{\dagger}M - Am)). \qquad (3.9)$$

At all except very low temperatures (T  $\ll$  1°K),  $\mathbf{P}_m$  is independent of m and this becomes

$$\langle U(0) U(t) \rangle = (2I+1)^{-1} \sum_{m,M} |U_{mM}|^2 \exp(it \langle S_z \rangle (A'M - Am)).$$
 (3.10)

Substituting the above expression into Eq. (3.7) one obtains

$$A(\omega) = \sum_{m,M} \frac{|U_{mM}|^2}{2\pi (2I+1)} \frac{\Gamma}{\Gamma^2/4 + [\omega - \langle S_z \rangle (A^*M - Am)]^2}, \qquad (3.11)$$

where

$$\Gamma = \Gamma_{\rm s} + \Gamma_{\rm a}. \tag{3.12}$$

The result, Eq. (3.12), for Fe<sup>57</sup> describes the familiar "six-finger spectrum". This consists of a superposition of six Lorentzian lines corresponding to the six non-zero values of  $U_{mM}$  (namely  $U_{\frac{1}{2}\frac{3}{2}}$ ,  $U_{\frac{1}{2}\frac{1}{2}}$ ,  $U_{\frac{1}{2}-\frac{3}{2}}$ ,  $U_{-\frac{1}{2}-\frac{1}{2}}$ ,  $U_$ 

(a) Equation (3.7) shows that a frequency, say  $\Omega$ , component of  $\langle U(0) U(t) \rangle$  displaces the absorption spectrum by  $\Omega$ . It follows that the high frequencies,  $\Omega \gg A \langle S_z \rangle$  can be ignored because they produce distant parts of the absorption spectrum, so far in the wings of the main absorption lines as to be undetectable. Now the frequency  $A \langle S_z \rangle$  is that for precession of the nuclear spin and corresponds in energy units to the energy required to orient nuclei. In most cases of interest this frequency and energy are very low compared to typical frequencies and energies of the electronic system. Hence in most cases Eq. (3.11), with the addition of quadrupole terms, is the appropriate one to use.

(b) Notwithstanding the fact that  $A\langle S_z \rangle$  is a low frequency, both Eqs.(3.7) and (3.11) show that useful information can be obtained only if  $\Gamma < A \langle S_z \rangle$ . Otherwise the natural width of the Lorentzian peaks is so great that no details due to magnetic effects can be detected. Fortunately in a number of cases, in particular Fe<sup>57</sup>, the nuclear state is sufficiently long lived for this condition to be well satisfied.

Because in most cases Eq. (3.11) is the appropriate formula to use, we see that the Mössbauer effect gives us information on  $\langle S_z \rangle$ , i.e. on the time-averaged spin values. Hence the Mössbauer effect gives us a similar kind of information to that derived from the strictly elastic magnetic scattering of neutrons (see Eq. (2.4)). In section 4 we shall discuss how such neutron and Mössbauer experiments can supplement one another but before leaving the general discussion it is worthwhile to give a brief account of the situations where Eq. (3.11) is not valid.

We have already commented that the Mössbauer effect can be used to study the time development of the electronic system only if this time development takes place slowly, corresponding to frequencies of the order of AS. It follows immediately that for such cases the system must be magnetically dilute because even the weak dipole-dipole forces between magnet moments, at reasonable concentrations, cause fluctuations, rapid compared to AS. (Thus, for a paramagnet for normal concentration Eq. (3.11) remains valid with  $\langle S_z \rangle$  zero for zero applied field.) Therefore as a first necessity we shall suppose the material has concentration 1% or less of magnetic atoms, i.e. sufficiently dilute that dipole-dipole forces can be ignored.

Next we note that in a dilute system the time fluctuations in the electron spin system will be provided by the spin-lattice relaxation. At high temperatures the spin-lattice relaxation time  $T_1$  will be short; the fluctuations in the electron spin orientation will be rapid compared to the nuclear precession and Eq. (3.11) remains valid. At low temperatures  $T_1$  is long; the fluctuations in the electron spin orientation are slow and Eq. (3.11) fails: instead the Mössbauer spectrum becomes that appropriate to an isolated ion. The change from one type of spectrum to another takes place at a temperature dependent on the nature of the electronic state involved. Thus for example Fe<sup>+++</sup> in Al<sub>2</sub>O<sub>3</sub> has a <sup>6</sup>S spectroscopic state with very weak coupling between the electron spin and the lattice vibrations. As a result  $T_1$ is long even at room temperature and the isolated ion Mössbauer spectrum is seen over a wide temperature range [4]. In contrast Fe<sup>+++</sup> in a cyanide complex has spin  $S = \frac{1}{2}$  and the spin lattice relaxation time can be rapid at high T. According to DAVIDS and WAGNER [5]  $Fe^{+++}$  in  $K_3Cr(CN)_6$  has, for M = 0,

$$1/T_1 = 4.3 \times 10^{-3} T^9 s^{-1}$$
 (3.13)

If we assume a hyperfine interaction, AS equivalent to say 200 kG, then the nuclear moment of 0.09  $\mu_N$  predicts a precession time  $T_p \sim 10^{-9}$  s. Hence for temperatures below about 20°K we expect  $T_1 \gg T_p$  and for temperatures above about 20°K we expect  $T_1 \ll T_p$ . The transition from "isolated ion spectrum" at low temperatures to "rapidly relaxed spectrum" at high temperatures has been observed by LANG [6] in haemoglobin cyanide where it is known that the Fe<sup>+++</sup> ion has  $S = \frac{1}{2}$  and the system is very dilute

indeed in magnetic ions. The low temperature spectrum is hard to interpret because in this case the hyperfine interaction is of an asymmetric tensor type with three principal values  $A_{xx}$ ,  $A_{yy}$  and  $A_{zz}$ . The high temperature spectrum shows just the quadrupole splitting.

When either the temperature is such that  $T_1$  is of order  $T_p$  or the concentration is such that the dipolar fluctuation time  $T_2$  is of order  $T_p$ , the Mössbauer spectrum poses an interesting theoretical problem which must be approached by applying the theory of cumulants to Eq. (3.7). This problem is not discussed here.

Similar remarks apply to Mössbauer ions distributed dilutely in metals or semiconductors. For example if  $Fe^{57}$  is added dilutely to a non-magnetic metal, say Cu, then at sufficient dilution the main relaxation process for the electron spin is caused by mutual spin flip with the conduction electrons. KORRINGA [7] has calculated

$$\frac{1}{T_1} \simeq \frac{\pi G^2}{\hbar} \left[ \frac{Z(E)}{N} \right]^2 kT, \qquad (3.14)$$

where G is the s-d exchange interaction and Z(E) the density of states. Using  $G \sim 0.5 \text{ eV}$  and  $E_f \sim 7 \text{eV}$  we calculate  $T_1 \sim 10^{-9}/T$  s for Fe in Cu. Assuming  $T_p \sim 10^{-9}$  s we conclude that a split Mössbauer spectrum would be seen only at T « 1°K. For Fe in a semiconductor the density of states would be so much smaller that a split spectrum could probably be seen at helium temperatures. Such a Mössbauer experiment has not been performed as far as the author is aware.

We conclude from this discussion that situations where the Mössbauer effect is used directly to study the dynamics of electron spin, fluctuations are of such a special character that they have no close connection with neutron scattering results. However Mössbauer experiments usually measure the time-averaged spin orientations and in such cases there is a direct connection with the strictly elastic magnetic neutron scattering which is discussed in the next section.

## 4. EXPERIMENTS ON FERROMAGNETIC ALLOYS

In studies on ferromagnetic alloys the use of neutron scattering, Mössbauer and nuclear magnetic resonance (NMR) experiments are closely related in principle, although at the present day the proper interpretation of Mössbauer and NMR experiments is only beginning to be clarified. Suppose the binary alloys have composition  $A_{1-c}B_c$  and suppose initially that the concentration c is small. Then each B atom is well separated from all other B atoms and effects due to one B atom do not interefere with those of another. Each B atom has a final moment and in addition each B atom affects its immediate environment so that A atoms near to it have moments different from A atoms which happen to be well isolated from all B atoms. If each B atom affects the moment of an A atom distance  $\vec{R}$  away, by an amount  $g(\vec{R})$  then a formal statement of the moment on a site  $\vec{n}$  is

$$\mu_{\vec{n}} = \mu_{h} + (\mu_{i} - \mu_{h})p_{\vec{n}} + \sum_{\vec{R}} g(\vec{n} - \vec{R})p_{\vec{R}}, \qquad (4.1)$$

where

$$p_{\vec{n}} = 1$$
 if a B atom is on site  $\vec{n}$   
 $p_{\vec{n}} = 0$  if an A atom is on site  $\vec{n}$ . (4.2)

In Eq. (4.1),  $\mu_h$  stands for the moment on undisturbed host (A) atoms and  $\mu_i$  for the moment on impurity (B) atoms.

Because the mean value of  $p_{\vec{n}}$  is c we have immediately

$$\langle \mu \rangle = \mu_{\rm b} + (\mu_{\rm i} - \mu_{\rm h})c + cG(0),$$
 (4.3)

where we have defined Fourier transforms by

$$G(\vec{K}) = \sum_{\vec{R}} \exp(i\vec{K} \cdot \vec{R})g(\vec{R}). \qquad (4.4)$$

From Eq. (4.3) we note that

$$\frac{d}{dc} \langle \mu \rangle = \mu_{i} - \mu_{h} + G(0) .$$
 (4.5)

The result in Eq.(4.1) is easily substituted into Eq.(2.4) to give for diffuse elastic scattering

$$\frac{d\sigma}{d\Omega'} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 [1 - \hat{K}_z^2] e^{-2W} |f(\vec{K})|^2 \operatorname{Nc}(1 - c) [\mu_i - \mu_h + G(\vec{K})]^2. \quad (4.6)$$

This formula has been used extensively by LOW and COLLINS [8,9] to determine  $\mu_i$  and  $G(\vec{K})$  for a wide variety of ferromagnetic alloys.

The theory can be extended to more concentrated alloys where the B atoms begin to affect one another. In this case we must replace Eq. (4.1) by the equations

$$\mu_{\vec{n}} = \langle \mu_A \rangle + \sum_{\vec{k}} g(\vec{n} - \vec{k}) [p_{\vec{k}} - c] \text{ for an A atom on } \vec{n}$$

$$\mu_{\vec{n}} = \langle \mu_{B} \rangle + \sum_{\vec{R}} h(\vec{n} - \vec{R})[p_{\vec{R}} - c] \quad \text{for a B atom on } \vec{n}.$$
(4.7)

These equations describe a superposition approximation: the effects of atoms

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on one another assumed to be independent within the statistical fluctuations allowed by the mean alloy concentration. Using this equation it is possible to derive the formula [10]

$$\frac{d\sigma}{d\Omega^{\dagger}} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 [1 - \hat{K}_z^2] e^{-2W} |f(\vec{K})|^2 \operatorname{Nc}(1 - c) \\ \times \{[\langle \mu_B \rangle - \langle \mu_A \rangle + G(\vec{K}) + cJ(\vec{K})]^2 + c(1 - c)[Q(0) + Q(\vec{K})]\}, \quad (4.8)$$

where

$$j(\vec{R}) = h(\vec{R}) - g(\vec{R})$$
 (4.9)

 $G(\vec{K})$ ,  $H(\vec{K})$  and  $J(\vec{K})$  are Fourier transforms defined by analogy to Eq. (4.4) and

$$Q(\vec{K}) = \sum_{\vec{R}} \exp(i\vec{K}\cdot\vec{R})[j(\vec{R})]^2. \qquad (4.10)$$

In principle Eq. (4.8) extends the value of neutron experiments into higher concentration regions (always provided there is no chemical short-range order present) but its validity has not yet been tested experimentally. The various parameters appearing in Eqs. (4.7) and (4.8) are linked by the equations

$$\frac{\mathrm{d}}{\mathrm{dc}} \langle \mu_{\mathrm{A}} \rangle = \mathrm{G}(0) \tag{4.11}$$

$$\frac{d}{dc} \langle \mu_{\rm B} \rangle = H(0) = G(0) + J(0)$$
(4.12)

$$\frac{\mathrm{d}}{\mathrm{dc}} \langle \mu \rangle = \langle \mu_{\mathrm{B}} \rangle - \langle \mu_{\mathrm{A}} \rangle + \mathrm{G}(0) + \mathrm{cJ}(0) . \qquad (4.13)$$

In principle the Mössbauer effect and NMR experiments can be used to supplement and confirm the neutron results because the hyperfine fields acting on any particular nucleus must, in the main, obey an equation exactly similar to Eq. (4.7), namely

$$H_{\vec{n}} = \langle H_A \rangle + \sum_{\vec{R}} g'(\vec{n} - \vec{R})(p_{\vec{R}} - c) \text{ for an A atom on } \vec{n}$$

$$H_{\vec{n}} = \langle H_B \rangle + \sum_{\vec{R}} h'(\vec{n} - \vec{R})(p_{\vec{R}} - c) \text{ for a B atom on } \vec{n}.$$
(4.14)

Hence, for example, the Mössbauer spectrum of the host atoms should show

a superposition of many "six-finger spectra" corresponding to the distribution defined by Eq. (4.7). Both the Mössbauer and NMR experiments measure the full distribution function of the hyperfine field and this can be deduced from Eq. (4.7) as follows.

For atoms of type A (the discussion for B atoms is identical) the distribution function defined by Eq. (4.7) is

$$\mathbf{p}(\mathbf{H}) = \left\langle \delta \left[ \mathbf{H} - \langle \mathbf{H}_{\mathbf{A}} \rangle + \mathbf{c} \mathbf{G'}(\mathbf{0}) - \sum_{\vec{\mathbf{R}}} \mathbf{g'}(\vec{\mathbf{R}}) \mathbf{p}_{\vec{\mathbf{R}}} \right] \right\rangle, \qquad (4.15)$$

where the averaging has to be applied to the positions of the B and A atoms. The Fourier transform of p(H) is

$$q(t) = \int_{-\infty}^{\infty} dH \exp(itH)p(H)$$

$$= \exp\left(it[\langle H_A \rangle - cG'(0)]\right) \left\langle \exp\left(it\sum_{\vec{R}} g'(\vec{R})p_{\vec{R}}\right) \right\rangle.$$
(4.16)
(4.17)

The averaging in Eq. (4.17) would be easy if all sites  $\vec{R}$  could be treated independently but we must recall the restriction that

$$\sum_{\vec{R}} p_{\vec{R}} = Nc.$$
 (4.18)

In the usual way we therefore use a grand canonical ensemble neglecting the restriction but weighting Eq. (4.17) properly. It is easy to show that Eq. (4.17) then becomes

$$q(t) = \exp\left(it[\langle H_A \rangle - cG'(0)]\right) \left\langle \exp\left(it\sum_{\vec{R}} g'(\vec{R})p_{\vec{R}}\right) \left(\frac{c}{1-c}\right)^{\sum_{\vec{R}} p_{\vec{R}}} \right\rangle_{Ave.} (1-c)^N,$$
(4.19)

where the average is now performed without restriction to give

$$q(t) = \exp\left(it[\langle H_A \rangle - cG'(0)]\right) \prod_{\vec{R}} \left\{ 1 + c\left[\exp\left(itg'(\vec{R})\right) - 1\right] \right\}$$
(4.20)

i.e.

$$\ln q(t) = \operatorname{it}[\langle H_{A} \rangle - cG'(0)] + \sum_{\vec{R}} \ln \left\{ 1 + c \left[ \exp(\operatorname{itg'}(\vec{R})) - 1 \right] \right\}.$$
(4.21)

Hence

$$p(H) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left(-it[H - \langle H_A \rangle + cG'(0)]\right) \exp\left[\ln\left\{1 + c\left[\exp\left(itg'(\vec{R})\right) - 1\right]\right\}\right]$$
(4.22)

which, though complicated, relates the observable p(H) to the quantity of interest,  $g'(\vec{R})$ . For example one result from Eq. (4.22), or directly from Eq. (4.14), is

$$\langle H^2 \rangle = \int_{-\infty}^{\infty} dH H^2 p(H) \approx \langle H_A \rangle^2 + c(1-c) \sum_{\vec{R}} [g'(\vec{R})]^2.$$
 (4.23)

Unfortunately this idea of relating Mössbauer or NMR experiments to neutron experiments is neither so simple nor so valuable as one might expect and we shall now list the reasons for this.

(a) The most serious difficulty is that the relation between magnetic moments and hyperfine fields is complex and there is only a rough proportionality between them. Therefore, even if we knew the hyperfine field values exactly, there would remain uncertainty about their interpretation in terms of magnetic moments. The simplest way to test this point is to use the Mössbauer effect to measure the mean host field. In a wide series of measurements CRANSHAW, JOHNSON and RIDOUT [11] (see also MARSHALL and JOHNSON [12]) have shown there is only a rough correlation between  $\langle H_A \rangle$  and  $\langle \mu_A \rangle$ .

(b) The second difficulty is that even in a crystal with overall cubic symmetry the Mössbauer spectrum is perturbed by dipolar-hyperfine fields and quadrupole fields. When an atom B is introduced into the host the charge cloud around those A atoms which happen to be near B atoms is perturbed, i.e. the B atom has disturbed the cubic symmetry in its immediate environment. This introduces both an electric field gradient and a dipolar magnetic field at the A nuclei. Both effects have a principal axis along the vector  $\vec{R}$  joining the B atom to the A atom in question. Thus in Eq. (4.14) it is necessary to add to  $g'(\vec{R})$  and  $h'(\vec{R})$  an additional term depending upon the relative orientation of  $\vec{R}$  and  $\vec{M}$ , the magnetization. Hence in place of Eq. (4.14) we have

$$H_{\vec{n}} = \langle H_{\vec{A}} \rangle + \sum_{\vec{R}} (p_{\vec{n}} + \vec{R}^{-} c) \left\{ g'(\vec{R}) + \lambda(\vec{R}) [3(\vec{R} \cdot \vec{M})^{2} - 1] \right\}. \quad (4.24)$$

The additional term makes the atoms in a shell of neighbours inequivalent to one another. In addition to this complication, a further splitting of the Mössbauer spectrum takes place through the quadrupole effect which accompanies the charge distortions. Both the dipolar and quadrupole terms have been observed in FeSi alloys by CRANSHAW, JOHNSON and RIDOUT [13] but their precise values have not yet been determined.

(c) The NMR experiments suffer from both the difficulties (a) and (b) listed above but in principle are capable of higher precision than either the neutron

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or Mössbauer experiments. Unfortunately they also have a difficulty of their own. In an NMR experiment the signal is completely dominated by nuclei which happen to be in the domain walls. This would be of no importance if the dipolar and quadrupolar effects mentioned above were absent: but in the presence of these effects the resonant frequency varies with the magnetization direction and therefore varies through the width of the domain wall. It is therefore important to determine which part of the domain wall gives the strongest signals. A new theory by MURRAY and MARSHALL [14] may help to interpret future NMR experiments but to date it has not proved possible to correlate any NMR experiment on a ferromagnetic alloy with neutron or Mössbauer results.

In view of these remarks a study of the dipolar field and quadrupole effects is indicated. Some beginning on this has been made using the Mössbauer effect [13, 15] but it is worthwhile describing one other result, for a rather different situation.

The magnetic moment density in hexagonal cobalt has been measured very accurately by MOON [16] using the Bragg scattering of polarized neutrons. The experiments are able to detect the asymmetry in the moment density and Moon concludes that

$$\mu(\vec{r}) = 0.394 \,\rho(E_{2g}) + 0.416 \,\rho(E_{1g}) + 0.190 \,\rho(A_{1g}), \qquad (4.25)$$

where  $\rho(\mathrm{E}_{2g})$  etc. are the densities with appropriate angular dependence. In terms of polar co-ordinates

$$\rho(E_{2g}) = \frac{3}{8} \sin^4 \theta \rho(\mathbf{r})$$

$$\rho(E_{1g}) = \frac{3}{2} \sin^2 \theta \cos^2 \theta \rho(\mathbf{r}) \qquad (4.26)$$

$$\rho(A_{1g}) = \frac{1}{4} (3 \cos^2 \theta - 1)^2 \rho(\mathbf{r}).$$

From this we get a measure of asymmetry from the result

$$\int d\vec{\mathbf{r}} \,\mu(\vec{\mathbf{r}}) (3\cos^2\theta - 1) = \frac{4}{7} [-0.394 + 0.208 + 0.190] \simeq 0.002. \quad (4.27)$$

This very small asymmetry is to be contrasted with the asymmetry parameter of 4/7 = 0.571 which would be given by a single 3d electron.

This asymmetry gives rise to a dipolar hyperfine field

$$H_{dip} = \mu_{Co} \int d\vec{r} \, \mu(\vec{r}) r^{-3} (3 \cos^2 \theta - 1) = 0.002 \langle r^{-3} \rangle \mu_{Co}$$
  

$$\approx 1.1 \text{ kG,} \qquad (4.28)$$

where we have used 1.7  $\mu_{\rm B}$  for the cobalt moment and 5.1  $a_0^{-3}$  for  $\langle r^{-3} \rangle$ .

This dipolar field is difficult to observe directly (because upon rotating the magnetization the g<sup>1</sup>-value, and hence the hyperfine field due to the orbital current, also changes) but the corresponding quadrupole field acting on Fe<sup>57</sup> in hexagonal cobalt has been measured in a very careful experiment by PERLOW et al. [17]. He finds the result

$$\frac{e^2 qQ}{2h} = 0.4 \text{ Mc/s.}$$
 (4.29)

Now the electric field gradient is

$$q = -\sum_{\text{electrons}} \langle \mathbf{r}^{-3} (3 \cos^2 \theta - 1) \rangle$$
$$= \sum_{\text{holes}} \langle \mathbf{r}^{-3} (3 \cos^2 \theta - 1) \rangle$$
$$= \left(\frac{\mu_{\text{Fe}}}{\mu_{\text{B}}}\right) \langle \mathbf{r}^{-3} \rangle \langle (3 \cos^2 \theta - 1) \rangle. \tag{4.30}$$

The moment on Fe in Co is known to be 2.8  $\mu_B$ . Using the same value for  $\langle r^{-3} \rangle$  and taking Q to be 0.12 b we deduce

$$\left\langle (3\cos^2\theta - 1) \right\rangle \simeq 0.002. \tag{4.31}$$

The agreement between Eqs. (4.27) and (4.31) is gratifying.

### 5. CONCLUSIONS

The relation between neutron scattering, Mössbauer absorption and NMR experiments has been reviewed. We have argued that the situations where the Mössbauer effect directly measures the time fluctuations in the electronic system are special and therefore the connection between these various techniques is close only when they study time-averaged quantities. It follows that an important area where all techniques are applicable is the study of ferromagnetic alloys. The neutron diffuse, magnetic scattering which is strictly elastic is of particular value in this field as the interpretation of Mössbauer and NMR experiments is complicated by dipolar and quadrupole effects.

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## DISCUSSION

K. P. SINHA: 1 would like to ask Dr. Elliott about the feasibility of a new type of experiment which combines the Mössbauer effect and optical absorption in a system containing a paramagnetic ion (e.g.  $Fe^{3+}$ ) in perfect octahedral surrounding. If by optical irradiation we go to an orbital state which is orbitally degenerate, we expect splitting of the excited state owing to electron vibration coupling. A Mössbauer measurement at this stage might give us some information about the nature of local distortion induced by electron-vibration coupling in the excited state. Of course, we are assuming that we have a system where the lifetime of the excited state is fairly long.

R.J. ELLIOTT: I think such an experiment would be interesting, but one would have to find an excited state of long lifetime, say,  $10^{-8}$  s. As you know, it was quite a problem to do paramagnetic resonance in such a system and under such conditions.

## DIFFUSE SCATTERING FROM ALLOYS AND DISORDERED SYSTEMS: EXPERIMENTAL TECHNIQUES AND POTENTIALITIES

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#### Abstract — Résumé — Аннотация — Resumen

DIFFUSE SCATTERING FROM ALLOYS AND DISORDERED SYSTEMS: EXPERIMENTAL TECHNIQUES AND POTENTIALITIES. The purpose of this paper is to review, both with regard to principles and practice, the types of information that may be obtained by studying the elastic diffuse scattering of neutrons. Attention will be concentrated on systems where there is a random arrangement of defects each of which may be assumed to be unaffected by the presence of its fellows, either because of dilution or because of an intrinsic lack of dependence on environment. In these circumstances the pattern of scattered intensity is proportional to the square of the modulus of a Fourier transform over the disturbance in scattering amplitude associated with a defect. Thus, information on the spatial distribution of defect scattering amplitude can be obtained by carrying out the relevant neutron scattering measurements and performing a Fourier inversion. In practice, because of the large number of processes contributing to the diffuse scattering background, measurements have so far been possible only in a limited number of fields. In particular considerable progress has been made in connection with magnetic defects in ferromagnets where the magnetic cross-section may be controlled by changing the direction of magnetization relative to the neutron scattering vector. In this way the scattering of interest can be isolated from the non-magnetic effects as a difference between two intensity measurements. A process contributing to the diffuse scattering background which is partly magnetic in character and therefore not eliminated by the above technique is multiple Bragg scattering in a magnetic polycrystal. This may be avoided by the use of a single -crystal specimen or by employing long wavelength neutrons such that no Bragg processes are possible. An instrument based on the latter principle has been developed at Harwell and used in connection with a wide range of measurements on dilute ferromagnetic alloys. These observations are discussed along with a number of other likely future developments in the field. Included among the latter are measurements of the diffuse magnetic scattering from paramagnetic salts. Observations of such scattering are of great interest since they contain direct information on the amount of spin transferred, as a result of covalency, from a magnetic ion on to the ligands which surround it.

DIFFUSION DANS LES ALLIAGES ET LES SYSTÈMES DÉSORDONNÉS; MÉTHODES EXPÉRIMENTALES ET POSSIBILITÉS D'APPLICATION. Le mémoire a pour objet d'examiner, du point de vue des principes et de la pratique, les divers renseignements que l'on peut obtenir en étudiant la diffusion élastique des neutrons. L'auteur traite surtout des systèmes comportant une disposition stochastique des défauts, au sujet desquels on peut supposer qu'aucun n'est affecté par la présence des autres, soit en raison de la dilution, soit en raison d'une indépendance intrinsèque à l'égard de l'environnement. Dans ces conditions, l'intensité diffusée est proportionnelle au carré du module d'une transformée de Fourier sur la perturbation de l'amplitude de diffusion associée à un défaut. On peut ainsi obtenir des renseignements sur la distribution spatiale de cette amplitude de diffusion en procédant aux mesures appropriées de diffusion des neutrons et en opérant une inversion de Fourier. En pratique, vu le grand nombre de phénomènes qui contribuent au bruit de fond de diffusion, on n'a pu jusqu'à présent faire des mesures que pour un petit nombre de champs. On a notamment réalisé des progrès considérables en ce qui concerne les défauts magnétiques dans les ferro-aimants où l'on peut faire varier la section efficace magnétique en modifiant la direction de magnétisation par rapport au vecteur de diffusion des neutrons. On parvient ainsi à séparer la diffusion considérée des effets non magnétiques sous la forme d'une différence entre les deux mesures d'intensité. Un phénomène qui contribue au bruit de fond de diffusion et qui possède un caractère partiellement magnétique et par conséquent n'est pas éliminé par la technique susmentionnée, est la diffusion multiple de Bragg dans un polycristal magnétique. On parvient à l'éviter en utilisant un échantillon monocristal ou en employant des neutrons ayant une longueur d'onde suffisante pour qu'aucun phénomène de Bragg ne puisse se produire. Un appareil fondé sur ce dernier principe

a été mis au point à Harwell et utilisé pour une gamme étendue de mesures portant sur des alliages ferromagnétiques dilués. L'auteur discute ces travaux ainsi que plusieurs autres qui pourraient être entrepris dans ce domaine. Parmi ces derniers figurent des mesures de la diffusion magnétique par les sels paramagnétiques. L'observation de cette diffusion revêt un grand intérêt car elle fournit des renseignements directs sur la fraction de spin transférée, par suite de la covalence, d'un ion magnétique aux coordinats qui l'entourent.

ДИФФУЗНОЕ РАССЕЯНИЕ НА СПЛАВАХ И РАЗУПОРЯДОЧЕННЫХ СИСТЕМАХ. ЭКС-ПЕРИМЕНТАЛЬНЫЕ МЕТОДЫ И ПОТЕНЦИАЛЬНЫЕ ВОЗМОЖНОСТИ. Задачей настоящей работы является рассмотрение как в принципе, так и с практической точки зрения тех видов данных, которые можно получить в результате изучения неупругого диффузного рассеяния нейтронов. Внимание сконцентрировано на тех системах, в которых имеется разупорядоченное расположение дефектов, каждый из которых можно условно считать не подверженным влиянию других имеющихся дефектов либо в результате разбавления, либо в результате отсутствия зависимости от окружения. При этих условиях интенсивность рассеяния пропорциональна квадрату модуля разложения Фурье по возмущению в амплитуде рассеяния, вызванному дефектом. Таким образом, данные об амплитуде пространственного распределения рассеяния дефектов могут быть получены в результате выполнения соответствующих измерений рассеяния нейтронов и произведения преобразования Фурье. На практике, в связи с тем, что большое количество процессов играет роль в создании фона диффузного рассеяния, измерения удалось пока произвести в ограниченном числе областей. В частности, значительные успехи достигнуты в области магнитных дефектов в ферромагнитных телах, в которых магнитные сечения могут контролироваться путем изменения направления намагничивания в отношении вектора рассеяния нейтронов. Таким образом, интересующее рассеяние может быть отделено от немагнитных эффектов путем определения разницы между результатами двух измерений интенсивности. Процессом, играющим роль в создании фона диффузного рассеяния, который является отчасти магнитным по своему характеру и не может быть поэтому исключен с помощью вышеуказанного метода, является брэгговское рассеяние на магнитном поликристалле. Этот процесс можно устранить путем использования монокристаллических образцов или таких длинноволновых нейтронов, при которых невозможен брэгговский процесс. Прибор, основанный на этом принципе, был разработан в Харуэлле и использовался для широкого круга измерений, связанных с разбавленными ферромагнитными сплавами. Эти вопросы рассматриваются вместе с некоторыми другими вопросами, касающимися возможных будущих разработок в этой области. В число этих последних входят измерения диффузного магнитного рассеяния на парамагнитных солях. Наблюдение такого рассеяния представляет большой интерес, поскольку позволяет получить непосредственные данные о величине спина, переданной в результате ковалентности от магнитного иона к окружающим его лигандам.

DISPERSIÓN DIFUSA EN ALEACIONES Y SISTEMAS DESORDENADOS; TÉCNICAS EXPERIMENTALES Y POSIBILIDADES. La finalidad de la memoria es analizar, desde el punto de vista de la teoría y de la práctica, las informaciones que pueden obtenerse estudiando la dispersión elástica difusa de neutrones. Se presta particular atención a los sistemas con distribución aleatoria de defectos, cada uno de los cuales puede considerarse aislado de los demás, bien por efecto de la dilución o bien por ser intrínsecamente independiente del medio. En estas condiciones, la intensidad dispersa es proporcional al cuadrado del módulo de una transformada de Fourier respecto de la perturbación de la amplitud de dispersión asociada al defecto. De este modo pueden obtenerse datos sobre la distribución espacial de la amplitud de dispersión por defectos realizando las mediciones pertinentes por dispersión neutrónica y efectuando una inversión de Fourier. En la práctica, dada la gran cantidad de procesos que contribuyen a la actividad de fondo debida a la dispersión difusa, sólo se han podido realizar determinados tipos de mediciones. En particular, se han logrado progresos considerables en lo que respecta a los defectos magnéticos de las sustancias ferromagnéticas en las que la sección eficaz magnética puede controlarse cambiando la dirección de magnetización con respecto al vector de dispersión neutrónica. De este modo, la dispersión de interés puede distinguirse de los efectos no magnéticos como diferencia entre dos intensidades medidas. Un proceso que contribuye al fondo de dispersión difusa, en parte de carácter magnético y que, por tanto, la mencionada técnica no elimina, es la dispersión multiple de Bragg en un policristal magnético. Puede prevenirse utilizando una muestra monocristalina o empleando neutrones de gran longitud de onda, de forma que impidan los procesos de Bragg. En Harwell se ha construido un instrumento basado en este principio, que se utiliza para una amplia serie de mediciones en aleaciones ferromagnéticas diluidas. Se examinan estos experimentos y otras novedades que cabe anticipar en la materia, entre ellas la medición de la dispersión magnética difusa en sales paramagnéticas. El estudio de esta dispersión reviste

enorme interés, pues proporciona información directa sobre la cantidad de spin transmitida por un ion magnético a los ligandos que le rodean como resultado de la covalencia,

#### 1. INTRODUCTION

The technique of crystal structure investigation by means of neutron diffraction has been well established for many years: more recently the study of quasi-particles such as phonons and magnons by neutron scattering has also received a considerable amount of attention. Both these types of experiment involve examination of neutrons coherently scattered from the whole of a specimen and the data collected contain information about the average properties of the crystal concerned, e.g. the average length of a lattice parameter or the average of the scattering amplitude distributions in the unit cells. The widths of the coherently scattered peaks in the neutron spectrum may indeed give some indication of the extent of deviations around this average. However, much more explicit information concerning departures from the mean is to be found in the diffusely scattered intensity.

The study of the latter, where solids are concerned, has on the whole received much less attention than the coherent diffraction. This is mainly because of experimental difficulties. As it is confined to small volumes in reciprocal space, a coherently scattered spectrum has high peak intensities leading to an easing of the experimental problem. Nevertheless examination of the diffusely scattered neutrons, although requiring rather more precise measurements of intensity, is well worth carrying out on account of the range of new information obtainable by this means. It is the purpose of this article to discuss some of the possibilities in this connection, but only those concerned with elastic diffuse scattering from a crystalline solid.

From the point of view of solid state physics there appear at the moment to be two general fields in which measurements of diffuse elastic scattering are particularly useful. First there is the examination of defects, both magnetic and non-magnetic, through observations of the appropriate crosssections. Secondly from measurements of the scattering from uncoupled electronic spins, an evaluation of the relevant form factors at small values of neutron scattering vector should be possible. In the case of non-metals this would be of considerable interest in view of the close connections linking such data with covalency effects (see [1]). (Strictly speaking no system of spins can ever be completely uncoupled and consequently paramagnetic spin scattering must always be inelastic. However, in the limit when the energy transfers are negligible compared with the energy of the incident neutrons, the scattering may be treated as elastic for all practical purposes.)

In the next section we discuss the cross-sections corresponding to scattering from both magnetic and non-magnetic defects and also from uncoupled electronic spins. It is assumed that the magnetic defects occur in a spin array which is collinear. More general formulae applicable to non-collinear spins are given in the Appendix. A discussion of scattering from partially aligned nuclear spins is also contained in the Appendix. In section 3 some comments are made concerning experimental difficulties involved in measurements of diffuse scattering. Recent results are referred to and some of the problems arising in connection with their analysis are discussed.

## 2. CROSS-SECTIONS FOR DIFFUSE ELASTIC SCATTERING FROM CRYSTALS

#### 2. 1. Defect scattering

We first consider the scattering of neutrons from defects in an otherwise perfectly periodic array of scattering centres. It is assumed that only one type of defect is present and that each defect is randomly sited<sup>1</sup> and not affected by the presence of its fellows. This latter assumption implies either, a sufficiently low concentration to ensure that regions of overlap between defects do not occur to any significant extent, or, if overlapping does take place, that the effects of the defect centres concerned superpose in an additive manner. We deal first explicitly with magnetic scattering following the discussion of Reference [4] but in fact our results are equally valid for non-magnetic defects.

The differential cross-section for the elastic scattering of unpolarized neutrons in an array of collinear spins is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left(\frac{\gamma \mathrm{e}^2}{2\mathrm{m}\mathrm{c}^2}\right)^2 \sin^2\alpha \left| \int_{\mathrm{V}_{\alpha}} \mathrm{d}\vec{\mathbf{r}} \,\rho\left(\vec{\mathbf{r}}\right) \mathrm{e}^{i\vec{k}\cdot\vec{\mathbf{r}}} \right|^2, \tag{1}$$

where the integral is over the volume of the specimen  $V_s$ . The value of the numerical constant on the right hand side is 0.073 b.  $\vec{k}$  is the scattering vector of the neutrons and  $\alpha$  is the angle between  $\vec{k}$  and the direction of the spins.  $\rho(\vec{r})$  represents the magnetic moment density in the specimen expressed in Bohr magneton units (an algebraic sign appropriate to the sense of the magnetic moment must be included). For a spin-only system the evaluation of  $\rho(\vec{r})$  is clearly straightforward, but in the presence of orbital effects there is some complication in the scattering (see e.g. [5]).

Under the conditions defined at the beginning of this section, Eq. (1) may be separated immediately into the sum of a Bragg and a disorder scattering cross-section. Thus, we have

$$\frac{d\sigma}{d\Omega} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 \sin^2 \alpha \left[\vec{d}^2\right] \sum_{\vec{m}} e^{i\vec{\kappa}\cdot\vec{m}} \left[^2 + \left|\sum_{\vec{m}} e^{i\vec{\kappa}\cdot\vec{m}}(d_{\vec{m}}-\vec{d})\right|^2\right], \quad (2)$$

where the  $\vec{m}$  denote sites on a basis lattice and

<sup>&</sup>lt;sup>1</sup> Scattering from a crystal in which it is appropriate to describe the departures from perfection in terms of a short range order parameter has been discussed elsewhere [2] and is not treated here. It may also be noted that a discussion concerned specifically with the scattering from dislocations in magnetic materials has been given by KRONMULLER et al. [3].

$$\mathbf{d}_{\vec{\mathbf{m}}} = \int_{\mathbf{V}_{\vec{\mathbf{m}}}} \mathbf{d} \vec{\mathbf{r}} \rho(\vec{\mathbf{r}}) e^{i\vec{\kappa} \cdot (\vec{\mathbf{r}} - \vec{\mathbf{m}})}, \qquad \vec{\mathbf{d}} = \frac{1}{N} \sum_{\vec{\mathbf{m}}} \mathbf{d}_{\vec{\mathbf{m}}},$$

the integration being over the volume of the unit cell at  $\vec{m}$ . The second term corresponds, of course, to the disorder scattering. Under the assumption made above that the defects do not interact, this part may be rewritten in the form

$$\frac{d\sigma^{defect}}{d\Omega} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 \sin^2(\alpha) \operatorname{Nc}(1-c) \left| \int_{V_c} d\vec{r} \rho^{\dagger}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \right|^2, \quad (3)$$

where c is the fractional concentration of defect sites in the basis lattice of N points.  $\rho'(\vec{r})$  represents the disturbance in magnetic moment density due to the presence in the specimen of a single defect. The reference level against which the disturbance is measured is the moment density corresponding to the unperturbed matrix.

Equation (3) may also be written in the form

$$Nc(1-c) \Big| \sum_{\vec{n}} d_{\vec{n}} e^{i\vec{k}\cdot\vec{n}} - \sum_{\vec{m}} d_{\vec{m}} e^{i\vec{k}\cdot\vec{m}} \Big|^{2}$$

$$= Nc(1-c) \Big\{ \sum_{\vec{n},\vec{m}'} d_{\vec{m}'} d_{\vec{m}'} e^{i\vec{k}\cdot(\vec{m}-\vec{m}')} + \sum_{\vec{n},\vec{n}'} d_{\vec{n}'} d_{\vec{n}} e^{i\vec{k}\cdot(\vec{n}-\vec{n}')} \Big| \Big\}, \qquad (4)$$

$$- \sum_{\vec{n},\vec{n}'} \Big[ d_{\vec{n}}^{*} d_{\vec{m}} e^{i\vec{k}\cdot(\vec{m}-\vec{n})} + d_{\vec{m}'}^{*} d_{\vec{n}} e^{i\vec{k}\cdot(\vec{n}-\vec{m})} \Big] \Big\},$$

where the first two factors on the right of Eq. (3) have been omitted. The sums over  $\vec{m}, \vec{m}'$  and  $\vec{n}, \vec{n}'$  correspond to sums over the basis lattice points in an unperturbed crystal and a specimen containing a single defect, respectively. Thus, in many cases, the sums can be limited to sites in the neighbourhood of this defect.

It is clear that exactly the same discussion as described above could be carried through with reference to nuclear scattering. In fact if d in Eq. (4) is replaced by  $\langle b \rangle e^{i\vec{k} \cdot \vec{u}}$ , where  $\langle b \rangle$  is the mean<sup>2</sup> nuclear scattering

<sup>&</sup>lt;sup>2</sup> It is assumed that the nuclear incoherent scattering is treated separately from the defect scattering and given by a set of sums of the form  $\sum_{n} c_{\eta}(<b_{\eta}^2 > -<b_{\eta} >^i)$  where each sum corresponds to one particular site in the unit cells and c represents the fractional concentration of the various nuclear species at this site.

length and  $\vec{u}_{f}$  relates a nucleus to its basis lattice site, we have the crosssection for nuclear defect scattering [6].

For a beam of polarized incident neutrons, a cross term between the magnetic and nuclear scattering amplitudes arises. This may be represented by replacing  $d_{\uparrow}^* d_{\uparrow}$  in Eq. (4) by (see Appendix)

$$\frac{\gamma e^2}{2mc^2} \left[ \left< b_j^* \right> e^{-i\vec{k}\cdot\vec{l}} \vec{j} \cdot \vec{f}_{i} \cdot \vec{k} \right) \vec{P} \cdot \vec{\mu}_{i}^{\perp} + \text{ complex conjugate } \right].$$
(5)

The vector  $\vec{\mu}_{\vec{1}}^{\perp} = \vec{\kappa} \times (\vec{\mu}_i \times \vec{\kappa})$  is the projection in the plane normal to  $\vec{\kappa}$  of  $\vec{\mu}_{\vec{1}}$ , the magnetic moment associated with the lattice site  $\vec{i}$ . Thus

$$\vec{\mu}_{\vec{i}} = \int_{V_{\vec{i}}} d\vec{r} \,\rho(\vec{r})$$
(6)

with an accompanying form factor of

$$\mathbf{f}_{\vec{i}}(\vec{\kappa}) = \frac{1}{\vec{\mu}_{\vec{i}}} \int_{V \to i} d\vec{\mathbf{r}} \,\rho(\vec{\mathbf{r}}) \,\mathbf{e}^{i\vec{\kappa}\cdot(\vec{r}-\vec{i})}$$
(7)

 $\vec{P}$  is a vector giving the direction and magnitude of the polarization of the neutrons in the incident beam (0 < P < 1). The absence of this cross term from an unpolarized neutron measurement is thus the result of an average over all polarizations leading to a zero effect.

If the above formulae are applied to the simple situation corresponding to a binary disordered system of collinear magnetic moments ( $\mu_1$  and  $\mu_2$ ) located at the basis lattice sites, the cross-section for magnetic disorder scattering is found to be [7]:

$$Nc(1 - c) \left(\frac{\gamma e^{2}}{2mc^{2}}\right)^{2} \sin^{2}(\alpha) \left| f_{1}(\vec{\kappa})\mu_{1} - f_{2}(\vec{\kappa})\mu_{2} \right|^{2} + Nc(1 - c) \frac{\gamma e^{2}}{2mc^{2}} \left\{ (\langle b_{1}^{*} \rangle - \langle b_{2}^{*} \rangle) [f_{1}(\vec{\kappa})\mu_{1} - f_{2}(\vec{\kappa})\mu_{2}] + [\langle b_{1} \rangle - \langle b_{2} \rangle] [f_{1}^{*}(\vec{\kappa})\mu_{1} - f_{2}^{*}(\vec{\kappa})\mu_{2}] \right\} \vec{P} \cdot \vec{\mu}^{\perp}.$$
(8)

#### 2. 2. Scattering from uncoupled spins

When used in connection with the present discussion, the term uncoupled is taken to imply that the energy required to reverse a spin in the presence of neighbouring spins but in the absence of a magnetic field is small compared with (a) the energy of an incident neutron and (b) the thermal energy kT. If (a) were applicable but not (b), the spin coupling present could be described by suitable correlation functions and the scattering from such

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a system treated by methods similar to those described in Reference [2]. The intention in the present paper is to discuss spins which are completely uncoupled in terms of the above definition. Consideration is given, however, to the effects of spin alignment resulting from the presence of a strong magnetic field. The discussion is always carried out in the quasi-elastic limit, though, so that, with the field applied, (a) above must remain valid.

The fully incoherent scattering of unpolarized neutrons from an uncoupled electronic spin in the presence of a magnetic field is given by (see Eq. (A15) in the Appendix)

$$\frac{1}{2}\left(\frac{\gamma e^2}{mc^2}\right)^2 \left[S(S+1)(1+\cos^2\alpha)+\langle (S^2)^2\rangle(1-3\,\cos^2\alpha)-2\langle S^2\rangle^2\sin^2\alpha\right]\left|f(\vec{k})\right|^2, (9)$$

where the z-axis corresponds to the direction of application of the field and  $\alpha$  now represents the angle between  $\vec{k}$  and  $\vec{H}$ . Note that for H = 0,  $\langle S^z \rangle = 0$  and  $\langle (S^z)^2 \rangle = \frac{1}{3}S(S+1)$  so that the above expression reduces to the familiar form

$$\frac{2}{3} \left( \frac{\gamma e^2}{mc^2} \right)^2 \quad S(S+1) \left| f(\vec{k}) \right|^2 \tag{10}$$

#### 3. EXPERIMENTAL METHODS AND ANALYSIS OF RESULTS

#### 3. 1. Experimental principles and apparatus

Clearly the difficulties arising in connection with the accurate measurement of diffusely scattered intensities result from the small differential cross-sections involved in many instances and the intrinsic background due to competing diffuse scattering processes. Where a background of nuclear incoherent scattering is particularly troublesome, it may be desirable to prepare specimens from separated isotopes. In any case a difference counting technique should be used in which a pair of measurements is made, one on a sample containing defects for example, and one on a defect-free specimen. The intensity of interest may then, in principle, be found by subtraction. Great care must be exercised, however, in order to ensure that all other conditions, apart from the presence of defects, are identical for the two measurements.

The principle just described has in fact been used by MARTIN and HENSON [8] in an examination of the defect scattering from irradiated graphite (similar work on BeO is in progress)<sup>3</sup>. The scattering from the irradiated sample was compared with that from an otherwise similar unirradiated specimen. The test sample was later annealed and again compared with the control specimen as a further check. The experiments were carried out using a liquid hydrogen source in the reactor DIDO at Harwell [13, 14].

<sup>&</sup>lt;sup>3</sup> Measurements of the total scattering from defects have been carried out by ANTAL <u>et al.</u> [9], ANTAL and GOLAND [10], MITCHELL and WEDEPOHL [11] and SABINE et al. [12].

It is apparent that, where scattering from defects in the electronic magnetic structure are concerned, several possible methods are available in which the difference counting technique may be applied to a single specimen (by varying, for example, the conditions of magnetization). Some of these are described below. However, it is of interest to note that a similar approach may, in principle, also be used in connection with non-magnetic defects, providing nuclear polarization can be effected and long-wavelength polarized neutrons are available (two almost prohibitive requirements). In these circumstances, it can be seen from Eq. (A9) in the Appendix that a reversal of the sign of the neutron polarization will isolate the cross-section proportional to  $b_i^* b_i^! P^2 I^2$ . With a knowledge of the various scattering amplitudes involved, this would allow nuclear displacements to be evaluated.

As mentioned above the defect scattering from electronic magnetic structures may be conveniently studied by difference counting techniques applied to a single sample. Obviously one method consists in the use of a polarized neutron beam in the same way as described above but with a view to isolating the terms of the type given in Eq. (5). Experiments using this principle have been carried out by COLLINS and FORSYTH on alloys of FeCo and FeNi [7].

The difference counting technique may also be applied by varying the conditions of magnetization of a ferromagnetic sample. Assuming that the magnetic moment in the specimen is all collinear, reference may be made to Eq. (3). For  $\vec{\mu}$  parallel to  $\vec{k}$  or perpendicular to  $\vec{k}$  or randomly oriented, as in the demagnetized state of a cubic crystal, the values of  $\sin^2 \alpha$  are 0, 1 and 2/3, respectively. Thus, the difference between two counts corresponding to any pair of these conditions may be used to isolate the scattering of interest.

As pointed out above, care must be taken to ensure that the only scattering intensity which is changed during a difference counting experiment is that which corresponds to the cross-section of interest. Thus, in connection with measurements in which the sign of neutron polarization or the magnetization of the specimen is changed, difficulties can arise because of multiple Bragg scattering involving magnetic interactions or of phenomena like the single transmission effect. These problems may be avoided by the use of single-crystal specimens or long-wavelength neutrons such that no Bragg effects are possible.

A piece of apparatus based on the latter principle has been developed at Harwell [4]. A diagram showing the main components is given in Fig. 1. The incident neutron beam passes through a filter consisting of polycrystalline beryllium and large single crystals of bismuth cooled in liquid nitrogen. Those neutrons whose wavelengths exceed the Bragg cut-off in Be are transmitted and pass on through a simple chopper spinning with axis parallel to the beam. Neutrons scattered in the specimen are recorded in a counter bank after traversing a flight path of approximately 1 m. The counters are gated in synchronism with the chopper with a delay corresponding to the time-of-flight of neutrons of about  $5-\text{\AA}$  wavelength. The gatewidth and chopper open time define a wavelength resolution of about 25% (full width at halfheight). The apparatus has been used to examine the impurity scattering from dilute alloys of Ni [4], of Fe [15] and of Pd [16] using a difference counting technique in which the direction of magnetization of a specimen is varied.


Schematic diagram of the apparatus for measuring magnetic defect scattering with long-wavelength neutrons

So far measurements of magnetic defect scattering have been confined to ferromagnetic metals. Similar experiments on non-metals containing magnetic defects are, of course, possible. If the difference counting technique in which the direction of magnetization of a sample is changed were used, it would be necessary to work on a ferromagnetic or ferrimagnetic salt or on an antiferromagnetic crystal with low anisotropy such that the spins could be forced away from the easy directions into a plane normal to an applied magnetic field of laboratory strength.

The second type of measurement of interest in solid state physics, mentioned in section 1, is that of the diffuse scattering associated with uncoupled electronic spins. The data concerned are directly related to the form factor  $f(\kappa)$  for the unpaired electrons in the scattering centres. As already pointed out, the evaluation of  $f(\kappa)$  at small  $\kappa$  for non-metals is of considerable interest because of the bearing it has on the degree of transfer of spin from the magnetic ions onto the surrounding ligands and the implications this has with regard to the theory of covalency. Measurements of the diffuse scattering from uncoupled spins can be carried out by a difference counting technique in which intensity determinations are made with and without a magnetic field applied to the sample. Thus, if the field were applied along the direction of  $\vec{\kappa}$ , the difference count would be proportional to (see Eqs. (9) and (10))

$$\left(\frac{\gamma e^2}{mc^2}\right)^2 \left[\langle (S^z)^2 \rangle - \frac{1}{3} S(S+1)\right].$$
(11)

The application of the field along the direction of  $\vec{k}$  ensures that there is no scattering by single Bragg processes (this is proportional to  $\sin^2 \alpha$ ). Such scattering would almost certainly be a troublesome contaminant in the present type of measurement as a large number of small-angle peaks are to be expected for any lattice of a sufficiently large spacing to contain uncoupled spins at low temperatures.

#### 3.2. The analysis of defect scattering data

Two general features of defect scattering are (a) that the scattering in the forward direction is dependent only on the square of the total change in scattering amplitude associated with each defect, and independent of the spatial distribution of the defect, and (b) that the scattering for values of  $\kappa \gg 1/a$ , where a is a lattice parameter, usually arises largely from the neighbourhood of the site at the centre of the defect. The first of these points In the case of magnetic defects in a can be seen by inspection of Eq. (1). ferromagnet the scattering in the forward direction is proportional to  $(d\overline{\mu}/dc)^2$ , where  $d\overline{\mu}/dc$  is the change of saturation magnetization per defect. For a continuous and slowly varying distribution of scattering amplitude density, the second statement follows from the fact that, if  $\kappa \gg 1/a$ , then  $e^{i\kappa r}$  fluctuates rapidly in sign for  $r \ge a$ , and almost no net contribution to the scattering results from this range of r. In a more realistic situation where the scattering amplitude is concentrated into small regions centred on basis lattice sites, the point (b) can best be seen by expansion of Eq. (4). Thus, if  $\delta d_{\vec{m}}$  represents the disturbance in scattering amplitude associated with lattice site  $\vec{m}$ , we may write the defect scattering as being proportional to

 $\sum_{\vec{m}} |\delta d_{\vec{m}}|^2 + \sum_{\vec{m},\vec{n}'} \delta d_{\vec{m}}^* \delta d_{\vec{m}} e^{i\vec{\kappa}\cdot(\vec{m}-\vec{m}')}.$ 

The value of the second sum is oscillatory in nature, tending to zero for large values of  $\kappa$ , so that in this range only the scattering corresponding to the first sum is significant. As  $\delta d$  for the site at the centre of a defect is usually considerably greater than the other scattering amplitude disturbances, the statement (b) follows.

In principle, provided an assumption can be made about the phase of the scattering, the entire spatial distribution of a defect may be found by Fourier inversion of scattering data obtained with a single crystal. However, no one has as yet attempted such an ambitious experiment. In fact two approaches to the analysis of defect scattering data have so far been employed. The first of these consists in the testing of various models for a defect by comparison of a calculated scattering pattern with the experimental data [4, 8]. This method is really only satisfactory if, besides the neutron observations, there are other results which provide some guidance in connection with the construction of suitable models for testing.

A second approach to the problem of data analysis is based on an approximation in which it is assumed that the defect has spherical symmetry. This method has been used in connection with scattering from polycrystalline samples of cubic materials (see [15] and [16]) and under these conditions the underlying approximation is probably quite reasonable except possibly in the region of the first co-ordination shell of neighbours. On the basis of an assumption of spherical symmetry the scattering can, of course, be analysed by standard one-dimensional Fourier methods (see, for example, [17]). Thus, we may write

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$$\frac{\mathbf{U}(\mathbf{r})}{\mathbf{r}} = \frac{2}{\pi} \int_{0}^{\infty} d\kappa \ \mathbf{A}(\kappa) \kappa \ \sin(\kappa \mathbf{r}), \qquad (12)$$

where U(r) is the amount of defect scattering amplitude per unit of the radial distance r and  $A(\kappa)$  is the square root of the scattered intensity corresponding to the scattering vector  $\kappa$ . (As implied above, there is, of course, a sign ambiguity associated with  $A(\kappa)$  but this can usually be resolved by the physics of the problem.)

In practice, to reduce the magnitude of spurious diffraction ring effects (Gibb's oscillations) in the transform, it is advisable to transform not  $A(\kappa)$ but  $[A(\kappa) - \delta d_0]$ , where  $\delta d_0$  represents the scattering amplitude disturbance on the central site in the defect. This is analogous to the process of Fourier difference synthesis used in crystallographic structure determinations. According to the discussion at the beginning of this section, the value of  $\delta d_0$ can usually be estimated from the scattering intensity for large  $\kappa$ . This procedure largely eliminates the Gibb's oscillations which would otherwise result from the absence of data in the region where  $\kappa$  exceeds  $\kappa_{max}$ , the largest scattering vector for which observations are available. In those cases where the scattered intensity is varying rapidly at the upper limit of the experimental k-range, Gibb's oscillations will persist, however. These may be suppressed by multiplying [A( $\kappa$ ) -  $\delta d_0$ ], before transformation, by  $G(\kappa) = \sin X/X$ , where  $X = \pi \kappa / \kappa_{max}$ . This corresponds to the use of an artificial temperature factor in crystallographic work. The transformed data now represent not U(r)/r but the convolution of U(r)/r with the function

$$g(\mathbf{r}) = \frac{2}{\pi} \int_{0}^{\kappa_{\text{max.}}} d\kappa \ G(\kappa) \cos (\kappa \mathbf{r}) . \qquad (13)$$

This is a function with a large central peak whose width is roughly  $\pi/\kappa_{\text{max}}$ . Thus, detail in U(r)/r on a scale smaller than this dimension is not resolved, as is to be expected in an experiment of restricted range in  $\kappa$ .

The errors on the transform 12 above,  $\sigma_T$  , are related to the errors on the experimental results  $\sigma_s$  by

$$\sigma_{\rm T}^2(\mathbf{r}) = \frac{2}{\pi^2} \int_{0}^{\kappa_{\rm max.}} d\kappa \ \kappa^2 \sin^2(\kappa \mathbf{r}) \sigma_{\rm s}^2(\kappa) \qquad (14)$$

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#### APPENDIX

Our purpose here is to examine the various types of term which enter into the cross-section for elastic or quasi-elastic diffuse scattering. The starting point is the cross-section

$$\left|\sum_{\vec{m}} e^{i\vec{k}\cdot\vec{m}} \sum_{\nu} d_{\vec{m}}(\nu)\right|^2$$
(A1)

where the  $\vec{m}$  represent the N points of a basis lattice and the sum  $\nu$  extends over the various types of scattering amplitude involved (we shall in fact consider explicitly four different types below). The amplitude  $d_{\vec{m}}$  is given by an integral over the unit cell at  $\vec{m}$ , i.e.

$$d_{\vec{m}}(\nu) = \int d\vec{r} e^{i\vec{k}\cdot(\vec{r}-\vec{m})} R(\vec{r},\nu), \qquad (A2)$$

where  $R(\vec{r}, \nu)$  represents the scattering amplitude density at  $\vec{r}$  of the process labelled by  $\nu$ . It is of course clear that a defect can give rise to scattering either because of changes in the scattering amplitudes at particular sites or because of phase shifts arising from positional changes due to lattice deformation. It will be noted that both of these effects are included in the definition of Eq. (A2). Thus, for a nuclear defect  $d = b e^{i\vec{k}\cdot\vec{l}}$  where  $\vec{u}$  represents the relaxation of an atom from its basis lattice position.

The Bragg scattering component in Eq. (A1) may be written as

$$\left|\sum_{\nu} \vec{d}(\nu)\right|^{2} \left|\sum_{\vec{n}} e^{i\vec{k}\cdot\vec{m}}\right|^{2}$$
(A3)

leaving a diffuse component of

$$\sum_{\vec{m}} e^{i\vec{k}\cdot\vec{m}} \sum_{\nu} [d_{\vec{m}}(\nu) - \vec{d}(\nu)]|^2, \qquad (A4)$$

where  $\overline{d}(\nu) = N^{-1} \sum_{n \neq 1} d_n(\nu)$ . In addition to the scattering from defects such as interstitials or vacancies or impurity atoms in a sample, we have also to envisage the possibility of disorder scattering arising from the presence of a range of isotopes or from randomly oriented uncoupled spins. We shall assume that distribution of isotopes is uncorrelated with the distribution of defects of the type named above. Let us use  $\langle d \rangle$  to indicate a mean value with respect to isotope distribution together with a thermal average over the orientations of any uncoupled spins in the system. We may now replace Eq. (A4) by two cross-sections. One of these corresponds to the scattering from defects such as interstitials etc. and hence will be referred to as the defect cross-section. This is given by

$$\left|\sum_{\vec{m}} e^{i\vec{k}\cdot\vec{m}} \sum_{\nu} [\langle d_{\vec{m}}(\nu) \rangle - \vec{d}(\nu)] \right|^2.$$
(A5)

The second cross-section, which we shall refer to as the fully incoherent cross-section, is given by

$$\sum_{\vec{n}} \left\{ \left| \sum_{\nu} d_{\vec{n}}(\nu) \right|^2 - \left| \sum_{\nu} \langle d_{\vec{n}}(\nu) \rangle \right|^2 \right\} .$$
 (A6)

Let us return to Eq. (A5). On the assumption that the defects are randomly distributed and non-interacting, we may after some manipulation rewrite the defect cross-section in the form

$$\operatorname{Nc}(1-c)\sum_{\nu,\mu}\left\{\sum_{\vec{m},\vec{m}'}\langle \mathbf{d}_{\vec{m}'}^{*}(\mu)\rangle\langle \mathbf{d}_{\vec{m}}(\nu)\rangle e^{i\vec{k}\cdot(\vec{m}-\vec{m}')} + \sum_{\vec{n},\vec{n}'}\langle \mathbf{d}_{\vec{n}'}^{*}(\mu)\rangle\langle \mathbf{d}_{\vec{n}}(\nu)\rangle e^{i\vec{k}\cdot(\vec{n}-\vec{n}')} - \sum_{\vec{n},\vec{n}}[\langle \mathbf{d}_{\vec{n}}^{*}(\mu)\rangle\langle \mathbf{d}_{\vec{n}}(\nu)\rangle e^{i\vec{k}\cdot(\vec{m}-\vec{n})} + \langle \mathbf{d}_{\vec{m}}^{*}(\mu)\rangle\langle \mathbf{d}_{\vec{n}}(\nu)\rangle e^{i\vec{k}\cdot(\vec{m}-\vec{n})}]\right\}$$
(A7)

where c is the fractional concentration of defects. The sums over  $\vec{m}, \vec{n'}$  and  $\vec{n}, \vec{n'}$  correspond now to sums over the basis lattice points in an unperturbed crystal and a specimen containing a single defect, respectively. Thus in many cases the sums can be limited to the immediate neighbourhood of this defect.

We shall examine the above cross-sections with regard to four particular types of scattering amplitude. These are as follows: (1) A spinindependent nuclear scattering amplitude b (the usual coherent scattering length). (2) A spin-dependent nuclear scattering amplitude b' such that the total scattering for a particular nucleus of spin I is given by (b + 2b' $\vec{S}^{n} \cdot \vec{I}$ ), where  $\mathbf{\vec{S}}^n$  is the spin of the neutron. The possibility that the nuclear spin may be partially polarized by a magnetic field applied in the z-direction. so that  $\langle I^z \rangle \neq 0$ , is taken into account in our discussions. (3) An amplitude arising from an electronic magnetic moment  $\vec{\mu}$  rigidly aligned in a crystal lattice by exchange or anisotropy forces. Thus, we have  $d \propto f(\vec{\kappa}) \vec{S}^n, \vec{\mu}^n$ , where the symbol  $\perp$  indicates that the vector concerned has been projected into the plane normal to  $\vec{k}$  and  $f(\vec{k})$  is an appropriate form factor (see Eq. (7)). (4) Finally, an amplitude corresponding to an uncoupled electronic spin  $\overline{S}$ which may be partially polarized in the z-direction by an applied external magnetic field. In this case we have that  $d \propto f(\vec{\kappa}) \vec{S}^n$ .

The above four types of scattering amplitude give rise to ten different forms of term  $\langle d t \rangle \langle d \rightarrow \rangle$  in the defect scattering cross-section. We shall detail these below and also the fully incoherent cross-sections arising from nuclear and electronic spins. As pointed out above a defect can give rise to scattering either because of changes in the scattering amplitudes at particular sites or because of phase shifts arising from positional changes due to lattice deformation. In writing down the form of the terms in  $\langle d_{j}^{*} \rangle \langle d_{l}^{*} \rangle$  below we shall, however, omit any differences in phase that might be present. Of the ten types of term mentioned above, three are purely nuclear products, i.e. we have

$$\langle \mathbf{b}_{i}^{*} \rangle \langle \mathbf{b}_{i} \rangle$$
 (A8)

$$\langle b_{j}^{*} \rangle P^{z} \langle b_{i}^{t} | l_{i}^{z} \rangle + \text{ complex conjugate}$$
 (A9)

and

$$4(\vec{S}^{n}, \langle \mathbf{b}_{j}^{!} \ast \vec{\Gamma}_{j}^{} \rangle) (\vec{S}^{n}, \langle \mathbf{b}_{j}^{!}, \vec{\Gamma}_{i}^{} \rangle)$$

$$= \langle \mathbf{b}_{j}^{!} \ast \vec{\Gamma}_{j}^{} \rangle \cdot \langle \mathbf{b}_{j}^{!}, \vec{\Gamma}_{i}^{} \rangle + i \vec{P} \cdot (\langle \mathbf{b}_{j}^{!} \ast \vec{\Gamma}_{j}^{} \rangle \times \langle \mathbf{b}_{j}^{!}, \vec{\Gamma}_{i}^{} \rangle)$$

$$= \langle \mathbf{b}_{j}^{!} \ast \vec{\Gamma}_{j}^{} \rangle \langle \mathbf{b}_{i}^{!}, \vec{\Gamma}_{i}^{} \rangle . \qquad (A10)$$

The vector  $\vec{P}$  gives the direction and magnitude of the neutron polarization (1 > P > 0).

The fully incoherent nuclear spin scattering cross-section per spin is given by

$$|\mathbf{b}|^{2} [\langle \vec{\mathbf{I}} \ \vec{\mathbf{I}} \rangle + i \vec{\mathbf{P}} \langle \vec{\mathbf{I}} \times \vec{\mathbf{I}} \rangle - \langle \mathbf{I}^{z} \rangle^{2}] = |\mathbf{b}|^{2} [\mathbf{I}(\mathbf{I}+1) - \mathbf{P}^{z} \langle \mathbf{I}^{z} \rangle - \langle \mathbf{I}^{z} \rangle^{2}].$$
(A11)

Thus, even for 100% polarization of the nuclei, incoherent scattering persists in the quasi-elastic limit unless  $P^z = 1$ . If more than one isotope is present, we must add to the incoherent cross-section a cross term of the form

$$P^{z}(\langle b*b' | I^{z} \rangle - \langle b* \rangle \langle b' | I^{z} \rangle) + complex conjugate.$$

The derivation of the expressions in Eqs.(A10) and (A11) calls for some discussion. First it may be noted that use has been made of the relationship

$$(\vec{\sigma}, \vec{a}) \ (\vec{\sigma}, \vec{b}) = \vec{a} \cdot \vec{b} + i\vec{\sigma} \cdot (\vec{a} \times \vec{b}),$$

where  $\vec{a}$  and  $\vec{b}$  are any pair of operators and  $\vec{\sigma}$  is the Pauli spin operator [18]. This is also employed in several of the derivations carried out below. A second point concerns the term in  $P^{z}\langle I^{z}\rangle$  in Eq. (A11). This term arises in connection with the fully incoherent scattering because in this case the two operators in the bracket of the polarization-dependent part of the cross-section do not commute. A similar effect appears in the cross-section for uncoupled electronic spins. When the case of scattering from rigidly aligned magnetic moments is considered, however, there is no question of non-commutation. This difference results from the fact that for the uncoupled spins one is working in the quasi-elastic approximation and calculating in this limit the total cross-section. This depends on a pair of identical operators with the same argument in time, say  $\vec{S}(t)$  and  $\vec{S}(t)$ . For the rigidly aligned moments, on the other hand, the calculation is of the truly elastic

scattering which depends on the non-identical operators  $\vec{\mu}(0)$  and  $\vec{\mu}(\infty)$ . Hence, we have commutation in the latter case.

In addition to the three nuclear cross-section terms given above, we may make the following purely electronically magnetic substitutions for  $\langle d_{\vec{k}} \rangle \langle d_{\vec{k}} \rangle$  in Eq. (A7): First a term depending on rigidly aligned magnetic moments  $\vec{\mu}$  alone. This is given by

$$4 \left(\frac{\gamma e^2}{2 m c^2}\right)^2 \underline{f}_{\vec{k}}^*(\vec{k}) \underline{f}_{\vec{i}}(\vec{k}) (\vec{S}^{\text{fh}}, \vec{\mu}_{\vec{j}}^{\perp}) (\vec{S}^{\text{fh}}, \vec{\mu}_{\vec{j}}^{\perp}) = \left(\frac{\gamma e^2}{2 m c^2}\right)^2 \underline{f}_{\vec{j}}^*(\vec{k}) \underline{f}_{\vec{i}}(\vec{k}) [\vec{\mu}_{\vec{j}}^{\perp}, \vec{\mu}_{\vec{i}}^{\perp} + i\vec{P}, (\vec{\mu}_{\vec{j}}^{\perp} \times \vec{\mu}_{\vec{i}}^{\perp})]$$
(A12)

where, it will be recalled,  $\vec{\mu}^{\perp} = \hat{\vec{\kappa}} \times (\vec{\mu} \times \hat{\vec{\kappa}})$  is the projection of  $\vec{\mu}$  in the plane normal to  $\vec{\kappa}$ . Next we may write down the form of the cross term between  $\vec{\mu}$  and an uncoupled electronic spin  $\vec{S}$  which is partially polarized in the zdirection. This is

$$2\left(\frac{\gamma e^{2}}{mc^{2}}\right)^{2} f_{j}^{*}(\vec{\kappa}) f_{j}(\vec{\kappa})(\vec{S}^{n}, \vec{\mu}_{j}^{\perp})(\vec{S}^{n}, \langle \vec{S}_{i}^{\perp} \rangle) + \text{ complex conjugate}$$

$$= \frac{1}{2} \left(\frac{\gamma e^{2}}{mc^{2}}\right)^{2} f_{j}^{*}(\vec{\kappa}) f_{j}(\vec{\kappa})[\vec{\mu}_{j}^{\perp}, \hat{H}^{\perp}\langle \vec{S}_{i}^{z} \rangle + i\vec{P}, (\vec{\mu}_{j}^{\perp} \times \hat{H}^{\perp}\langle \vec{S}_{i}^{z} \rangle)]$$

$$+ \text{ complex conjugate}. \qquad (A13)$$

Also we have the term corresponding to a pair of uncoupled electronic spins

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$$4 \left(\frac{\gamma e^2}{mc^2}\right)^2 f_{\vec{x}}^*(\vec{\kappa}) f_{\vec{t}}(\vec{\kappa}) (\vec{S}^n \langle \vec{S}_{\vec{t}}^{\perp} \rangle) (\vec{S}^n \langle \vec{S}_{\vec{t}}^{\perp} \rangle)$$

$$= \left(\frac{\gamma e^2}{mc^2}\right)^2 f_{\vec{t}}^*(\vec{\kappa}) f_{\vec{t}}(\vec{\kappa}) [\langle \vec{S}_{\vec{t}}^{\perp} \rangle, \langle \vec{S}_{\vec{t}}^{\perp} \rangle + i\vec{P} \cdot \langle \vec{S}_{\vec{t}}^{\perp} \rangle \times \langle \vec{S}_{\vec{t}}^{\perp} \rangle)]$$

$$= \left(\frac{\gamma e^2}{mc^2}\right)^2 f_{\vec{t}}^*(\vec{\kappa}) f_{\vec{t}}(\vec{\kappa}) \sin^2 \alpha \langle \vec{S}_{\vec{t}}^z \rangle \langle \vec{S}_{\vec{t}}^z \rangle$$
(A14)

where  $\alpha$  now denotes the angle between  $\vec{\kappa}$  and  $\vec{H}$  the applied magnetic field (i. e. the z-direction).

The fully incoherent paramagnetic spin scattering is given by

$$\frac{1}{2} \left(\frac{\gamma e^2}{mc^2}\right)^2 |\mathbf{f}(\vec{\kappa})|^2 [(1 + \cos^2 \alpha) \mathrm{S}(\mathrm{S} + 1) + (1 - 3 \cos^2 \alpha) \langle (\mathrm{S}^z)^2 \rangle - 2(\vec{\mathbf{P}}, \vec{\kappa}) \cos \alpha \langle \mathrm{S}^z \rangle - 2 \sin^2 \alpha \langle \mathrm{S}^z \rangle^2].$$
(A15)

We note the appearance of a polarization-dependent term just as was found in the case of nuclear spins. In evaluating the above cross-sections use has been made of the following thermal average

$$\langle (S^{\gamma})^{2} \rangle = \langle (S^{z})^{2} \rangle \delta_{\gamma z} + \frac{1}{2} [S(S+1) - \langle (S^{z})^{2} \rangle] (\delta_{\gamma n} + \delta_{\gamma y}).$$

The remaining four terms in our series of ten are all cross terms between nuclear and electronic scattering amplitudes. Thus, we have cross terms with b, the coherent nuclear amplitude, of

$$\frac{\gamma e^2}{mc^2} f_{\vec{i}}(\vec{k}) \langle b_{\vec{j}}^* \rangle (\vec{S}^n, \vec{\mu}_{\vec{i}}^\perp) + \text{ complex conjugate}$$
$$= \frac{\gamma e^2}{2mc^2} f_{\vec{i}}(\vec{k}) \langle b_{\vec{j}}^* \rangle \vec{P}, \vec{\mu}_{\vec{i}}^\perp + \text{ complex conjugate}$$
(A16)

and

$$\frac{2 \gamma e^2}{mc^2} f_{\overrightarrow{i}}(\vec{k}) \langle \underline{b}_{\overrightarrow{j}}^* \rangle \langle \mathbf{\hat{S}}^n, \langle \mathbf{\hat{S}}_{\overrightarrow{i}}^\perp \rangle + \text{ complex conjugate}$$
$$= \frac{\gamma e^2}{mc^2} f_{\overrightarrow{i}}(\vec{k}) \langle \underline{b}_{\overrightarrow{j}}^* \rangle P^z \langle \mathbf{S}_{\overrightarrow{i}}^z \rangle + \text{ complex conjugate}.$$
(A17)

Finally we have the cross terms with b', the spin-dependent nuclear scattering amplitude. These are:

$$\frac{2\gamma e^2}{mc^2} f_{\vec{i}}(\vec{k})(\vec{S}^n, \langle b_{\vec{j}}^{1*}, \vec{l}_{\vec{j}} \rangle)(\vec{S}^n, \vec{\mu}_{\vec{i}}^{\perp}) + \text{ complex conjugate}$$

$$= \frac{\gamma e^2}{2mc^2} f_{\vec{i}}(\vec{k}) [\langle b_{\vec{j}}^{1*}, \vec{l}_{\vec{j}}^2 \rangle \hat{\vec{H}}, \vec{\mu}_{\vec{i}}^{\perp} + i\vec{P}, (\langle b_{\vec{j}}^{1*}, \vec{l}_{\vec{j}}^2 \rangle \hat{\vec{H}} \times \vec{\mu}_{\vec{i}}^{\perp})] + \text{ complex conjugate}$$
(A18)

and

$$\frac{4\gamma e^{2}}{mc^{2}} \mathbf{f}_{\vec{i}}(\vec{\kappa})(\vec{S}^{n} \langle \mathbf{b}_{j}^{1} \ast \vec{L}_{j} \rangle)(\vec{S}^{n} \langle \vec{S}_{\vec{i}}^{1} \rangle) + \text{ complex conjugate}$$

$$= \frac{\gamma e^{2}}{mc^{2}} \mathbf{f}_{\vec{i}}(\vec{\kappa})[\langle \mathbf{b}_{j}^{1} \ast \vec{L}_{j} \rangle, \langle \vec{S}_{\vec{i}}^{1} \rangle + i\vec{P}.(\langle \mathbf{b}_{j}^{1} \ast \vec{L}_{j} \rangle \times \langle \vec{S}_{\vec{i}}^{1} \rangle)] + \text{ complex conjugate}$$

$$= \frac{\gamma e^{2}}{mc^{2}} \mathbf{f}_{\vec{i}}(\vec{\kappa}) \langle \mathbf{b}_{j}^{1} \ast \vec{L}_{j}^{2} \rangle \langle \vec{S}_{\vec{i}}^{2} \rangle [\sin^{2}\alpha + i\vec{P}.(\vec{H} \times \vec{H}^{1})] + \text{ complex conjugate}.$$
(A19)

This completes the set of ten terms, namely Eqs.(A8), (A9), (A10), (A12), (A13), (A14), (A16), (A17), (A18) and (A19).

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#### DISCUSSION

J.J. RUSH: To what wavelength does your intensity allow you to go with this type of experiment?

G.G. LOW: In measurements made by Martin at Harwell, which I mentioned in the oral presentation, the results were obtained with 7.5 Å neutrons. The results for the alloys were obtained at around 5 Å. I do not think we can go much beyond that with our present set-up, which does not include a cold source. Martin did have a cold source.

N.S. SATYA MURTHY: Have you made any attempt to correlate the square of the form factor in nickel-vanadium and nickel-chromium alloys with changes in the d-electron density distribution in the alloys, i.e. on the nickel sites, when impurities are introduced?

G.G. LOW: We have carried out the Fourier transforms which I mentioned in the oral presentation and which indicate the distribution of the disturbance in the magnetic moment around these sites. This is in accordance with certain theoretical suggestions made by Friedel some years ago, before we carried out the experiments. This is why we chose the nickel system to start with. As I have said, there is a correlation between the neutron scattering we observed and the behaviour of the Slater-Pauling curve.

N.S. SATYA MURTHY: Do you think that, apart from being used merely to demonstrate the fact that the addition of vanadium or chromium disturbs the magnetic moment on the nickel sites out to large distances, diffuse scattering measurements could also be used to get detailed information concerning the nature or cause of the disturbances?

G.G. LOW: No, I do not. I think it is now a matter for the theoreticians. In any case, Friedel's discussion in terms of bound states more or less covers this point, at least from the qualitative point of view. R.J. ELLIOTT: I might point out that Hubbard and his co-workers at Harwell are trying to make more detailed calculations of the shape of the density, using Green's function methods, but it amounts to the same thing as Friedel's approach, except that the procedure is more detailed. I believe they found that if you only change the potential on the impurity site itself, you have some difficulty in explaining the extension, and so they are now trying to extend this by changing the potential and the coupling to neighbouring atoms as well.

G. VENKATARAMAN: I notice that by your Fourier-transform method you are able to get the distribution of the disturbance from beyond a certain distance. In other words, you don't get any points near the origin and are able to get values only beyond a certain distance. But do you think that you could get a point near the origin, say, by using Mössbauer techniques, which also measure the unpaired distribution? In this way you could, to some extent, complete the whole curve.

G.G.LOW: If the impurity had a nucleus which enabled you to do so, you could certainly use the Mössbauer effect, but then you would have the problem, as Dr. Elliott mentioned, of knowing what the hyperfine interaction is, in order to get the moment. So the technique is not unambiguous, you still have one further step to take.

N.S. SATYA MURTHY: Since the kind of experiment described by Dr. Low is not dissimilar to the elastic diffuse scattering measurements made by Venkataraman and others on the ammonium halides, I would like to ask the crystal spectrometer people whether similar experiments on elastic diffuse scattering from magnetic alloys could be made by crystal spectrometry techniques. Would anything be gained by this? With a chopper and time-of-flight methods, one usually gets into a lot of complicated electronics. I was therefore wondering if crystal spectrometer techniques could be used.

G. CAGLIOTI: Considering what Dr. Low has to say in his paper regarding the use of measurements of the diffuse magnetic intensity of elastically diffracted neutrons to study covalency parameters in perfect paramagnetic single crystals, it seems to me that the three-axis spectrometer, using an elastic arrangement, would be a very valuable tool because it could help discriminate against dynamical contributions to the scattering.

G.G. LOW: I think there is a difficulty in using crystal instruments to carry out measurements at long wavelengths because, in order to get the intensity you want, you have to relax the collimation. This is of course feasible but normally you can't relax the mosaic spread in the crystals sufficiently to match the relaxation in collimation and hence there is a proportionate loss in intensity. We should like to use a crystal monochromator because it would even give us the possibility of using polarized neutrons at long wavelengths. Unfortunately, however, a loss of intensity is involved. We have not yet found a practical way of getting around this problem.

H. PALEVSKY: Could Dr. Elliott tell us whether these experiments on dilute alloys could be done with energy analysis, that is, if one could pick out the inelastic part? How much more would we learn with regard to the theoretical discussion that he gave?

R.J. ELLIOTT: I do not think there is any theory at present that could pretend to say what you would get. No real theory exists even in respect of

the magnetic excitations in transition metals, so it is too much to expect a theory covering alloys. Nor is there any very good theory dealing with liquids, even though lots of interesting experiments are carried out on the subject. I think the approach you suggest would be very interesting, but I wouldn't like to hazard a guess as to what one might see.

## NEUTRON SCATTERING BY PARAMAGNETICS

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#### Abstract — Résumé — Аннотация — Resumen

NEUTRON SCATTERING BY PARAMAGNETICS. The scattering of cold neutrons by paramagnetic MnO has been studied using a rotating crystal spectrometer. Energy distributions have been obtained at several scattering angles and temperatures. Some measurements have also been made at thermal energies. The cold neutron data indicate that there is considerable inelasticity in the scattering, the details of which are determined by the nature of the time-dependent spin-correlation functions. First and second neighbour exchange integrals have been evaluated from the second moments of the energy distribution at large scattering angles. A damped magnon model has been suggested to explain the details of the observed energy spectra. Results on KMnF<sub>3</sub> are also presented.

DIFUSION DES NEUTRONS PAR DES MATIÈRES PARAMAGNÉTIQUES. Les auteurs ont étudié la diffusion des neutrons froids par MnO paramagnétique, à l'aide d'un spectromètre à cristal tournant. Ils ont déterminé les distributions d'énergie pour plusieurs angles et températures de diffusion. Ils ont également fait des mesures avec des neutrons thermiques. Les données relatives aux neutrons froids indiquent qu'il y a une forte inélasticité dans la diffusion, dont les caractéristiques sont déterminées par la nature des fonctions de corrélation du spin qui dépendent du temps. Les auteurs ont évalué les intégrales d'échange des premier et deuxième voisins d'après les moments du deuxième ordre de la distribution d'énergie pour de grands angles de diffusion. Ils proposent un modèle de magnon amorti pour expliquer les détails des spectres d'énergie observés. Ils donnent également les résultats obtenus avec KMnF<sub>3</sub>.

РАССЕЯНИЕ НЕЙТРОНОВ НА ПАРАМАГНИТНЫХ ВЕЩЕСТВАХ. Рассеяние холодных нейтронов на парамагнитном MnO было изучено с помощью вращающегося кристаллического спектрометра. Были получены распределения энергии при целом ряде углов рассеяния и температур. Некоторые измерения были также проведены при тепловых энергиях. Данные по холодным нейтронам показывают, что в рассеянии имеется значительная неупругость, подробности которой определяются характером функций спиновой корреляции, зависящих от времени. Первый и второй члены обменных интегралов были вычислены по вторым моментам распределения энергии при больших углах рассеяния. Для объяснения подробностей наблюдаемых энергетических спектров предложена модель матнона с уменьшенной амплитудой колебания. Будут также представлены результаты по KMnF<sub>3</sub>.

DISPERSIÓN NEUTRÓNICA EN SUSTANCIAS PARAMAGNÉTICAS. Los autores han estudiado la dispersión de neutrones fríos en el MnO paramagnético, con ayuda de un espectrómetro de cristal giratorio. Han obtenido las distribuciones energéticas para diversos ángulos de dispersión y temperaturas. También realizaron algunas mediciones a energías térmicas. Los datos correspondientes a los neutrones fríos indican que existe una considerable inelasticidad en la dispersión, cuyas características dependen de la naturaleza de las funciones de correlación del spin con respecto al tiempo. Partiendo de los momentos secundarios de la distribución de la energía para amplios ángulos de dispersión, se han calculado las integrales de intercambio de los átomos de primero y de segundo orden de proximidad. Se ha propuesto un modelo de magnón amortiguado para explicar la estructura fina de los espectros energéticos observados. También se exponen los resultados obtenidos con el KMnF<sub>8</sub>.

#### I. INTRODUCTION

It has long been recognized that studies on the inelastic scattering of slow neutrons from paramagnetics can lead to a knowledge of spin fluctuations in these substances. Experimental work in this direction has, however, been meagre. The early investigations [1] motivated by the pioneering calculations of VAN VLECK [2], were carried out using cyclotron neutron sources and did not prove very informative. In 1957, using crystal spectrometer techniques, BROCKHOUSE [3] demonstrated for the first time that inelastic scattering does occur provided the exchange coupling is large enough. Subsequently, IYENGAR and BROCKHOUSE [4] studied the scattering from MnO at several temperatures (above the Néel temperature) and showed the effects of short range magnetic ordering. More recently CRIBIER and JACROT [5] have carried out similar investigation of  $MnF_2$  using cold neutrons. The present experiments extend the work of Iyengar and Brockhouse to the cold neutron region.

Paramagnetic MnO is an interesting substance for experimental investigation though it is complicated from the standpoint of theoretical interpretation. Neutron diffraction experiments [6,7] have shown that there is considerable short range magnetic ordering even at room temperature which is well above the Néel temperature of 122°K. It is interesting to see if there is any resemblance between the spectrum of magnetic excitations in the ordered state and that in the partially ordered state just as there is a similarity between the vibrational spectrum of solids and liquids. The cold neutron scattering technique by virtue of its high resolution offers a means of examining this point.

#### II. EXPERIMENT

A rotating crystal spectrometer at the Canada-India Reactor at Trombay has been used for most of the measurements. The spectrometer gives bursts of neutrons of wavelength 4.1 Å produced by reflection from the (111) planes of a spinning aluminium crystal and the scattered neutron energy is measured by the time-of-flight technique. The neutrons scattered by the sample are detected by a set of six  $B^{10}F_2$  counters. The resolution of the spectrometer is 3.6% in wavelength or 0.36 meV at the incident energy.

The time-of-flight distribution (after five-point smoothing) obtained at six scattering angles  $\phi$  which correspond to values of  $Q_0$  ( $Q_0=(4\pi/\lambda)\sin(\phi/2)$  equal to 0.51, 0.82, 1.04, 1.21, 1.46 and 1.76 Å<sup>-1</sup> are shown in Fig.1. These distributions have been converted to energy spectra with corrections for the instrumental factors, for the factor k'/k<sub>0</sub> (where k<sub>0</sub> and k' refer to the incident and scattered neutron wave vectors, respectively) and for the variation of the Mn<sup>++</sup> form factor with the wave vector transfer Q. These are shown in Fig.2. The inset shows the diffraction pattern over the range of the peak arising from the short-range ordering. In each of the spectra, except the one for  $Q_0 = 1.76$  Å<sup>-1</sup>, a distinct inelastic peak is seen whose position shifts with  $Q_0$ . It has a minimum value for  $Q_0 = 1.21$  Å<sup>-1</sup>, the diffraction maximum. The energy transfers  $\epsilon$  at the peaks of the distributions are given in Table I.



Fig.1

Time-of-flight distributions of 4. 1-Å neutrons scattered by MnO at room temperature

Figure 3 shows energy distributions taken at  $Q_0 = 1.04$  Å<sup>-1</sup> at 220, 300 and 480°K. It is seen that the peak of the distribution shifts towards the elastic at the low temperature and away from the elastic at 480°K, the maxima occuring at  $\epsilon = 2.4$ , 2.9 and 3.5 meV, respectively. In all these energy distributions no corrections have been made for the phonon contribution to the scattering but estimates made on a Debye model taking a Debye temperature of 500°K (estimated from Lindemann's relation) indicate that it is unimportant at these small energy transfers.

Some measurements have also been made at  $Q_0 = 1.36$  Å<sup>-1</sup> using a tripleaxis spectrometer with incident neutrons of wavelength 1.74 Å. The observed spectrum is shown in Fig.4, the broken line indicating the resolution which is 5.2 meV. The spectrum shows merely a broadening about the elastic position instead of a separate inelastic peak. This is due to the poorer resolution of the measurement. IYENGAR and BROCKHOUSE [4] have made similar measurements at several scattering angles and temperatures. They find that this broadening is at a minimum at  $Q_0 = 1.29$  Å<sup>-1</sup>.

#### III. DISCUSSION

As remarked earlier, magnetic inelastic scattering arises due to spin fluctuations. These spin fluctuations are most conveniently expressed



Fig.2

Energy spectra of neutrons scattered by MnO at room temperature. The spectra was obtained after applying corrections to the distributions of Fig. 1 ( $E_0$  = 4.87 meV). Inset shows positions on the diffraction patterns at which the distributions have been obtained.

through the time-dependent spin correlation function  $\langle S^{\alpha}_{0}(0) S^{\beta}_{R}(t) \rangle_{T}$ , where  $S^{\alpha}_{0}(0)$  and  $S^{\beta}_{R}(t)$  denote respectively the  $\alpha$ - and  $\beta$ -component of the spin operators at the lattice sites 0 and R. Following the works of VAN HOVE [8], de GENNES [9] and SÁENZ [10] the differential cross-section for slow neutron scattering can now be expressed in terms of the spin correlation function as

#### TABLE I

| MEAN ENERGY TRANSFER |                              |  |  |  |  |  |  |  |
|----------------------|------------------------------|--|--|--|--|--|--|--|
| AS A                 | FUNCTION OF SCATTERING ANGLE |  |  |  |  |  |  |  |

| ø(deg)                            | 19.25 | 31.0 | 39.5 | 46.5 | 57.0 | 70.0 |
|-----------------------------------|-------|------|------|------|------|------|
| Q <sub>0</sub> (Å <sup>-1</sup> ) | 0.51  | 0.82 | 1.04 | 1.21 | 1.46 | 1.76 |
| €(meV)                            | 5.6   | 3.8  | 2.9  | 2.4  | 2.4  | -    |



Temperature dependence of the energy distribution in MnO at  $Q_0 = 1.04 \text{ Å}^{-1}$ 

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\epsilon\,\mathrm{d}\Omega} = \frac{2}{3} \left(\frac{\mathrm{e}^{2}\gamma}{\mathrm{mc}^{2}}\right)^{2} \frac{1}{\hbar} |\mathbf{F}(\vec{Q})|^{2} \frac{\mathrm{k}'}{\mathrm{k}_{0}} \sum_{\vec{R}} \mathrm{e}^{i\vec{Q}\cdot\vec{R}} \int \mathrm{e}^{-i\epsilon t/\hbar} \mathrm{d}t \langle \vec{S}_{0}(0), \vec{S}_{R}(t) \rangle.$$
(1)

From Eq.(1) it is clear that the spin correlation can, in principle, be deduced by Fourier inversion of the experimental data even as the space correlation function  $G(\vec{r}, t)$  is obtained from liquid scattering experiments. Such a procedure, however, demands data of high precision extending over wide ranges of Q and  $\omega$ . In view of this, attempts to obtain  $\langle \vec{S}_0(0), \vec{S}_R(t) \rangle_T$ by Fourier inversion have not been made so far although in a few cases, the instantaneous correlation function  $\langle \vec{S}_0(0), \vec{S}_R(0) \rangle_T$  has been obtained by an analysis of critical scattering data [11, 12]. With limited experimental data, an understanding of spin fluctuations must of necessity be based on a 'model' approach.

However, we might remark that some information about the spin system can be obtained by just considering the moments of the distribution alone. Moment calculations were first made by VAN VLECK [2] under the assumption that both static and dynamic correlation between different spins could be ignored, i.e.

$$\langle \vec{\mathbf{S}}_{0}(0) \cdot \vec{\mathbf{S}}_{R}(0) \rangle_{\mathrm{T}} = \langle \vec{\mathbf{S}}_{0}(0) \cdot \vec{\mathbf{S}}_{R}(t) \rangle_{\mathrm{T}} = 0, \quad \mathrm{R} \neq 0$$

De GENNES [9] improved on this calculation by admitting the possibility of dynamical correlations. He showed that the second moment of the energy distribution at large momentum transfers (where  $Qb \gtrsim \pi$ , b being the interatomic distance) is given by

$$\langle \epsilon^2 \rangle = \frac{2}{3} \operatorname{S}(\mathrm{S}+1) \sum_i \operatorname{Z}_i (2\mathrm{J}_i)^2,$$
 (2)



Energy distribution taken on triple-axis spectrometer and at room temperature using 1.74 Å at  $Q_0 = 1.36 Å^{-1}$ The broken line shows the resolution (~5.2 meV).

where  $Z_i$  is the number of the i-th neighbour and  $J_i$  is the i-th neighbour exchange integral, S being the spin of the ion.

In spite of the short-range ordering exhibited by MnO, we might expect the de Gennes' formula to be applicable at large values of  $Q_0$  where the effects of spatial ordering are known to be small. Using the value of the moment at  $Q_0 = 1.46$  Å<sup>-1</sup> and the molecular field relation for the paramagnetic Curie temperature ( $\theta_c = 360^{\circ}$ K as given by de Gennes from a fit to the diffraction curve of Iyengar and Brockhouse),  $J_1$  and  $J_2$  have been evaluated as:  $J_1 = -0.33$  meV (3.8°K) and  $J_2 = -0.20$  meV (2.3°K). The errors in these estimates are believed to be about 15%. The agreement with other reported values [13, 14] is considered fair.

To explain the details of the observed spectrum, we consider a model for the spin fluctuations. The most striking feature of the pattern is the occurrence of a distinct inelastic peak somewhat similar to what one would expect in the ordered state. This suggests that the magnetic excitations in the partially ordered state may perhaps be described in terms of highly damped magnons. The damping could arise from magnon-magnon interactions (resulting in frequency blurring) as well as from the lack of longrange order (which introduces momentum blurring). Similar damping mechanisms have been used for phonons by BUTTERWORTH and MARSHALL [15] and by EGELSTAFF [16] in discussing scattering from liquids. We have applied these ideas in deriving an expression for the differential crosssection for the inelastic scattering from exchange-coupled lattices such as MnO. For simplicity only momentum blurring is considered. Following SÁENZ [10], we have for the cross-section for single magnon annihilation in an antiferromagnet (with exchange forces only)

$$\frac{1}{2} \left(\frac{\mathrm{e}^2 \gamma}{\mathrm{mc}^2}\right)^2 \mathrm{SF}^2(\mathrm{Q}) \frac{\mathrm{k}!}{\mathrm{k}_0} \left(1 + \overline{\mathbf{e}} \cdot \vec{\mu}^2\right) \left\langle \mathrm{n}_{\mathsf{q}} \right\rangle \delta\left(\mathbf{\epsilon} - \boldsymbol{\epsilon}_{\mathsf{q}}\right) \sum_{\tau} \left\{ \left[\mathrm{f}_{\vec{\mathsf{q}}} - \mathrm{g}_{\vec{\mathsf{q}}}\right]^2 \delta(\vec{\mathrm{Q}} - \vec{\mathsf{q}} - 2\pi\vec{\tau}) \right\}$$

$$+ \left[ f_{\vec{q}} + g_{\vec{q}} \right]^2 \delta(\vec{Q} - \vec{q} - 2\pi \vec{w} - 2\pi \vec{\tau}) \}$$
(3)

The notation here is the same as that of Sáenz with the difference that a  $\vec{q}, \vec{q}$  and  $2\pi\vec{w}$  replace respectively his  $\vec{q}, \vec{\kappa}$  and  $\vec{w}$ . For the case of the polycrystal we take the average value of  $[1+\vec{e}\cdot\vec{\mu}^2] = 1/3$ , replace the delta functions by their average values using the method of Egelstaff and write for the cross-section

$$\frac{2}{3} \left(\frac{e^2 \gamma}{mc^2}\right)^2 \operatorname{SF}^2(\mathbf{Q}) \frac{k'}{k_0} \langle \bar{\mathbf{n}}_q \rangle \delta(\epsilon - \epsilon_q) \left\{ [\bar{\mathbf{f}}_{\vec{q}} - \bar{\mathbf{g}}_{\vec{q}}]^2 \sum_{\tau} \frac{1}{16\pi^2 \tau \mathbf{Q} \mathbf{q}} + [\bar{\mathbf{f}}_{\vec{q}} + \bar{\mathbf{g}}_{\vec{q}}]^2 \sum_{\chi} \frac{1}{16\pi^2 \chi \mathbf{Q} \mathbf{q}} \right\} 4\pi \mathbf{q}^2, \tag{4}$$

where  $2\pi \vec{X} = 2\pi \vec{w} + 2\pi \vec{\tau}$ .

The bars indicate that the quantities correspond to the average dispersion relation assumed for the magnons. It is reasonable to assume that the predominant contribution to the inelastic cross-section comes from the neighbourhood of a  $\vec{w}$  point (i.e. an antiferromagnetic or super-lattice reflection) and the first term may be neglected in a first-order approximation. We can then write

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\epsilon\mathrm{d}\Omega} = \frac{2}{3} \left(\frac{\mathrm{e}^2\gamma}{\mathrm{m}\,\mathrm{c}^2}\right)^2 \mathrm{SF}^2(\mathrm{Q}) \frac{\mathrm{k}^{\,\prime}}{\mathrm{k}_0} \langle \bar{\mathrm{n}}_{\mathfrak{q}} \rangle \delta(\epsilon - \epsilon_{\mathfrak{q}}) \left\{ [\bar{\mathrm{f}}_{\mathfrak{q}}^{-1} + \overline{\mathrm{g}}_{\mathfrak{q}}^{-1}]^2 \sum_{\tau} \frac{1}{16\pi^2 \chi \mathrm{Q}\mathrm{q}} \right\} 4\pi \mathrm{q}^2 \frac{\mathrm{d}\mathrm{q}}{\mathrm{d}\epsilon} (5)$$

This formula is now modified to the case of a paramagnetic medium with residual short-range ordering, by taking account of (a) the spin disorder and (b) the damping of the magnons in a manner similar to that used by Egelstaff for the case of metals above their melting points. The summation is replaced by an integral which involves a structure factor f(X) representing

the measured angular distribution arising from the short-range order. We then have

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\epsilon\mathrm{d}\Omega} = \frac{2}{3} \left(\frac{\mathrm{e}^2\gamma}{\mathrm{m}\,\mathrm{c}^2}\right)^2 \mathrm{SF}^2(\mathrm{Q}) \frac{\mathrm{k}!}{\mathrm{k}_0} \langle \overline{\mathrm{n}}_q \rangle \delta(\epsilon - \epsilon_q) \left\{ \left[\overline{\mathrm{f}}_q + \overline{\mathrm{g}}_q^2\right]^2 \int \chi f(\chi) \mathrm{d}\chi \right\} \frac{1}{\mathrm{Q}} q \frac{\mathrm{d}q}{\mathrm{d}\epsilon} .$$
(6)

We now introduce momentum blurring of the magnons by replacing q by  $q_0$ -i $\Gamma$ , where  $q_0$  corresponds to the undamped case and  $\Gamma$  is the damping constant. The cross-section is then given by

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\epsilon \mathrm{d}\Omega} = \frac{2}{3} \left(\frac{\mathrm{e}^2 \gamma}{\mathrm{mc}^2}\right)^2 \mathrm{SF}^2(\mathrm{Q}) \frac{\mathrm{k}^{\prime}}{\mathrm{k}_0} \langle \bar{\mathrm{n}}_{\mathrm{q}_0} \rangle \delta(\epsilon - \epsilon_{\mathrm{q}_0}) \left[ \bar{\mathrm{f}}_{\mathrm{q}_0} + \overline{\mathrm{g}}_{\mathrm{q}_0} \right]^2 \frac{1}{\mathrm{Q}} q_0 \frac{\mathrm{d}q_0}{\mathrm{d}\epsilon} \int \frac{\Gamma \chi f(\chi) \mathrm{d}q \mathrm{d}\chi}{\pi [q_0 - q)^2 + \Gamma^2}$$
(7)

No detailed calculations have yet been made on the basis of the proposed model.

#### KMnF<sub>3</sub>

Besides MnO, we have also done some experiments on  $\rm KMnF_3$ , preliminary results of which are described here.  $\rm KMnF_3$  belongs to a large class of compounds having the perovskite-like structure in which the magnetic ions form a simple cubic lattice. It is antiferromagnetic below 88°K.



Semi-logarithmic plot of the scattered neutron intensity against the square of the energy transfer for KMnF<sub>3</sub> at room temperature showing the Gaussian character of the distribution

$$(Q_0 = 0.79 \text{ Å}^{-1})$$

The inset shows the raw time-of-flight spectrum.

Neutron diffraction investigations show that the only important interaction is the super-exchange among first-neighbour Mn ions which are at a distance of 4.186 Å apart, with intervening oxygen ions. Further, at room temperature there is practically no evidence of any short-range ordering as seen in a diffraction pattern.

A time-of-flight distribution has been taken at  $Q_0 = 0.79$  Å<sup>-1</sup>, for which  $Qb > \pi$ . After application of the corrections described earlier, the energy spectrum was found to be a Gaussian centred around the incident energy as shown in Fig.5. The inset shows the measured time-of-flight spectrum. The absence of a distinct inelastic peak such as that observed in MnO reflects the weaker coupling of the spins.

The exchange integral can be calculated from the observed spectrum using Eq.(2). From the slope of the straight line in Fig.5 the standard deviation of the energy transfer is found to be  $\langle \epsilon^2 \rangle^{\frac{1}{2}} = 3.46$  meV, which on substitution yields for the first neighbour exchange integral a value of  $J_1 = -0.292$  meV. This is in good agreement with the values quoted by ANDERSON [17].

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# DISCUSSION

K.P. SINHA: Have you compared your values of  $J_{nn}$  and  $J_{nm}$  with those which Owen obtained by EPR measurements of Mn-doped MgO?

N.S. SATYA MURTHY: The value of  $J_1$ , obtained by Harris and Owen in the case of Mn-doped MgO is 0.63 meV and is much larger than the value given by neutron measurements. Our values are in good agreement with those quoted by Collins from his spin wave measurements.

K. P. SINHA: What specific type of damping mechanism have you taken for magnons? It seems to me that phonon-magnon interaction effects would be quite important.

N.S. SATYA MURTHY: Magnon-magnon interactions may cause considerable damping of the spin waves.

N. KROÓ: I think that even the old measurements of Brockhouse and Iyengar show that, in the case of MnO, coherent scattering effects must be involved. This is much more pronounced in your measurements, where even breaks occur, as in the single-phonon scattering picture of a polycrystal. It seems to me from your  $39.5^{\circ}$  measurement that even the energy-gap at q = 0 for magnons can be seen. I am wondering whether you have tried to derive an average dispersion relation for the quasi-magnons from the breaks you observed and whether, since the slope of the breaks is related to the lifetime of the excitations, you have tried to estimate these lifetimes?

N.S. SATYA MURTHY: All we have done is to make a preliminary suggestion concerning a possible theoretical approach. We have not attempted the sophisticated analysis that you are suggesting.

M.G. ZEMLYANOV: What processes are involved in the scattering of neutrons in a paramagnetic substance - nuclear scattering or magnetic scattering? And how can one distinguish between the influence of each of these processes?

N.S. SATYA MURTHY: For the region of interest in this experiment there is no interference from nuclear scattering. The magnetic scattering that is analysed here is concentrated around a  $\vec{w}$ -point which is purely of magnetic origin.

# NEUTRON INVESTIGATION OF MAGNON SPECTRUM IN HAEMATITE

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#### (Presented by J.A. Janik)

#### Abstract — Résumé — Аннотация — Resumen

NEUTRON INVESTIGATION OF MAGNON SPECTRUM IN HAEMATITE. Measurements were done in Vinča on the RA reactor using a crystal neutron spectrometer. Monochromatic neutrons ( $\lambda$ = 1.314 Å) were scattered on a large single crystal of haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The angular distributions of inelastically scattered neutrons were investigated. For a number of different crystal missetting angles  $\Delta \theta$ , the width  $\Gamma$  of the scattered neutron beam (so-called scattering cone) was measured. This scattering cone was ascribed to the magnon scattering surface surrounding the (111) reciprocal lattice point. For several magnon velocities the  $\Gamma$  versus missetting angle dependence was calculated and compared with the experimental points. The value of the velocity in the [111] direction was found to be equal to 25.5±1.0 km/s. Structural anisotropy of the magnon dispersion relation was discovered. The velocity was found to be higher for the directions of propagation parallel to the [111] axis in qualitative agreement with the earlier measurements (Riste and others) giving v = 38 km/s. It was not possible to reveal the existence of an energy gap Eg in the acoustic magnon energy band. It was estimated that the  $E_g$  value must be below 1 meV. Using the formalism of Wallace the magnon dispersion relations in haematite were calculated. This was done under the assumption that there exist two non-vanishing exchange integrals  $J_1$  and  $J_2$ .  $J_1$  and  $J_2$  denote the superexchange energy coupling between the spins of neighbouring iron ions bonded via an oxygen ion. The Fe-O-Fe angles of the bonds taken into consideration are correspondingly 132 and 126°. Satisfactory agreement between the theory and existing experimental data is obtained when  $SJ_1 = SJ_2 = 5.1$  meV. Apart from the acoustic magnon branch, the calculations revealed the existence of an optic branch but this was not accessible to investigation by the neutron diffraction technique.

ETUDE DU SPECTRE DE MAGNONS DANS L'HÉMATITE. AU MOYEN DES NEUTRONS. Les mesures ont été faites à Vinča, dans le réacteur RA, au moyen d'un spectromètre à cristal. Des neutrons monochromatiques  $(\lambda = 1.314 \text{ Å})$  ont été diffusés par un grand monocristal d'hématite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). Les auteurs ont étudié la distribution angulaire des neutrons diffusés inélastiquement. Pour plusieurs angles de décalage  $\Delta \theta$  du cristal, ils ont mesuré la largeur  $\Gamma$  du faisceau de neutrons diffusés (appelé cône de diffusion). Ils ont attribué ce cône à la surface de diffusion des magnons qui entoure le point du réseau réciproque (1,1,1). Pour plusieurs vitesses de magnons, ils ont mesuré  $\Gamma$ , en fonction de l'angle de décalage, et l'ont comparée aux points expérimentaux. Ils ont constaté que dans la direction [111], la vitesse avait une valeur égale à 25,5±1,0 km/s. Ils ont découvert une anisotropie structurelle de la relation de dispersion des magnons. Ils ont noté que la vitesse était plus élevée pour les directions de propagation parallèles à l'axe [111], ce qui concorde qualitativement avec les mesures antérieures (faites par Riste et d'autres) qui ont donné v = 38 km/s. Il n'a pas été possible de mettre en évidence l'existence d'une discontinuité Eg dans la bande acoustique de l'énergie des magnons. Selon les évaluations, Eg doit avoir une valeur inférieure à 1 meV. En utilisant le formalisme de Wallace, les auteurs ont calculé les relations de dispersion des magnons dans l'hématite. A cet effet, ils ont admis l'existence de deux intégrales d'échange  $J_1$  et  $J_2$  qui ne disparaissent pas.  $J_1$  et  $J_2$  expriment le couplage à superéchange d'énergie entre les spins d'ions Fe voisins liés par l'intermédiaire d'un ion oxygène. Les angles Fe-O-Fe des liaisons considérées sont respectivement de 132 et 126°. Les résultats théoriques et les données expérimentales actuelles concordent de façon satisfaisante lorsque  $SJ_1 = SJ_2 = 5,1$  meV. Outre la branche acoustique des magnons, les calculs ont révélé l'existence d'une branche optique qui, toutefois, ne se prête pas aux recherches par la méthode de la diffusion des neutrons.

НЕЙТРОННОЕ ИССЛЕДОВАНИЕ СПЕКТРА МАГНОНА В ГЕМАТИТЕ. Измерения были проведены в Винча на реакторе RA с использованием кристалдического нейтронного

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спектрометра. Рассеяние монохроматических нейтронов ( $\lambda = 1,314$  А) производилось на крупном монокристалле гематита ( $lpha-{
m Fe_2O_3}$ ). Исследовались угловые распределения неупруго рассеянных нейтронов. Для ряда различных неправильных углов кристалла  $\Delta heta$  была измерена ширина Г пучка рассеянных нейтронов (так называемого конуса рассеяния). Этот конус рассеяния был приписан явлению поверхностного рассеяния магнона вокруг точки обратной решетки [1,1,1]. Для ряда скоростей магнона была рассчитана и сравнена с экспериментальными точками зависимость Г от неправильного угла. Установлено, что величина скорости в направлении [111] равна 25,5 ±1,0 км/сек. Была обнаружена структурная анизотропия дисперсионного соотношения магнона. Было найдено, что скорость является более высокой в направлениях распространения параллельных оси [111] и что качественно она хорошо согласуется с более ранними измерениями (Ристе и др.), дающими v = 38 км/сек. Обнаружить в акустической области энергии магнона существование разрыва энергетической кривой Ед не удалось. Было рассчитано, что величина Е должна быть ниже 1 Мэв. При помощи формализма Уолласе были рассчитаны дисперсионные соотношения магнона в гематите. При этом исходили из предположения, что существуют два не стремящихся к нулю интеграла обмена  $J_1$  и  $J_2$ .  $J_1$  и  $J_2$  означают связь сверхобменной энергии между спинами соседних ионов железа, связанных ионом кислорода. Углы связи Fe-O-Fe, принятые в расчет, составляют соответственно 132° и 126°. Получено удовлетворительное согласие между теорией и существующими экспериментальными данными, когда  $SJ_1 = SJ_2 = -5,1$  Мэв. Помимо акустической ветви магнона, расчеты показали наличие оптической ветви, но с помощью метода нейтронной дифракции исследовать это не представилось возможным.

ESTUDIO, POR METODOS NEUTRONICOS, DEL ESPECTRO DE MAGNONES EN LA HEMATITA. Los autores realizaron sus mediciones en el reactor RA de Vinča con ayuda de un espectrómetro neutrónico de cristal. Los neutrones monocromáticos ( $\lambda$ = 1,314 Å) se dispersaron en un monocristal de hematita (Fe<sub>2</sub>O<sub>3</sub> $\alpha$ ) de gran tamaño. Se estudiaron las distribuciones angulares de los neutrones inelásticamente dispersos, midiendo para un cierto número de ángulos distintos de desplazamiento del cristal.  $\Delta \theta$ , la anchura  $\Gamma$  del haz de neutrones dispersos (el llamado cono de dispersión), que fue adscrito a la superfície de dispersión magnónica que envolvía al punto (1,1,1) de la red recíproca. Se calcularon y compararon con los puntos obtenidos experimentalmente los valores de  $\Gamma$  en función de la variación del ángulo de desplazamiento para diversas velocidades de los magnones. Se comprobó que el valor de la velocidad en la dirección [111] era igual a 25,5±1,0 km/s. descubriéndose así la anisotropía estructural de la relación de dispersión magnónica. Se encontró que la velocidad era superior para las direcciones de propagación paralelas al eje [111], lo que está cualitativamente de acuerdo con anteriores mediciones (Riste y otros) que daban una velocidad v=38 km/s. No fue posible poner de manifiesto la existencia de una laguna energética Eg en la banda de las energías magnónicas acústicas. Se calculó que el valor de Eg tiene que ser inferior a 1 meV. Utilizando las fórmulas propuestas por Wallace se calcularon las relaciones de dispersión de los magnones en la hematita. Este cálculo se efectuó en el supuesto de que existan dos integrales de intercambio que no desaparecen: J1 y J2, que indican el acoplamiento energético de superintercambio entre los spins de los iones hierro próximos, enlazados por un ion oxígeno. Los ángulos de los enlaces Fe-O-Fe tenidos en cuenta son de 132º y 126º, respectivamente. Un acuerdo satisfactorio entre la teoría y los datos experimentales disponibles se tiene cuando  $SJ_1 = SJ_2 = 5,1$  meV. Además de la rama magnónica àcústica, los cálculos han revelado la existencia de una rama óptica, pero el estudio de ésta no pudo llevarse a cabo por el método de difracción neutrónica.

#### INTRODUCTION

An account of the first and hitherto sole measurements reported on the subject was published by GOEDKOOP and RISTE [1] and RISTE and WANIC [2]. This work was done in Kjeller using the neutron diffraction technique [3] and white neutron beam. The resolution of such a technique is specified by the  $\Gamma_0$ , i.e. the width of elastic reflection (Bragg or Laue type) peak as measured at half its height. This was equal to 1.9° which resulted in a comparatively poor accuracy of obtained data. Since the Cracow Neutron Spectrometer described in [4] and used for the investigations of magnon spectrum

in pyrrhotite [5] allowed the obtainment of  $\Gamma_0 = 0.4^\circ$  it seemed worth while to repeat the measurements on haematite. These were performed in Vinča, Yugoslavia, using the monochromatic neutron beam from the horizontal beam hole marked B of the heavy-water moderated reactor RA (TVRS) with  $\sim 5 \times 10^{13} n/cm^2$  s central neutron flux.

#### STRUCTURE AND GEOMETRY OF THE SAMPLE

The static structure of haematite is fairly well known [6,7,8]. It belongs to the R3c (No.167) space group. The parameters of the rhombohedral primitive unit cell are: a = (5.420 ± 0.010) Å,  $\alpha$  = 55°17'. The rhombohedral co-ordinates of the ions are: Fe<sup>+</sup>+<sup>+</sup>: ( $\overline{w}$ ,  $\overline{w}$ ), (w, w, w), ( $\frac{1}{2}$  +  $\overline{w}$ ,  $\frac{1}{2}$  +  $\overline{w}$ ), ( $\frac{1}{2}$  + w,  $\frac{1}{2}$  + w,  $\frac{1}{2}$  + w) and 0<sup>-</sup>: (u, u, 0), (u, 0, u), (0, u, u); ( $\frac{1}{2}$  +  $\overline{u}$ ,  $\frac{1}{2}$  +  $\overline{u}$ ), ( $\frac{1}{2}$  +  $\overline{u}$ ,  $\frac{1}{2}$  +  $\overline{u}$ ), ( $\frac{1}{2}$ ,  $\frac{1}{2}$  +  $\overline{u}$ ,  $\frac{1}{2}$  + u), where w = 0.105 ± 0.0010 and u = 0.292 ± 0.007.

The spins of iron ions, S = 5/2, are coupled antiferromagnetically (see Fig.1). The critical point of this spin ordering  $T_N$  equals 969%. At room



Magnetic structure of haematite above Morin transition temperature

temperatures and higher, haematite exhibits a weak spontaneous ferromagnetism which disappears after cooling the crystal below the so-called Morin transition temperature, about -20°C, the value of which depends to some extent on the origin of the sample. The presence of the weak ferromagnetism was explained by DZYALOSHINSKY [7] as a natural consequence of magnetic symmetry when anisotropic interactions are present. Thus, strictly speaking, haematite is a collinear antiferromagnet only below Morin transition temperature. But the distortion of the collinear antiparallel arrangement of spins above this temperature is very small. It amounts to about 4 min of arc when expressed in the deviation angle  $\varphi$  (see Fig.1).

For the experiments a single crystal of haematite of natural origin, from Elba, was used. It had the form of a rectangular platelet 25 mm high, 20 mm wide and about 2 mm thick. The [111] rhombohedral axis was normal to its

surface. The mosaic-spread parameter was immeasurable, being certainly less than  $0.05^{\circ}$ .

#### MEASUREMENTS AND RESULTS

Measurements were done using the Cracow Neutron Spectrometer [4]. The monochromatic beam of neutrons ( $\lambda = 1.314$  Å) was obtained by reflection from an aluminium crystal monochromator. This beam impinged upon the sample crystal which was mounted, with its longest edge vertical, on a goniometer head fixed rigidly on the main table of the spectrometer. The angular distribution of neutrons scattered within the magnon scattering cone connected with the reciprocal lattice point  $\tau = (1, 1, 1)$  was studied. This was done in the same manner as was described in the paper on pyrrhotite [5] and with identical collimators used in the whole arrangement. It should only be emphasized that the scanning of the scattering cone was this time performed in a horizontal plane and not in the vertical one as during the work in Kjeller [2]. Thus the directions of the magnon wave vectors which defined the angular width  $\Gamma$  of the scattering cone were different from the previous case (see Fig. 2). Since the crystal was almost ideal it was possible to measure the width  $\Gamma$  of inelastic peaks for low missetting angles  $\Delta \theta$ . The peaks for sufficiently high  $\Delta \theta$  had typical trapezoidal shapes and none of them had any elastic contamination superposed. Thus, unlike the case in the work on pyrrhotite [5], it was permissible to rely on the measurements of the widths at the half height of the peaks. Such a width should be directly equal to the width of the scattering cone when the latter is sufficiently wide in comparison with the experimental resolution curve and then need not be corrected. This was checked by performing a number of convolutions of the presumed rectangular peaks with the real resolution curve having a triangle-like shape. Only for  $|\Delta \theta| < 10^\circ$  was it necessary to make corresponding corrections for instrumental broadening of the peaks. The widths so obtained could be plotted versus the missetting angle  $\Delta \theta$  (see Fig. 3). The error bars marked on several points in this figure are to a certain degree arbitrary, since there is no prescribed procedure for such a case. .The relative uncertainties of the represented widths are certainly greater for higher and lower  $\Delta\theta$ -values, because of statistics and corrections, respectively, than for the middle range of  $\Delta \theta$ -values. These data could be compared with theoretical curves based on the assumption that the dispersion relation of magnons in the investigated region of reciprocal space is linear, i.e. E = hvq, where E is the magnon energy,  $q = 1/\lambda$ , the magnon wave vector and v, the magnon velocity. In such a case the application of the conservation rules of momentum and energy alone leads to the exact equation for  $\Gamma(\Delta\theta)$  dependence. (See Eq.(1.17) of Reference [9]). The curves presented in Fig. 3 were calculated by an electronic computer and correspond to particular specified values of magnon velocity. As can be seen, the curves expressing the  $\Gamma(\Delta\theta)$  dependence are not the same for positive and negative  $\Delta\theta$ -values, contrary to the dependence predicted by the approximate Eq.(7) of Reference [2]. The accurate data of the present measurements in both cases (+ and  $-\Delta\theta$ ), although following different curves, fit the same velocity



Fig. 2

Cross-section in the  $(1\overline{1}0)$  plane of the neutron-magnon scattering in reciprocal space Magnitude of the scattering surfaces is exaggerated.



Fig. 3

Comparison of the experimental data with the theoretical curves calculated as explained in the text.

Ο Δθ >0 x Δθ <0 v =  $(25.5 \pm 1)$ km/s, if not too high  $|\Delta\theta|$  values are considered. Further inspection of the data represented in Fig. 3 reveals two interesting facts:

(a) For  $|\Delta \theta| \ge 40^{\circ}$  the experimental points start to deviate from the theoretical constant velocity curve. This deviation cannot be explained as the result of a growing discrepancy between the exact dispersion curve (see Fig. 4) and the linear approximation, because the deviation caused by this



Fig. 4

Calculated dispersion curves showing the anisotropy of the magnon dispersion relation

discrepancy, if seen at all, should have just the opposite sign, i.e. the experimental points for  $\Delta\theta$  should have fallen on the side of smaller velocities. The observed deviation can be explained only as a consequence of the structural anisotropy of the magnon dispersion relation in haematite. Such a conclusion is in qualitative agreement with the results of previous [2], less accurate measurements which gave v = 38 km/s. This velocity was found for magnons propagating in a direction normal to the [111] axis. In the present investigation, due to different geometry of scanning, the magnon vectors for not too high  $\Delta\theta$  values were roughly parallel to the direction [111]. But when the modulus of the missetting angle increases beyond a certain value, the angle  $\Psi$  between the q-vector determining the width  $\Gamma$  and the direction [111] becomes so large that it is not justifiable to neglect its influence upon the dispersion relation (see Fig.2).

(b) Within the attained accuracy no deviation from the linear behaviour of the magnon dispersion relation for small q-values could be detected. This means that the energy gap of the acoustical magnon band is small in comparison with the situation existing in other antiferromagnets. The upper limit of the energy gap  $E_g$  was estimated as being less than 1 meV. It is worth mentioning that a sufficiently low value of  $E_g$  is a necessary condition for the successful application of the diffraction technique in the investigation of magnon scattering.

#### CALCULATIONS

The magnon dispersion relations were obtained using the method of WALLACE [10] and neglecting the very small non-collinearity of the spin ordering. Following the suggestions of Reference [11] only the two presumably strongest interactions (via oxygen ions) were taken into account. These were the superexchange integrals  $J_1$ , between the ions belonging to different unit cells marked 1 and 3, 2 and 4, and  $J_2$ , between the ions 1 and 2, 3 and 4. These pairs of ions had the largest Fe-O-Fe angles, 132° and 126° for  $J_1$  and  $J_2$  respectively. Wallace's formalism gave the fourth order equation for the magnon energies. On account of the crystal symmetry this equation appeared to be biquadratic and two magnon branches resulted

$$E_1 = E_2 = JS \{A^2 - BB^* - CC^* - 2\sqrt{BB^*CC^*}\}^2$$
 (1)

$$E_3 = E_4 = JS \{A^2 - BB^* - CC^* + 2\sqrt{BB^*CC^*}\}^2,$$
 (2)

where

$$A^2 = \{12 + 6p + \rho\}^2$$
(3)

$$BB^{*} = 4p^{2} \{ 3 + 2[\cos(\alpha - \beta) + \cos(\beta - \gamma) + \cos(\gamma - \alpha)]$$
(4)

$$CC^* = 4\left\{6 + 4\left[\cos\alpha + \cos\beta + \cos\gamma\right] + 4\left[\cos\left(\alpha - \beta\right) + \cos\left(\beta - \gamma\right) + \cos\left(\gamma - \alpha\right)\right]\right\}$$

$$+2[\cos(\alpha-\beta-\gamma)+\cos(\beta-\gamma-\alpha)+\cos(\gamma-\alpha-\beta)]\},$$
(5)

where

 $\alpha = 2\pi \vec{q} \cdot \vec{a}, \quad \beta = 2\pi \vec{q} \cdot \vec{b}, \quad \gamma = 2\pi \vec{q} \cdot \vec{c}$ (6)

and  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  are the unit translation vectors of the rhombohedral cell of haematite;  $J = J_1$ ,  $J_2 = pJ_1$ , and the anisotropy energy factor  $\rho = E_a/JS$  ( $E_a = g\mu_{\beta} H_a$ , the energy of anisotropy per spin). Equation (1) reduces to a simple form for the [111] and [110] directions, then (see Fig. 4) for  $\rho = 0$ 

$$E_{[111]} = 12JS [p(1 - |\cos(\alpha/2)| + \sin^2(\alpha/2)]^{\frac{1}{2}}$$
(7)

$$E_{[1\bar{1}0]} = \sqrt{24} JS \left[ 1 - \frac{2}{3} \cos \alpha - \frac{1}{3} \cos 2\alpha \right]^{\frac{1}{2}} (p+2) .$$
(8)

In order to check how the anisotropy factor would distort the linear behaviour of the acoustical dispersion relation, the dispersion curve for small



Fig. 5

Effect of the internal effective anisotropy field expressed by  $\rho$  on the magnon dispersion relation in the [111] direction and for p = 1.

q-values was calculated for several non-zero values of  $\rho$  (see Fig. 5). It was estimated that the actual value of  $\rho$  must be lower than  $10^{-3}$ . Then Eq.(1) was rewritten in polar co-ordinates  $\varphi, \psi$  and q and the cos x functions replaced by  $[1 - x^2/2]$ . It appeared that in such an approximation, valid for small q-values, the dispersion relation for  $\rho = 0$  is linear and not dependent on  $\varphi$  but only on  $\psi$ . Hence the magnon velocity could be defined. The ratio of the velocities in the direction [111] and one normal to it is

$$v_{[1\bar{1}0]}/v_{[111]} = 0.634 \sqrt{p+2}.$$
 (9)

Taking p = 1 one obtains from the measured  $v_{[111]}$  that  $J = J_1 = J_2 = 5.1/S$  meV, where S is the effective spin quantum number of the Fe ion. The largest uncertainty lies in the p-factor. The localization of the optical magnon branch would be of much help because it is very sensitive to p.

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#### DISCUSSION

K.P. SINHA: Has the neutron scattering technique yielded any experimental evidence of the existence of higher branches of spin waves which are analogous to optical modes of lattice vibrations?

J.A. JANIK: Yes, it has, for instance in the case of phyrrhotite.

# COMPARISON OF SPIN WAVE THEORY WITH NEUTRON SCATTERING RESULTS FOR MnF<sub>2</sub>

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#### Abstract — Résumé — Аннотация — Resumen

COMPARISON OF SPIN WAVE THEORY WITH NEUTRON SCATTERING RESULTS FOR MnF2. Recent inelastic neutron scattering experiments carried out by Okazaki and Turberfield have provided a direct measure of spin wave dispersion in  $MnF_2$  both at 4.2°K and at higher temperatures approaching the Néel point. The low temperature results taken together with other magnetic data allow the various exchange constants in  $MnF_2$ to be evaluated with some precision. Using these constants, the spin wave formalism for anti-ferromagnets described by Oguchi has been employed to predict theoretically the temperature dependence of the spin wave dispersion. No disposable parameters are involved and theoretical dispersion curves may be compared with the experimental results for higher temperatures as a test of the spin wave theory. The spin wave energies were evaluated numerically and integrations over the Brillouin zone were carried out, thus avoiding the use of some form of series expansion in temperature. Account was taken of dynamical interactions between pairs of spin waves but kinematical effects were neglected. Renormalization of the spin wave energies was performed. This is an important factor for  $T/T_N \ge \frac{1}{4}$ . The agreement between theory and experiment is in fact remarkably good up to temperatures corresponding to about 90% of the Néel point. It would be dangerous to extrapolate this result to systems of lower spin as kinematical effects are likely to play a much greater part in such cases. For MnF<sub>2</sub> where S = 5/2 a rough estimate suggests that kinematical effects will not be important until M/M<sub>G</sub><sup>20%</sup> and this occurs only within a degree or so of the Néel point. A brief discussion of the likely consequences of a biquadratic exchange term in MnF2 is given and it is concluded that, if present, such exchange is quite small.

COMPARAISON ENTRE LA THÉORIE DE L'ONDE DE SPIN ET LES RÉSULTATS OBTENUS PAR LA DIF-FUSION DES NEUTRONS DANS MnF2. Des expériences récentes, exécutées par Okazaki et Turberfield au moyen de la diffusion inélastique des neutrons, ont fourni une mesure directe de la dispersion de l'onde de spin dans MnF<sub>2</sub>, à 4,2°K et à des températures supérieures approchant le point de Néel. Les résultats obtenus à basse température, complétés par des données sur les caractéristiques magnétiques, ont permis d'évaluer les diverses constantes d'échange dans MnF2 avec une certaine précision. En utilisant ces constantes, l'auteur a employé le formalisme de l'onde de spin pour substances antiferromagnétiques, décrit par Oguchi, pour prévoir théoriquement comment varie la dispersion de l'onde de spin en fonction de la température. Aucun des paramètres mis en jeu n'est superflu, et les courbes théoriques de dispersion peuvent être comparées aux résultats expérimentaux pour des températures plus élevées en vue de vérifier la théorie de l'onde de spin. L'auteur a évalué numériquement les énergies d'onde de spin et intégré sur la zone de Brillouin, évitant ainsi tout développement en série selon la température. Il a tenu compte des interactions dynamiques entre paires d'ondes de spin, mais il a négligé les effets cinématiques. Les énergies d'onde de spin ont fait l'objet d'une renormalisation. C'est là un facteur important pour  $T/T_N \ge \frac{1}{4}$ . La concordance entre la théorie et les résultats expérimentaux demeure, en fait, remarquable jusqu'à des températures correspondant à environ 90% du point de Néel. Il serait dangereux d'extrapoler ces résultats en vue de les utiliser pour des systèmes à spin plus faible, car les effets cinématiques joueraient probablement un rôle beaucoup plus important dans ces cas. En ce qui concerne  $MnF_2$ , où S = 5/2, une évaluation grossière laisse supposer que les effets cinématiques seront peu importants jusqu'à M/M $_{
m O}$  - 20%, ce qui ne se produit que dans les limites d'un degré environ du point de Néel. L'auteur discute brièvement les conséquences que peut avoir un terme d'échange biquadratique dans MnF, ; il conclut que, si cet échange existe, il est très faible.

СРАВНЕНИЕ ТЕОРИЙ СПИНОВОЙ ВОЛНЫ С РЕЗУЛЬТАТАМИ РАССЕЯНИЯ НЕЙ-ТРОНОВ ДЛЯ MnF<sub>2</sub>. В результате экспериментов по неупругому рассеянию, которые провели недавно Оказаки и Турберфильд, получена прямая мера дисперсии спиновой волны в MnF2 и при 4;2°К и при более высоких температурах, приближающихся к точке Нила. Низкотемпературные результаты вместе с другими магнитными свойствами позволяют оценить с некоторой точностью различные обменные константы в MnF<sub>2</sub>. Используя эти константы, был применен описанный Огучи формализм теории спиновой волны для антиферромагнетиков в целях теоретического предсказания зависимости дисперсии спиновой волны от температуры. Ни один из имеющихся параметров не затрагивается, и теоретические кривые дисперсии можно сравнить с экспериментальными результатами в отношении более высоких температур в качестве проверки теории спиновой волны. Были приняты в расчет численные значения энергии спиновых воли и были взяты интегралы по зоне Бриллюзна, и тем самым удалось избежать использования некоторой формы разложения в ряд по температуре. Учтены динамические взаимодействия между парами спиновых волн, однако кинематические эффекты не принимались во внимание. Была произведена перенормировка энергий спиновых волн. Это-важный фактор для  $T/T_N \sim \frac{1}{4}$ . Фактически теоретические и экспериментальные данные в значительной степени совпадают при температурах, соответствующих приблизительно 90% точки Нила. Опасно экстраполировать этот результат к системам с меньшими спинами, поскольку, вероятно, кинематические эффекты играют значительно большую роль в таких случаях. Для MnF2, где S = 5/2, согласно приблизительной оценке, кинематические эффекты не играют существенной роли до М/М₀ ~20%, что происходит только на расстоянии примерно одного градуса от точки Нила. Кратко обсуждаются вероятные последствия биквадратного члена обмена в MnF<sub>2</sub> и делается вывод о том, что такой обмен, если он присутствует, является довольно незначительным.

ESTUDIO COMPARATIVO, EN EL MNF2, DE LA TEORIA ONDULATORIA DEL SPIN Y DE LOS RESULTADOS DE LA DISPERSIÓN NEUTRONICA. Los experimentos de dispersión inelástica de neutrones, realizados recientemente por Okazaki y Tuberfield, han proporcionado un medio de medir directamente la dispersión de las ondas de spin en el MnF2, tanto a 4,2°K como a temperaturas más elevadas próximas al punto de Néel. Los resultados obtenidos a bajas temperaturas, considerados conjuntamente con otros datos magnéticos, permiten evaluar con cierta precisión las diversas constantes de intercambio en el MnF<sub>a</sub>. Haciendo uso de estas constantes, se ha empleado el formalismo de las ondas de spin para sustancias antiferromagnéticas descrito por Oguchi para predecir teóricamente la dispersión de las ondas de spin en función de la temperatura. No intervienen parámetros redundantes y las curvas de dispersión teóricas pueden compararse con los resultados experimentales obtenidos a temperaturas más elevadas, como prueba de la teoría ondulatoria del spin. Se han evaluado numericamente las energías de las ondas de spin y se han realizado integraciones que abarcan la zona de Brillouin, por lo que no es preciso emplear alguna forma de desarrollo en serie en función de la temperatura. Se tuvieron en cuenta las interacciones dinámicas entre pares de ondas de spin, pero se despreciaron los efectos cinemáticos. Se procedió a renormalizar las energías de las ondas de spin. Esto constituye un importante factor en el caso de  $T/T_N \ge \frac{1}{4}$ . La concordancia entre los datos teóricos y los resultados experimentales es, de hecho, notable hasta temperaturas correspondientes a un 90% aproximadamente del punto de Néel. Extrapolar este resultado a sistemas de spin más bajo sería arriesgado, ya que en esos casos es probable que los efectos cinemáticos desempeñen un papel mucho más importante. Para el MnFz, en el que S=5/2, un cálculo aproximado sugiere que los efectos cinemáticos no tendrán importancia hasta llegar a un valor de  $M/M_O$  ~ 20%, y esto ocurre únicamente a menos de un grado, aproximadamente, del punto de Néel. Et autor describe sucintamente las probables consecuencias de un término bicuadrático de intercambio en el MnF, y llega a la conclusión de que tal intercambio, de producirse, es muy pequeño.

#### 1. INTRODUCTION

Investigations of spin wave dispersion by means of inelastic neutron scattering appear, at the moment, to be valuable in two rather different general connections. On the one hand pioneer experiments giving the overall form of the dispersion in a ferromagnetic metal over a large fraction of the Brillouin zone dimension would be of great interest as far as the theory of the metallic state is concerned. On the other hand, precise measurements of spin wave energies in non-metals, as a function both of wave vector and temperature, allow the fairly detailed magnetic theory available in these cases to be tested rather sensitively against experiment.

A useful material for examination in an experiment of the second type is  $MnF_2$ . It is a simple compound both electronically and crystallographically so that a discussion of its low-temperature magnetic properties is expected to be well within the capabilities of standard spin wave theory. A series of measurements of spin wave dispersion in  $MnF_2$  have in fact recently been carried out by Okazaki and Turberfield in References [1] and [2] and it is the purpose of this paper to use these to test the predictions of the spin wave theory for antiferromagnets described by OGUCHI [3].

# 2. METHOD OF EVALUATING THE THEORETICAL SPIN WAVE ENERGIES

 $MnF_2$  has the rutile structure and the Mn ions which are in S-states with a spin of 5/2 lie on a body-centred tetragonal lattice. In the antiferromagnetic state the two sets of antiparallel spins which are aligned along the c-axis may be regarded as belonging to two interpenetrating simple tetragonal sub-lattices. This form of antiferromagnetic structure can thus be described as the CsCl type. The dominant exchange interaction is between an ion and its eight nearest neighbours on the second sub-lattice. The exchange constant corresponding to this interaction is denoted as  $J_2$ , while  $J_1$  signifies the interactions between nearest-neighbour ions which lie along the c-axis and on the same sub-lattice. The possibility of a third exchange interaction  $J_3$  between third neighbours (second neighbours on the same sublattice) must also be envisaged. The convention will be adopted that a positive sign for J corresponds to ferromagnetic exchange.

The antiferromagnetic resonance data of JOHNSON and NETHERCOT [4] taken together with the value for the perpendicular susceptibility obtained at low temperatures by TRAPP and STOUT [5] allow  $J_2$  and the effective anisotropy field at zero wave vector  $H_a$  to be determined. The values obtained are  $J_2 = -1.76^{\circ}$ K and  $g \mu_{\beta} H_a = 1.06^{\circ}$ K [5]. Having fixed these parameters, the low-temperature spin wave dispersion results of Okazaki and Turberfield enable an evaluation of  $J_1$  and  $J_3$  to be carried out. It is found that  $J_1 = 0.3 \pm 0.1^{\circ}$ K and  $J_3 = 0 \pm 0.05^{\circ}$ K [1].

If the above values for these parameters are accepted and if it is assumed that their temperature dependence is either known or insignificant below the Néel point, the magnetic behaviour of  $MnF_2$  in the antiferromagnetic region is in principle completely determined, as no disposable parameters remain. As already indicated the purpose of this paper is to examine the extent of the agreement with experiment of predictions based on simple spin wave theory. The calculations carried out take account of dynamical interactions between pairs of spin waves and of energy renormalization but neglect kinematical effects.

The method of calculation follows the numerical procedure described by LOW [6]. Briefly, on the basis of the spin wave expressions developed by OGUCHI [3] which take into account terms to the fourth power in the spin wave operators, it is possible to write the energy of a spin wave at a finite temperature in the form

$$\mathbf{E}(\mathbf{T}) = \mathbf{E}[\mathbf{1} - \Delta(\mathbf{T})], \tag{1}$$

where  $\Delta(T)$  is almost independent of wave vector  $\vec{q}$  (except close to  $T_N$ ), E is the energy at 0°K of a spin wave of identical wave vector and

$$\Delta_{\vec{q}'}(T) = \frac{\alpha_{q'}}{NS} \sum_{\vec{q}} \alpha_{\vec{q}} \left[ (1+\epsilon)^2 - \gamma^2 \right]^{\frac{1}{2}} / \left[ \exp\left(\frac{E(T)}{kT}\right) - 1 \right], \quad (2)$$

where

$$\alpha_{\vec{q}} = \frac{1+\epsilon-\gamma^2}{(1+\epsilon)^2-\gamma^2}$$
(3)

and

 $\gamma = \cos\left(\frac{1}{2}\operatorname{aq}_{x}\right)\cos\left(\frac{1}{2}\operatorname{aq}_{y}\right)\cos\left(\frac{1}{2}\operatorname{cq}_{z}\right).$ (4)

N is the number of Mn ions in one sub-lattice. The sum in the expression for  $\Delta(T)$  is over all  $\vec{q}$  in the first Brillouin zone and the  $\alpha_{\vec{q}}$  inside the sum takes on values corresponding to these wave vectors. The  $\alpha_{\vec{q}}$  outside the summation sign has a value corresponding to the wave vector of the spin wave of which the energy E(T) is being sought (hence the weak dependence of  $\Delta(T)$  on wave vector except at very small  $\vec{q}$  or for temperatures close to  $T_N$ ). a and c are the lattice parameters for the tetragonal MnF<sub>2</sub> structure and  $q_x$ ,  $q_y$  and  $q_z$  the components of the wave vector  $\vec{q}$ . The energy of a spin wave at 0°K is given by

$$E = 2Sz_2 | J_2 | [(1+\epsilon)^2 - \gamma^2]^{\frac{1}{2}} (1+\alpha_{\frac{1}{4}} \frac{0.073}{2S}), \qquad (5)$$

where the second factor on the right has its origin in the fact that the ordered state of an antiferromagnet is not the ground state.  $z_1$ ,  $z_2$  and  $z_3$ refer to the number of neighbouring ions concerned in the exchange interactions denoted by  $J_1$ ,  $J_2$  and  $J_3$  respectively.

The quantity  $\epsilon$  is given by

$$\epsilon = \frac{g\mu_{\beta}H_{a}}{2Sz_{2}\left[J_{2}\right]} - \frac{2z_{1}J_{1}}{z_{2}J_{2}}\sin^{2}(\frac{1}{2}cq_{z}) - \frac{z_{3}J_{3}}{z_{2}J_{2}}[\sin^{2}(\frac{1}{2}aq_{x}) + \sin^{2}(\frac{1}{2}aq_{y})]$$
(6)

so that it is through this parameter that the subsidiary exchange interactions  $J_1$  and  $J_3$  are introduced. In fact Oguchi's expressions are for an antiferromagnet in which there is one set of exchange interactions only, i.e. the  $J_2$  type. However, calculations of the effect of temperature on spin wave dispersion have been carried out using Eqs (1) to (5) in conjunction with Eq. (6). This approximation neglects small terms to the fourth power in the spin wave operators which arise from the presence of  $J_1$  etc., but the consequent error in interaction energy (i.e. in  $\Delta(T)$ ) is estimated to be a few per cent only (see below).
In the course of the calculations the anisotropy energy  $g\mu_{B}H_{a}$  was modified to take account of the experimentally observed variation of antiferromagnetic resonance frequency with temperature [4]. Thus,

$$\epsilon(\mathbf{T}) \sim \frac{g\mu_{\beta}H_{a}}{2Sz_{2}|J_{2}|} \left(\frac{M}{M_{0}}\right)^{2.9} [1 - \Delta(\mathbf{T})]^{-2} + \dots, \qquad (7)$$

where  $M/M_0$  is the fractional sub-lattice magnetization at the temperature concerned. This form of approximation for the temperature dependence of the anisotropy energy differs from that used in connection with calculations on macroscopic properties such as sub-lattice magnetization etc. [6] in that previously the term in  $(1 - \Delta(T))$  was omitted. This has no significant effect on the values for the macroscopic properties computed. However, it clearly leads to appreciably different spin wave energies at small  $\vec{q}$  and this is of some importance in the present case where direct comparison with experimentally observed spin wave dispersion is carried out. It should be noted that  $g_{\mu R}H_{a}$  also has a dependence on wave vector  $\vec{q}$ . This arises because by far the largest contribution to H<sub>a</sub> comes from dipole-dipole interactions among the Mn ions. The  $\vec{q}$ -dependence of anisotropy fields of this type has been discussed by ZIMAN [7] and his expressions were used to estimate the variation of  $H_a$  for MnF<sub>2</sub>. It appears that the  $\vec{q}$ -dependence of  $H_a$  is associated almost entirely with the magnitude of  $q_z$ . Allowance was made for this in the present calculations but the effects on the actual spin wave energies are rather small, i.e. roughly a 1% reduction when q<sub>2</sub> has its maximum value.

Numerical solutions of Eq. (1) for E(T) were found on a 7030 computer using an iterative procedure involving the renormalization of the spin wave energies [6]. Dispersion curves corresponding to propagation in a [001] direction calculated on the above basis are shown in the Fig. 1. The two lower solid lines relate to temperatures of 49.5 and 62.0°K and may be compared with the experimental data for these temperatures obtained by Okazaki and Turberfield in Reference [2]. Considering the number of approximations that have been made the agreement of theory with experiment is good. The pair of dashed lines associated with each of the lower solid curves indicates the additional lowering of spin wave energy which results if  $\Delta(T)$  in Eq. (1) is multiplied by the factors of slightly more than unity which are indicated on the figure. It would seem from these that an increase in the spin wave interaction term of about 5% gives the best agreement with both sets of experimental data simultaneously. Crude estimates suggest that such an increase is not inconsistent with the additional interaction terms expected to result from the presence of the subsidiary exchange interaction  $J_1$  (see above). Thus, it would appear that the predictions of simple spin wave theory taking account only of dynamical interactions between pairs of magnons are in good agreement with experiment.

### 3. CONCLUSIONS

The outstanding conclusion from a comparison of the present series of calculations with experiment is that surprisingly high accuracy is achieved





Diagram showing the spin wave dispersion in  $MnF_2$  for propagation along the c-axis The experimental results of OKAZAKI et al. [2] for three temperatures are shown together with theoretical curves which take into account dynamical interactions between pairs of spin waves and include renormalization of the spin wave energies. The dashed curves show the effect of increasing the spin wave interaction term by the factors indicated

Temp. (°K): □ 4.2; ▲ 49.5; ● 62

by taking into account only dynamical interactions between pairs of spin waves. In fact it would be dangerous to extrapolate this result to systems of lower spin. A rough estimate suggests that for S = 5/2, kinematical effects will not be important until  $M/M_0 \sim 20\%$  and this occurs only within a degree or so of the Néel point. The fact that third and higher order interaction events do not seem to contribute at higher temperatures is more puzzling, and difficult to understand unless it results from some sort of cancellation among these terms. That such terms are not important, however, is strongly suggested by the agreement obtained with experimental spin wave energies both at 49.5 and 62.0°K. If present, any terms of this nature would rapidly increase with temperature and be expected to lead to discrepancies of very different magnitudes at these two points.

Consideration was given to the effects which would arise if a biquadratic exchange term were present in  $MnF_2$ , i. e. if a term of the form  $-2j \sum_{\langle m,n \rangle} (\vec{S}_m, \vec{S}_n)^2$ 

were added to the Hamiltonian, where j is the biquadratic exchange constant between an ion and its nearest neighbours on the second sub-lattice. The effect of j, as far as terms quadratic in the spin wave operators are concerned is to add  $+ 2S_{j}^{2}$  to a term in  $|J_{2}|^{*}$ . The effect on the spin wave interaction terms is less obvious but apparently it can be summed up roughly in the form of a factor in front of  $\Delta(T)$ . Thus, the presence of a non-zero

<sup>\*</sup> This has been pointed out independently by Dr. R. Orbach.

value of j can be distinguished from a change in the value of  $J_2$  only by the temperature dependence of E(T). Estimates suggest in fact that the spin wave interaction term is quite sensitive to j. Thus, as agreement with experiment is obtained using the original Hamiltonian which contains only the bilinear form of exchange, it would appear that any biquadratic term is rather small. Although one hesitates in setting limits in this matter because of the approximations involved in the calculations, a value of  $j/J_2$  of more than about one per cent is probably inconsistent with the temperature dependence of the experimental dispersion data.

Brief reference should perhaps be made to calculated values for macroscopic properties, for example fractional sub-lattice magnetization, such as were discussed previously [6]. These earlier computations have been repeated taking into account the slightly different expressions and parameters described in this paper. The resulting values for magnetization and parallel susceptibility are very similar to those already published. It has been pointed out by Kanamori (Eq. (14) and Fig. 5, Ref. [6]) that the previous calculations for specific heat are in error because the expression used as a basis for computation did not incorporate the temperature dependence of the interaction energy correctly. A corrected expression gives a larger magnetic specific heat and at higher temperatures the calculated values are considerably enhanced and in fair agreement with experiment. Thus, it appears that in general the spin wave approximation is capable of reasonably accurately reproducing a number of the properties of manganese fluoride up to temperatures within ten per cent or so of the Néel point. This is presumably true also in the case of other non-metallic magnets with high spin values.

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### DISCUSSION

R.J. ELLIOTT: Have you analysed the data to find the effective J as a function of T?

G.G.LOW: As you suggest, it would be possible to express the temperature dependence of the spin wave energies in terms of exchange parameters which have an effective temperature dependence, but in fact this type of analysis has not been carried out. In the present discussion it has been assumed that the only source of temperature dependence lies in the spin wave interactions, and any variations in exchange energy arising from lattice expansion with increasing T have been neglected. Justification for this assumption can be found in the measurements relating to the pressure dependence of  $T_N$  by Benedek and Kushida\* taken together with data on the compressibility and thermal expansion of MnF<sub>2</sub>. These suggest that the variation in  $|J_2|$  due to thermal expansion in going from 0 to 60°K is less than one per cent.

A.W. JOSHI: In your paper you mention that the anisotropy field  $H_a$  depends on the wave vector  $\vec{q}$ . What sort of dependence is this?

G.G. LOW: The anisotropy energy arises mainly from dipolar interactions among the manganese ions and calculation of the relevant lattice sums as written down by Ziman suggests that  $H_a$  is roughly independent of  $q_x$  and  $q_y$  but falls off appreciably with increasing  $q_z$ .

A.W. JOSHI: The value of  $J_3$  reported in the paper is  $0 \pm 0.05^{\circ}$  K, which means that it could be positive or negative. Is it not possible to determine accurately whether the interaction between two Mn atoms on the same sublattice is ferromagnetic or antiferromagnetic?

G.G. LOW: It does not at the moment appear to be possible to fix the value of  $J_3$  any more accurately than already indicated and therefore the sign of exchange in the a-axis direction between nearest-neighbour Mn ions on the same sub-lattice remains undetermined. Exchange in the direction of the c-axis  $(J_1)$  is, of course, positive as first demonstrated by J.Owen and others at Oxford in their resonance experiments.

<sup>\*</sup> BENEDEK, G.B. and KUSHIDA, T., Phys. Rev. 118 (1960) 46.

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