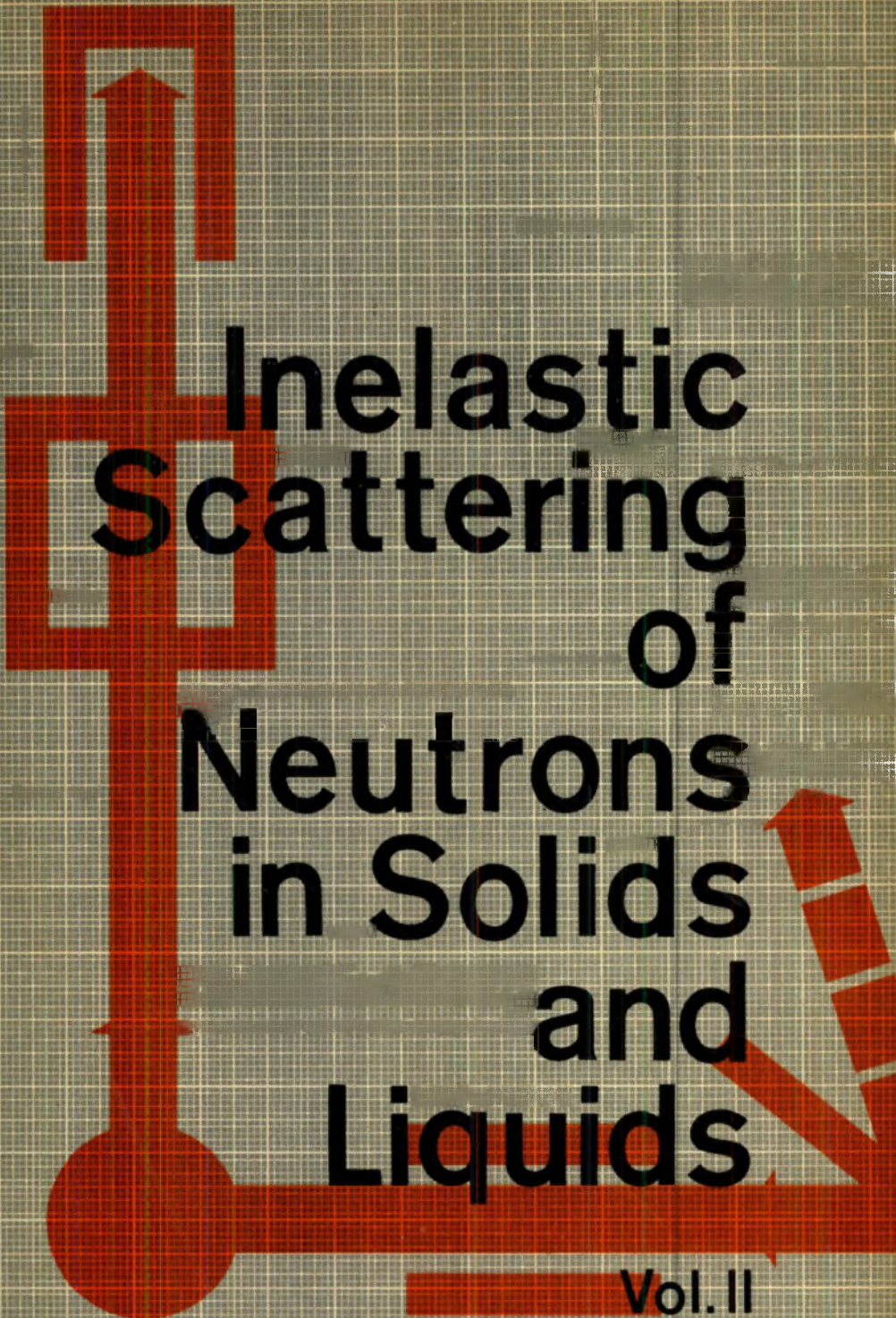




Inelastic Scattering of Neutrons in Solids and Liquids

Vol. II

PROCEEDINGS OF A SYMPOSIUM, CHALK RIVER, 10-14 SEPTEMBER 1962

SECTION FRANÇAISE



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA 1963

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INELASTIC SCATTERING OF NEUTRONS
IN SOLIDS AND LIQUIDS

Vol. II

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PROCEEDINGS SERIES

INELASTIC SCATTERING
OF NEUTRONS
IN SOLIDS AND LIQUIDS

II

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FOREWORD

The Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids was the International Atomic Energy Agency's second symposium held on this subject. The previous one was held in 1960 in Vienna and the very first international meeting in this field took place in 1957 in Stockholm. At the Stockholm meeting only 11 papers from six countries were presented; this was the very beginning of a rapidly developing new branch of physics. At the Vienna Symposium there were 50 papers from 12 countries. At Chalk River 67 papers from 13 countries and three international organizations, the European Atomic Energy Community, the Joint Institute for Nuclear Research and the International Atomic Energy Agency, were presented and discussed. In several other countries, either research in this field has already begun or preparations to start it are under way. This is an indication that the interest in using inelastic scattering of neutrons as a method to study the internal dynamics of solids, liquids and molecules is continuously increasing. On the other hand, a deeper knowledge of the dynamic properties of moderators plays an important role in the understanding of the process of thermalization of neutrons. The latter study is of special importance in promoting advances in nuclear reactor technology.

In the light of these developments the International Atomic Energy Agency, with the co-sponsorship of the United Nations Educational, Scientific and Cultural Organization, organized the Symposium at Chalk River from 10 to 14 September 1962 on the generous invitation of the Government of Canada and Atomic Energy of Canada Limited.

The proceedings now published contain all the 67 papers and the records of the discussions.

December 1962

SIGVARD EKLUND
Director General

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IV

SOLIDS

CRYSTAL DYNAMICS FROM NEUTRON SPECTROMETRY

A. D. B. WOODS

ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

CRYSTAL DYNAMICS FROM NEUTRON SPECTROMETRY. This paper reviews investigations carried out at Chalk River on the lattice dynamics of various crystals including lead, sodium, alkali halides, semi-conductors, and other more complex compounds. Analysis of the low temperature results ($\sim 100^\circ\text{K}$) gives considerable insight into the nature of the interatomic forces. In sodium, a simple metal, the interatomic forces are very nearly derivable from a potential. Lead, a more complicated metal, has extremely long range forces accompanied by strong electronic effects. At higher temperatures anharmonic effects are very pronounced in both metals, especially in lead. The alkali halide results can be interpreted on a "shell" model, with polarizable ions. Even at low temperature neutron groups corresponding to the longitudinal optical modes have temperature dependent widths which are not yet fully understood.

ÉTUDE DE LA DYNAMIQUE DES CRISTAUX PAR LA SPECTROMÉTRIE NEUTRONIQUE. Dans ce mémoire, l'auteur décrit les recherches faites à Chalk River sur la dynamique des réseaux de certains cristaux, y compris le plomb, le sodium, les halogénures alcalins, les semi-conducteurs et d'autres composés complexes. L'analyse des résultats obtenus à basse température (environ 100°K) fournit de nombreux renseignements sur la nature des forces interatomiques. Dans le sodium (métal simple), les forces interatomiques peuvent presque être dérivées d'un potentiel. Dans un métal plus compliqué, tel que le plomb, on trouve des forces ayant une portée extrêmement grande et comportant des effets électroniques marqués. A des températures plus élevées, il se produit des effets anharmoniques très prononcés dans les deux métaux et particulièrement dans le plomb. On peut interpréter les résultats obtenus pour les halogénures alcalins en se fondant sur le modèle en couche comportant des ions polarisables. Même aux basses températures, les groupes de neutrons correspondant aux modes optiques longitudinaux possèdent des largeurs dépendant de la température, que l'on ne comprend pas encore parfaitement.

ИЗУЧЕНИЕ ВОПРОСОВ ДИНАМИКИ КРИСТАЛЛОВ МЕТОДАМИ НЕЙТРОННОЙ СПЕКТРОМЕТРИИ. Дается обзор исследований в Чок Ривер динамики решетки различных кристаллов, включая свинец, натрий, щелочные галоидные соединения, полупроводники и другие более сложные соединения. Анализ результатов исследований при низких температурах (около 100°K) приводит в значительной степени к пониманию природы межатомных сил. В натрии, простом металле, межатомные силы весьма аналогичны силам, возникающим из потенциала. Свинец, более сложный металл, обладает исключительно дальнедействующими силами, сопровождаемыми сильными электронными явлениями. При более высоких температурах в обоих металлах, особенно в свинце, отчетливо проявляются негармонические явления. Результаты исследования щелочных галоидных соединений могут быть объяснены "оболочечной" моделью с поляризуемыми ионами. Даже при низкой температуре нейтронные группы, соответствующие продольным оптическим формам, имеют длины, зависящие от температуры, которые еще не поняты полностью.

ESTUDIO DE LA DINÁMICA DE REDES CRISTALINAS POR ESPECTROMETRÍA NEUTRÓNICA. Los autores pasan revista a las investigaciones realizadas en Chalk River sobre la dinámica reticular de varios cristales, entre ellos plomo, sodio, haluros alcalinos, semiconductores y otros compuestos más complejos. El análisis de los resultados obtenidos a baja temperatura ($\sim 100^\circ\text{K}$) permite formarse una idea más cabal de la naturaleza de las fuerzas interatómicas. En el sodio, metal simple, dichas fuerzas pueden deducirse con considerable precisión a partir de un potencial. En el plomo, metal más complejo, existen fuerzas de largo alcance acompañadas de fuertes efectos electrónicos. A temperaturas más elevadas, los efectos anarmónicos son muy pronunciados en ambos metales, sobre todo en el plomo. Los resultados obtenidos con los haluros alcalinos pueden interpretarse según el modelo de capas con iones polarizables. Incluso a bajas temperaturas, los grupos de

neutrones correspondientes a los modos ópticos longitudinales presentan amplitudes dependientes de la temperatura que aún no se han podido interpretar en detalle.

I. INTRODUCTION

Inelastic neutron scattering from single crystals has become, over the past few years, an established technique for obtaining accurate and detailed information on the frequency versus wave vector dispersion relations for the lattice vibrations in the crystal. In the experiments the neutrons interact with the crystal, the interaction resulting in the production or annihilation of a single normal mode of vibration (phonon) of the crystalline lattice according to the conservation relations

$$E_0 - E' = \pm h\nu \quad (1)$$

$$\mathbf{k}_0 - \mathbf{k}' = 2\pi \underline{\tau} - \mathbf{q} \quad (2)$$

In these equations E_0 and E' are the initial and final energies and $\mathbf{k}_0$ and $\mathbf{k}'$ the initial and final wave vectors, respectively, of the neutron, ν is the phonon frequency, $\underline{\tau}$ is any reciprocal lattice vector and $\mathbf{q}$ is the phonon wave vector. The ambiguous sign differentiates between phonon creation (+) and phonon annihilation (-). The existence of the dispersion relation

$$\nu = \nu(\mathbf{q}) \quad (3)$$

causes the coherently scattered neutrons to occur in groups. In order to determine the dispersion relations it is only necessary to measure the quantities involved in Eqs. (1) and (2); it is not necessary to make detailed intensity measurements (but see BROCKHOUSE et al. [1, 2]).

Methods for measuring the dispersion relations have been discussed in detail by BROCKHOUSE [3] and involve either neutron choppers plus time-of-flight, or crystal spectrometers. The crystal spectrometer method has a distinct advantage, particularly for single crystal work, because of its constant momentum transfer mode of operation which greatly facilitates accumulation and interpretation of the experimental data.

This paper is mainly a discussion of such experimental results obtained over the last few years at Chalk River. The Born - von Kármán theory and specific dynamical models are briefly reviewed and then related to the experimental results. The results are also related to various other physical properties of the crystals. The materials specifically discussed are: (1) the pair of metals, lead and sodium, (2) the alkali halides, sodium iodide and potassium bromide, and (3) some molecular compounds such as hexamethylene tetramine and cyclohexane. Other materials such as diamond structure semi-conductors and crystals with ferroelectric properties are discussed in other papers in these proceedings [4, 5].

II. THEORY OF LATTICE DYNAMICS

Introduction

The theory of the lattice dynamics of simple crystals has been extensively treated in the literature in the last twenty-five years. Most calculations have been within the framework of the Born - von Kármán theory formulated many years previously. The essential approximations in this theory are that the atoms in a lattice vibrate harmonically about their equilibrium position and that the electron in the lattice follow the atomic motions adiabatically, that is they are always in equilibrium with their surroundings. The theory has been discussed quite generally by BORN and HUANG [6] but they did not apply it extensively to particular cases. Most of the applications by other workers have been to cubic or hexagonal crystals with one or two atoms per unit cell. Except for a few specific cases, the usual models have involved central forces between first and second neighbours only or similar simple force systems. As will be seen later, such simple systems are very rarely adequate to reproduce the experimental results, particularly the detailed frequency versus wave vector dispersion relations; in most cases, it is necessary to include interactions out to distant neighbours.

Born - von Kármán theory with general forces

In the Born-von Kármán theory of lattice dynamics [6], the equation of motion of the K^{th} atom in the ℓ^{th} unit cell is given by

$$M_K \ddot{U}_x (K; \ell) = \sum_y \sum_{\ell'} \sum_{K'} \Phi_{xy} (KK'; \ell\ell') U_y (K'; \ell'). \quad (4)$$

In this equation M_K is the mass of the atom of type K , U_x is the displacement of the atom from equilibrium and direction x , ℓ indicates the unit cell position and $\Phi_{xy} (KK'; \ell\ell')$ is the force in direction x on the K^{th} atom in the ℓ^{th} unit cell when the K'^{th} atom in the ℓ'^{th} cell is moved unit distance in the y direction. These Φ_{xy} 's are the interatomic force constants. In this paper they will be referred to by $\alpha_1, \beta_1, \alpha_2$, etc. where the subscript indicates the order of the neighbour and the α 's and β 's are convenient labels. The force constant matrices are defined in Table I.

The solution of Eq. (4) can be written in terms of plane waves of frequency (ν), wave vector (q) and polarization vector (ξ_K). The general solutions for eigenfrequencies can be very involved but for symmetric directions in cubic crystals with one atom per unit cell the expression for ν^2 reduces to a simple linear equation. For example, for longitudinal waves propagating along the cube edge ($[100]$ direction) the equations become (assuming interactions out to fifth neighbours)

$$\begin{aligned} 4\pi^2 M\nu^2 = & (8\alpha_1 + 16\beta_4)(1 - \cos[\pi q/q_{\text{max}}]) \\ & + (2\alpha_2 + 8\alpha_3 + 8\alpha_5)(1 - \cos[2\pi q/q_{\text{max}}]) \\ & + (8\alpha_4)(1 - \cos[3\pi q/q_{\text{max}}]) \end{aligned}$$

for a body-centred cubic crystal, and

$$\begin{aligned}
 4 \pi^2 M v^2 = & (8\alpha_1 + 16\beta_3 + 8\beta_5)(1 - \cos[\pi q/q_{\max}]) \\
 & + (2\alpha_2 + 8\alpha_3 + 8\alpha_4)(1 - \cos[2\pi q/q_{\max}]) \\
 & + 8\alpha_5(1 - \cos[3\pi q/q_{\max}])
 \end{aligned}$$

for a face-centred cubic crystal. Similar linear relations exist for the other symmetric branches.

TABLE I

FORCE CONSTANT MATRICES FOR BODY-CENTRED CUBIC
AND FACE-CENTRED CUBIC LATTICES FOR INTERACTIONS
OUT TO FIFTH NEIGHBOURS

Body-centred cubic		Face-centred cubic	
Atom position	Force constant matrix	Atom position	Force constant matrix
$\frac{a}{2}(1, 1, 1)$	$ \begin{bmatrix} \alpha_1 & \beta_1 & \beta_1 \\ \beta_1 & \alpha_1 & \beta_1 \\ \beta_1 & \beta_1 & \alpha_1 \end{bmatrix} $	$\frac{a}{2}(1, 1, 0)$	$ \begin{bmatrix} \alpha_1 & \gamma_1 & 0 \\ \gamma_1 & \alpha_1 & 0 \\ 0 & 0 & \beta_1 \end{bmatrix} $
$\frac{a}{2}(2, 0, 0)$	$ \begin{bmatrix} \alpha_2 & 0 & 0 \\ 0 & \beta_2 & 0 \\ 0 & 0 & \beta_2 \end{bmatrix} $	$\frac{a}{2}(2, 0, 0)$	$ \begin{bmatrix} \alpha_2 & 0 & 0 \\ 0 & \beta_2 & 0 \\ 0 & 0 & \beta_2 \end{bmatrix} $
$\frac{a}{2}(2, 2, 0)$	$ \begin{bmatrix} \alpha_3 & \gamma_3 & 0 \\ \gamma_3 & \alpha_3 & 0 \\ 0 & 0 & \beta_3 \end{bmatrix} $	$\frac{a}{2}(2, 1, 1)$	$ \begin{bmatrix} \alpha_3 & \delta_3 & \delta_3 \\ \delta_3 & \beta_3 & \gamma_3 \\ \delta_3 & \gamma_3 & \beta_3 \end{bmatrix} $
$\frac{a}{2}(3, 1, 1)$	$ \begin{bmatrix} \alpha_4 & \delta_4 & \delta_4 \\ \delta_4 & \beta_4 & \gamma_4 \\ \delta_4 & \gamma_4 & \beta_4 \end{bmatrix} $	$\frac{a}{2}(2, 2, 0)$	$ \begin{bmatrix} \alpha_4 & \gamma_4 & 0 \\ \gamma_4 & \alpha_4 & 0 \\ 0 & 0 & \beta_4 \end{bmatrix} $
$\frac{a}{2}(2, 2, 2)$	$ \begin{bmatrix} \alpha_5 & \beta_5 & \beta_5 \\ \beta_5 & \alpha_5 & \beta_5 \\ \beta_5 & \beta_5 & \alpha_5 \end{bmatrix} $	$\frac{a}{2}(3, 1, 0)$	$ \begin{bmatrix} \alpha_5 & \delta_5 & 0 \\ \delta_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{bmatrix} $

Born von Kármán theory with central forces

In the models discussed above, no restrictions have been placed on the nature of the interatomic forces, and the number of independent force constants depends only on the symmetry of the atoms in question. If, however, there are specific assumptions made concerning the nature of the interatomic forces, then there may exist relationships between the force constants. In particular, for the case of central forces, where the interaction between two atoms is described by a potential, V , a function only of their distance, r , apart, these relationships reduce the number of independent force constants to two per atom. Thus, for first neighbour interactions in a face-centred cubic lattice, Eq. (29.3) of [6] leads to $\alpha_1 - \beta_1 = \gamma_1$; other relationships are readily derived. In addition, the conditions for the crystal to be in equilibrium under central forces, given by Eq. (29.8) and (29.17) of [6], further reduce the number of independent force constants. The first condition determines the structure of the unit cell and is automatically satisfied for the simple structures which we are considering since every atom is at a centre of symmetry. The second condition (29.17) states that there is no net force on any single atom; it essentially determines the size of the unit cell. For interactions out to fifth neighbours, this condition reduces to

$$\alpha_1 - \beta_1 + \beta_2 + 4\beta_3 + 11(\beta_4 - \gamma_4) + 4(\alpha_5 - \beta_5) = 0$$

for a body-centre cubic lattice, and to

$$\beta_1 + \beta_2 + 6(\beta_3 - \gamma_3) + 4\beta_4 + 10\gamma_5 = 0$$

for a face-centred cubic lattice. Thus, in the case of central forces, there are $(2n-1)$ independent force constants, where n is the number of neighbours considered.

Specific models

The models discussed above make no explicit assumptions about the detailed functional form of the interatomic forces. Several calculations based on particular force models have been carried out and applied to various substances; the alkali halides and some monovalent metals are examples.

KELLERMANN [7] made calculations on sodium chloride taking into account directly the electrostatic interactions in addition to short range repulsive forces between the ions. This model did not take into account the polarizability of the ions. Subsequently, a model proposed by DICK and OVERHAUSER [8] was applied to lattice dynamics by COCHRAN [9] to take the polarizability of the ions into account in a particularly simple way. This model was used [10] to calculate the $\nu(q)$ dispersion relations for sodium iodide and to compare these calculations with experiment. In its simplest form this model pictured each ion as a central hard core surrounded by a shell consisting of the outermost electrons. The shell and core have the same equilibrium positions but can move relative to one another. The adiabatic approximation is retained in the equations of motion by setting the

mass of the shell of electrons equal to zero. This model can be regarded as the first approximation (dipole approximation) in a more general theory in which distortions of the electronic configuration are represented by a series of electric multipole moments. In its more complicated forms the dipole approximation has been applied with considerable success to both ionic crystals [11] and to semi-conductors [12, 4]. Somewhat similar developments have been carried out by TOLPYGO and co-workers [13] and by HARDY [14].

TOYA [15] has made some basic calculations which he applied to sodium. He attempted to calculate directly the contribution of the electron-phonon interaction to the interatomic potential. The resulting $\nu(q)$ dispersion relations have previously been shown to agree quite well with experiment [16].

III. LATTICE VIBRATIONS, EXPERIMENTAL

Metals

The two metals, lead and sodium, have been studied and compared quite extensively over a considerable range of temperature. These metals are very different in many of their properties and their intercomparison is quite instructive. Lead has four valence electrons and a high electron-phonon interaction; it becomes a superconductor at the relative high temperature of 7°K. Sodium, on the other hand, has a single valence electron which appears to be almost free. Its lattice structure (body-centred cubic) is more open than that of lead (face-centred cubic) and it is not known to become superconducting. The elastic constants for the two metals also lead to some interesting considerations. One of the conditions for interatomic forces to be central [6] is that the Cauchy relation ($C_{12} = C_{44}$) be satisfied. For lead $C_{12} > 2C_{44}$ both at 300°K and 4.2°K [17] whereas for sodium C_{12} and C_{44} are within 15% of each other [18, 19], probably at all temperatures. Thus the interatomic forces in lead cannot be derived from a potential $V = V(r)$, but the elastic constants do not preclude the possibility that such a potential is a good approximation for sodium. The consequences of this relation to the Born-von Kármán theory of lattice dynamics will be discussed later.

Dispersion curves for lead and sodium at low temperatures

Measurements of the dispersion curves for both lead and sodium in the principal symmetry directions have previously been reported [20, 16]. Measurements have been made in the symmetric $[00\bar{1}]$, $[\bar{1}\bar{1}0]$ and $[\bar{1}\bar{1}\bar{1}]$ directions. These curves are illustrated in Fig. 1 (lead at 100°K) and Fig. 2 (sodium at 90°K) and their comparison shows some striking features. Some of the more obvious differences, such as the degeneracies at various zone boundaries and the unusual shape of the Na $[\bar{1}\bar{1}\bar{1}]$ L branch, are consequences for the crystal structures. In addition to phonons propagating in the three principal directions, other symmetric modes (eg. those labelled $[\bar{1}\bar{1}0]$ for lead), and also non-symmetric modes, were measured for both lead and sodium.

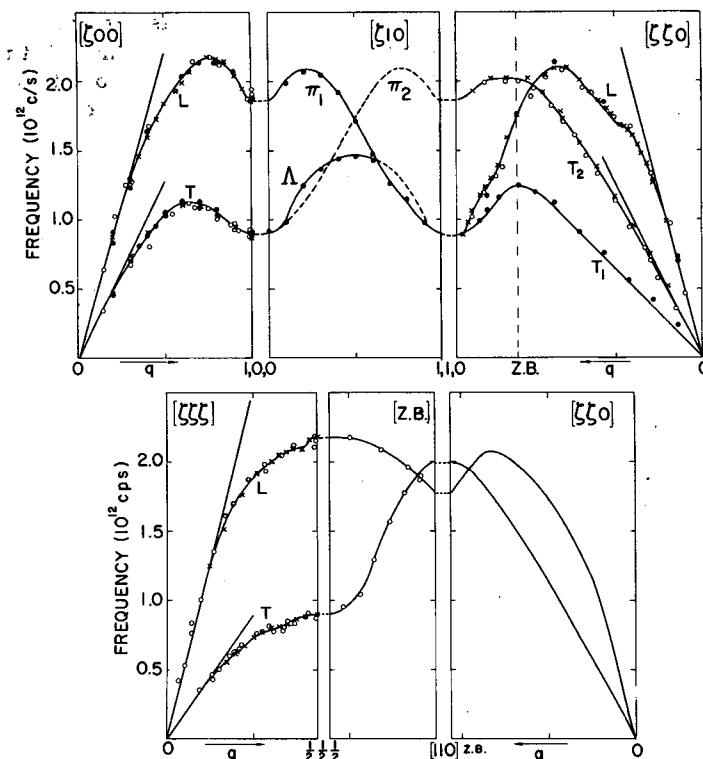


Fig.1

The dispersion curves for the lattice vibrations in lead measured at 100° K.

The dispersion curves show some gross features which emphasize the difference between the two metals. Of special interest in the lead results are the pronounced dips for $[00\zeta]$ L and T branches. A qualitative interpretation of these shapes in terms of the Born-von Kármán theory of lattice dynamics shows immediately that the effect of distant neighbours is important. The dip in the $[00\zeta]$ L branch is the more spectacular one and the analysis of it in terms of a Fourier series (FOREMAN and LOMER [21], BROCK HOUSE *et al.* [20]) indicates that the forces are significant as far as the thirteenth neighbour, at least. Similarly the shapes of the $[\zeta\zeta\zeta]$ L and $[\zeta\zeta 0]$ L branches imply extremely long range forces. On the other hand, the $[00\zeta]$ and $[\zeta\zeta 0]$ branches for sodium are qualitatively similar to simple sine curves and hence imply no obvious long range interactions. Detailed analysis of these curves do, however, indicate that forces out to about fifth neighbours are necessary to fit the finer details of the curves.

The analysis for both the lead and sodium data was carried out as described previously for lead [20]; the squares of the frequencies were fitted to a Fourier series of the form

$$4\pi^2 M v^2 = \sum_{\pi}^N \Phi_n (1 - \cos n\pi\zeta/\zeta_{\max})$$

where, for the symmetry directions in simple materials such as these, the Φ_n are linear combinations of the interatomic force constants. If the value of N (the number of terms in the Fourier series) necessary to obtain an adequate fit to the data is sufficiently small, then the number of interatomic

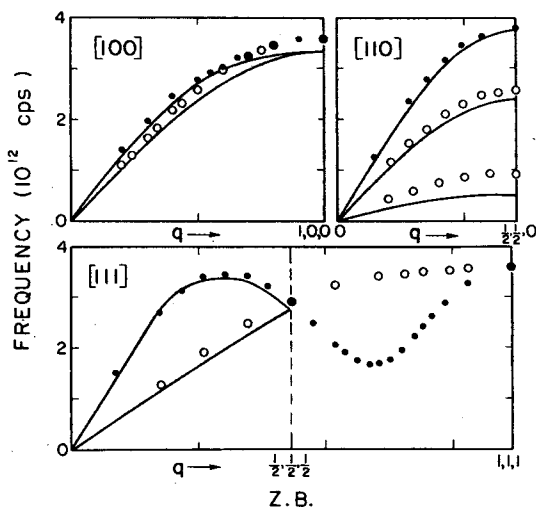


Fig. 2

The dispersion curves for the lattice vibrations in sodium measured at 90° K.

- Longitudinal -- Toya
- Transverse

force constants involved is also small, and they may be deduced from a system of simultaneous linear equations. For the case of sodium this is possible, and the values for the interatomic force constants are shown in Table II. These have been calculated under the assumptions of both and general forces out to fifth neighbours. The central force model gives very nearly as good a fit as does the general force model. For lead, on the other hand, the Fourier series analysis shows that the forces extend beyond fifth neighbours and hence the number of interatomic force constants involved is too large for this analysis to be carried out. The analysis could be done if more independent $\nu(q)$ information were available. Methods for doing this have been described by BROCKHOUSE [3].

The analysis of these dispersion curves in terms of the Born von Kármán theory is unsatisfactory for lead and a new approach is therefore desirable. KOHN [22] has predicted that a discontinuity in the slope of a dispersion curve for a metal should occur for those values of the wave vector, q , given by the equation (for free electrons)

$$2 K_F = |2\pi \underline{\tau} + \underline{q}|$$

where K_F is the radius of the Fermi surface. Such an effect is expected to be small except possible in those metals which have a high electron-pho-

TABLE II

FORCE CONSTANTS (UNITS DYNES/CM) CALCULATED
FROM MEASURED DISPERSION CURVES.
ESTIMATED PROBABLE ERROR IS ± 10 EXCEPT
WHERE INDICATED

Force constant	General forces	Central forces
$\alpha_1, < x, x >$	1178	1173
$\alpha_1, < x, x >$	1320	1319
$\alpha_2, < x, x >$	472 ± 30	431 ± 20
$\beta_2, < y, y >$	104 ± 30	110 ± 20
$\alpha_3, < x, x >$	-38	-47
$\beta_3, < z, z >$	-0.4 ± 30	20
$\gamma_3, < x, y >$	-65	-67
$\alpha_4, < x, x >$	52 ± 20	44
$\beta_4, < y, y >$	-7	0.5
$\gamma_4, < y, z >$	3	5
$\delta_4, < x, y >$	14	16
$\alpha_5, < x, x >$	17	17
$\beta_5, < x, y >$	33	17

non interaction. Lead has a high superconducting temperature and hence probably satisfies the conditions for a large Kohn effect. It is believed [23] that the abrupt changes in the shape of the $[\xi\xi 0]$ L near $aq/2\pi = 0.45$ and $[\xi\xi\xi]$ L near $aq/2\pi = 0.75$ are indeed these anomalies, and that the pronounced dip in the $[00\xi]$ L branch near the zone boundary is also connected with this effect. The existence of these anomalies implies extremely long range forces; the Fourier series analysis of the dispersion curves for a metal may be an effective method for their initial detection. The positions of these anomalies leads to information about the shape of the Fermi surface.

Similar effects have been sought in the dispersion curves of sodium but no evidence for their existence has been seen. Thus the effects seems to be much smaller than in lead. This is not unexpected since the electron-phonon interaction in sodium is probably much smaller. The small size of these anomalies in sodium is also reflected by the fact that the Fourier series analysis reveals no strong long range forces.

As indicated above, analysis based on the Born-von Kármán theory is quite profitable in the case of sodium, and the fifth neighbour fits for both central and general force models are within the experimental errors. The good fit for the central force model suggests that it might be instructive to derive an interatomic potential [24] whose derivatives are related to the force constants (29.3 of [6]). This will not be accurate since the condition on the elastic constants, $C_{12} = C_{44}$, is not satisfied exactly; hence a comp-

licated and detailed fit to a potential curve is not justified. A simple two-term potential of the form

$$V = Ar^{-n} - Br^{-m}$$

was fitted to the force constants for the first three neighbours for selected pairs of values of m and n . The values $m = 3.5$ and $n = 7$ gave roughly the best fit. This potential function is shown in Fig. 3.

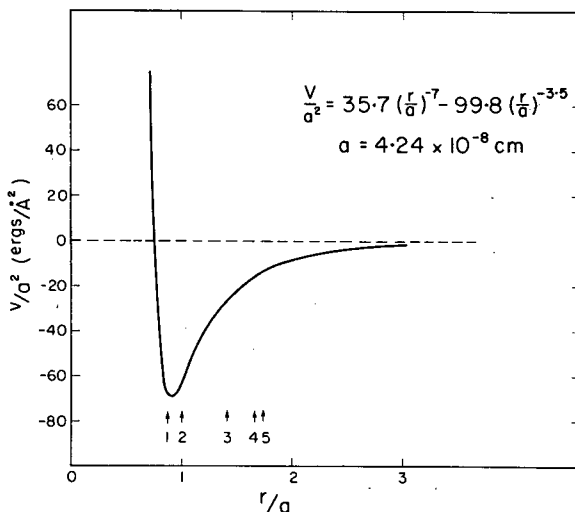


Fig. 3

A simple interatomic potential for sodium fitted to the force constants for the first three neighbours. The positions of the first five neighbours are indicated by the small arrows.

An attempt was made to use this simple potential to calculate several of the other properties of the sodium lattice. If the only change with temperature is the positions of the atoms on the potential curve, that is, if the shape of the curve itself does not change with temperature, then it should be possible to calculate quantities like the change in compressibility and of phonon frequency with temperature. Such calculations give results which are only in qualitative agreement with observation; calculated changes in the elastic constants between 90° K and 296° K are typically about 70% of the observed changes.

The fifth neighbour general force model was also used by DIXON *et al.*, [25] to calculate the frequency distribution function ($g(\nu)$) for sodium at 90° K . Frequencies were calculated, using the Chalk River Bendix G-20 computer, for 23821 points in the irreducible volume in Q space ($1/48$ of the full Brillouin one). A frequency interval of $\Delta\nu = 0.04 \times 10^{12}$ cycles/s was used. The resulting frequency distribution is shown in Fig. 4. Several interesting features are to be noted: (1) The sharp change in slope just below $\nu = 1.0$ is probably real. The frequency corresponds with that of the $[\zeta\zeta 0]$ T_1 branch as it approaches the zone boundary; (2) Critical points are also

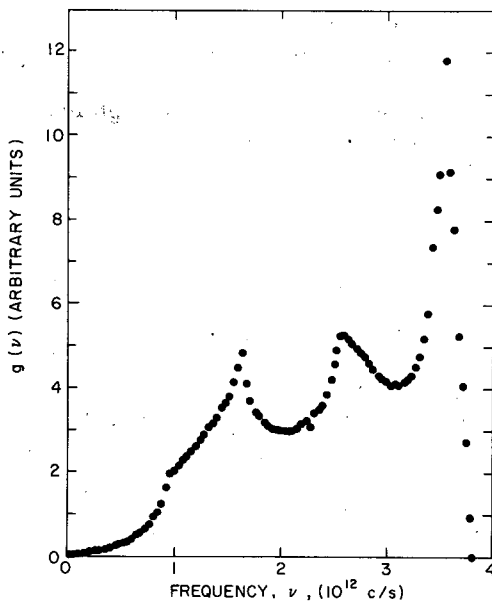


Fig. 4

The frequency distribution function for sodium calculated from the parameters of the fifth neighbour general force model which was fitted to the neutron data. Phonon frequencies were calculated at 23821 positions in $1/48$ of the Brillouin zone.

apparent near $\nu = 1.65$ (this is near the minimum in the $[\xi\xi\xi]$ L branch), $\nu = 2.56$ ($[1/2, 1/2, 0]$ T_2), and $\nu = 3.58$ ($[1, 0, 0]$ L and T). It is likely that other critical points are also present, particularly on each side of $\nu = 3.58$.

It is also possible at the present time to carry out a similar calculation for lead because the number of force constants involved is too large for the fit to the $\nu(q)$ data to be performed.

Temperature effects in metals

The effect of temperature changes on the frequencies and lifetimes of phonons has also been investigated for both lead and sodium. The results for lead have indicated that the effect of the long range forces decreases with increasing temperature and that the phonon lifetimes at 425° K are remarkably short [20]. Experiments were also carried out at 5° K and 9° K to see if there was any change in certain specific modes accompanying the onset of superconductivity [26]; none was observed within an accuracy of about 1/4%. In addition, it was shown that the shape of the $[00\xi]$ T branch at 5° K was very similar to that at 100° suggesting that anharmonic effects are small at the higher temperature.

A similar investigation has been carried out for sodium. Because of the martensitic transformation below 35° K, it was not possible to make measurements at very low temperatures. High temperature measurements were made at 215° K and 296° K. The phonon frequencies decreased by a few

per cent and the widths of the neutron groups increased between 90° K and 296° K. The analysis of the neutron line widths into phonon lifetimes was similar to that described for lead [20]. The phonon lifetimes in sodium were difficult to measure because of the high incoherent inelastic background under the peaks. Neutron groups for the mode $[0.3, 0.3, 0] T_2$ are shown in Fig. 5 for temperatures of 90° K and 296° K. The frequency at 296° K

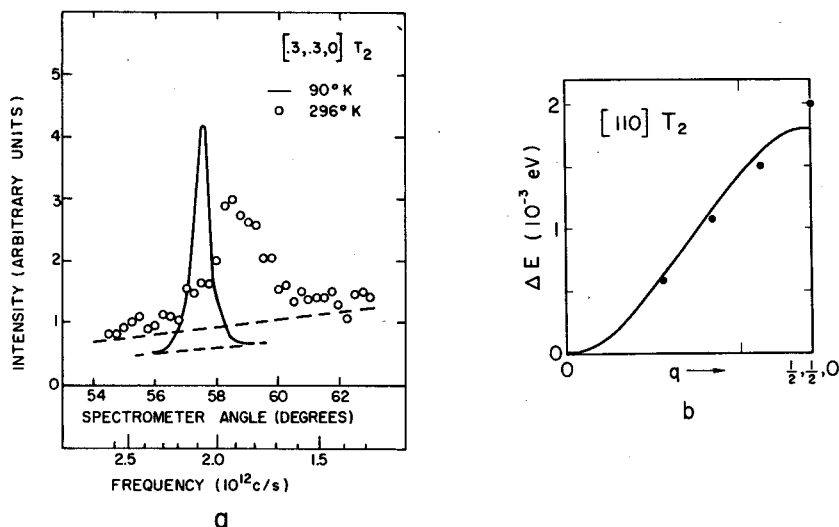


Fig. 5

- (a) Neutron distributions from sodium for the mode $[0.3, 0.3, 0] T_2$, observed at 90° K and 296° K.
 (b) Phonon widths at 296° K using the 90° K distributions as the instrument resolution function.

is slightly lower but the change in width of the neutron group is quite marked. The energy widths as a function of q for the $[\xi\xi 0] T_2$ branch are also shown. This temperature is about three-quarters of the melting temperatures of sodium but the relative lifetime (about two vibrational periods) is considerably longer than that for the $[0, 0, 1] T$ mode in lead at 425° K (less than one vibrational period at two-thirds of the melting temperature). The solid curve is the simple cosine curve which might be expected on the basis of the discussion given previously [20].

Alkali halides

A programme for the study of ionic crystals has resulted in the determination of the complete dispersion curves for the principle symmetry directions in sodium iodide and potassium bromide. The results for the $[00\xi]$, $[\xi\xi 0]$ and $[\xi\xi\xi]$ directions of sodium iodide [10, 11] are shown in Fig. 6. Similar results have been obtained for potassium bromide [27]. All of the data for KBr and the more recent of the data for NaI were obtained using the constant Q method [3]. The dashed lines have been derived using the BORN-KELLERMANN (point ion) model [7]. Substantial improvement in the agreement between experiment and theory can be obtained by taking into account the polarizability of the ions as discussed earlier. The solid

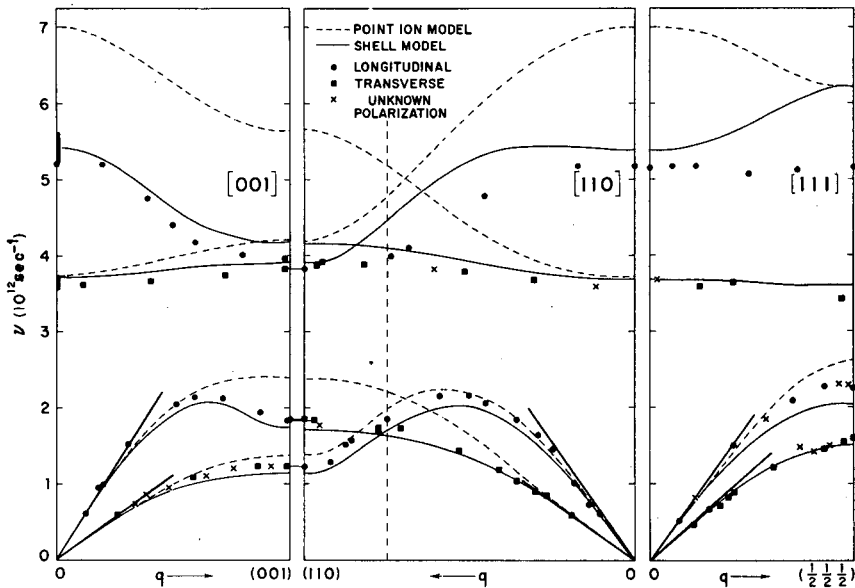


Fig. 6

The dispersion curves for sodium iodide for the three principal symmetry directions.

line in Fig. 6 illustrates this for the case of sodium iodide [10]. This simple model took account of the polarizability of the large negative iodine ion only and was not able to give a good fit to all of the data, particularly for the $[111]$ longitudinal optical (LO) branch. Subsequent refinements of the model [11, 28] took into account first and second neighbours short range forces, variable ionic charge and variable polarizability (of both ions). This model gave fits to the data for both NaI and KBr which were well within the experimental error. Some of the parameters in this model, however, have values which appear unreasonable for a simple physical picture of the shell model as a description of the dynamical behaviour of the crystal. This is perhaps a reflection of the need for including higher order multipoles in the calculations, particularly for discussing certain branches, such as $[111]$ LO.

This model with the best fit parameters, and the simple shell model were then compared with the experimental measurements of some phonons in non-symmetric directions in KBr. The comparison which is shown in Fig. 7 definitely favours the more complicated model.

Also of importance in these results is the agreement between the ratio of the longitudinal optical (LO) and transverse optical (TO) modes at $q = 0$ and the ratio calculated from the expression (LYDDANE *et al.* [29])

$$(\nu_{LO}/\nu_{TO})_{q=0}^2 = \epsilon_0 / \epsilon$$

where ϵ_0 and ϵ are the low and high frequency dielectric constants. The agreement for both sodium iodide and potassium bromide is within the experimental error.

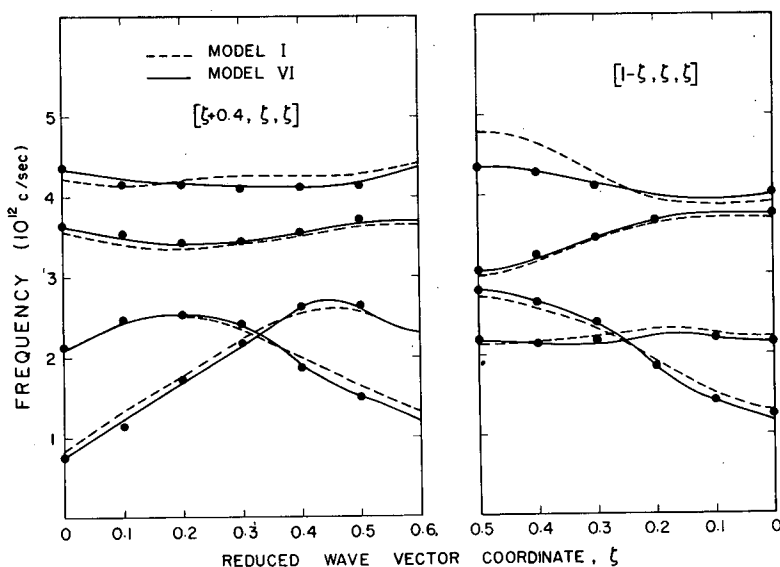


Fig. 7

The $[\zeta+0.4, \zeta, \zeta]$ and $[1-\zeta, \zeta, \zeta]$ branches in KBr at 90°K .
The dashed lines have been calculated from the "simple" shell model
and the solid line from the "best" shell model.

One of the outstanding problems connected with these measurements is the behaviour of the longitudinal optical phonons, particularly those of small wave number. In the original sodium iodide report [10] it was noted that the behaviour of these LO modes had some peculiar characteristics; well defined neutron groups were not observed but instead the groups were broad and their width appeared to increase with decreasing q . The experiment suffered from two major disadvantages: (1) as the neutron energy transfer was varied the momentum transfer (Q) also varied and (2) the large incoherent scattering from the sodium produced a peak in every energy distribution corresponding to the energy of the almost flat transverse branches, and thus contaminated all the useful peaks due to coherent scattering. Subsequent experiments, using potassium bromides as the specimen and the constant Q crystal spectrometer, largely overcame both of these difficulties. The resulting neutron groups for the LO phonons were now quite well defined but their widths were still greater than expected and appeared to increase as $q \rightarrow 0$. Furthermore, measurements using the original sodium iodide specimen and the constant Q spectrometer gave results which were still unsatisfactory. A new sodium iodide specimen with a mosaic spread of about 0.1° was used under similar conditions (the original sodium iodide crystal had a mosaic spread of about 1.3°), and results similar to those observed for KBr were obtained. The results for the LO modes shown in Fig. 6 were obtained with this specimen. In addition some acoustical modes were also remeasured with this specimen and are included in Fig. 6; no significant difference was observed between the two specimens for the acoustical modes. Thus we are forced to the conclusion that the behaviour of the LO modes of

small wave numbers is sensitive to the specimen characteristics. Analysis of the original specimen showed no impurities thought likely to cause trouble.

It was felt that the temperature dependence of the widths of the neutron groups, in particular those for the LO modes, might give some valuable information. Several LO modes along the $[\xi\xi\xi]$ direction in KBr were chosen for detailed study; these were $[0, 0, 0]$ LO, $[0.1, 0.1, 0.1]$ LO and $[0.37, 0.37, 0.37]$ LO. Measurements were carried out at 8° K, 90° K, 200° K, 296° K, and 400° K. The neutron groups all showed significant broadening between 8° K or 90° K and 200° K and were much broader at higher temperatures. The groups for the mode $[0.1, 0.1, 0.1]$ LO obtained at 8° K and 200° K shown in Fig. 8 illustrate this broadening. By contrast, the acoustical modes

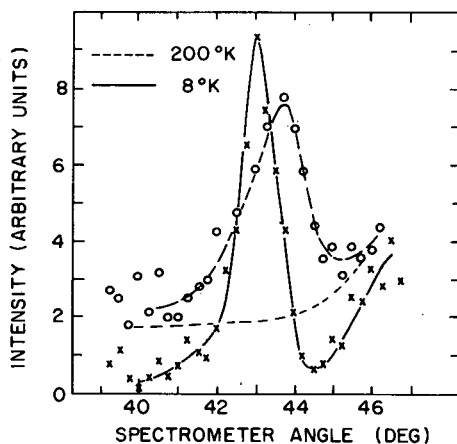


Fig. 8

Neutron distributions from potassium bromide for the mode $[0.1, 0.1, 0.1]$ LO observed at 8° K and 200° K.

show no detectable broadening and the transverse optical modes only very slight broadening at temperatures of 400° K.

It thus appears that there is real temperature dependent energy broadening for the LO modes even at low temperatures. For one specimen at least (the original sodium iodide), the odd behaviour of these LO modes is more pronounced. This is not understood but it possibly depends on the crystal history. It is hoped to study this aspect further. The other principal features of the dispersion curves have been satisfactorily fitted by the dipole approximation model discussed above. In addition this model was used to calculate the frequency distribution function and the specific heat of both NaI and KBr. Good agreement with the measured specific heat and Debye temperature were obtained [28].

Molecular compounds and other materials

Another class of experiments which has recently been carried out has been concerned with the behaviour of more complex molecular systems.

Some of these involving hydrogen vibrations have already been reported [30]. Recently BECKA [31] has studied hexamethylenetetramine (HMT) powder to look for peaks in the frequency distribution. In addition, he has investigated the effects of phase transitions on molecular motions in globular compounds [32]. These experiments were mostly done using the rotating crystal spectrometer [3].

Fig. 9 shows a neutron energy distribution obtained [31] from scattering 4.06 Å neutrons from a sample of HMT at 80°K and 300°K. Peaks are

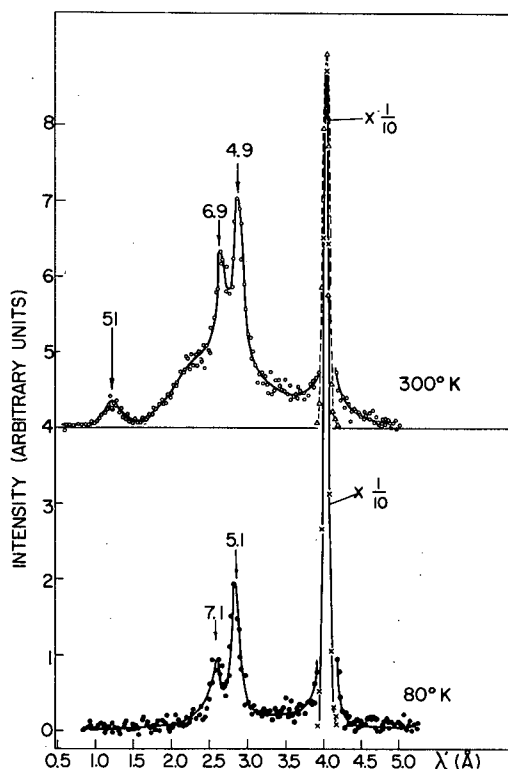


Fig. 9

Wavelength distributions of initially 4.06 Å neutrons scattered from hexamethylenetetramine at 300°K and 80°K.

apparent at 5.7 and 51 meV. These probably correspond to peaks in the frequency distribution function and are consistent with inferences drawn from other data [31].

The distribution of neutrons scattered from the globular compounds cyclohexane, 2-2-dimethylbutane and 1-4-diazobicyclo-(2.2.2)-octane (DABCO) has been used [32] to determine some aspects of the dynamical behaviour of these compounds above and below transition temperatures. Both cyclohexane and 2-2-dimethylbutane show a broadened elastic peak above the transition temperature which becomes narrower as the angle of scattering decreases. This has been interpreted as evidence of "quasi-free

rotation" above the transition temperature. The disappearance of well defined inelastic peaks above the transition temperature has been interpreted as evidence of dynamical disorder in the high temperature phase. The third material, DABCO, showed none of these effects.

An interesting substance which has recently been studied by DOLLING and BROCKHOUSE [33] is pyrolytic graphite which consists of approximately parallel hexagonal planes, randomly oriented about the c-axis. The dispersion curve for the longitudinal vibrations propagating the c-axis has been measured and yields results which are in good agreement with the measured elastic constant C_{33} .

IV. SUMMARY

This paper has been a short report on the work on the lattice dynamics of crystals which has been carried out at Chalk River over the last four years. Aspects of this work not discussed are reported in other papers in those proceedings [2, 4, 5]. The paper has attempted to show how the current theories on lattice dynamics are related to the experimental measurements which have so far been carried out.

ACKNOWLEDGEMENTS

The author is sincerely grateful for the opportunity of participating in this work under the guidance of Dr. B.N. Brockhouse who has been a constant source of inspiration throughout. It has also been a pleasure to work with his other collaborators of the past four years, T. Arase, L.N. Becka, R. Bowers, G. Caglioti, W. Cochran, R.A. Cowley, B.A. Dasannacharya, A.E. Dixon, G. Dolling, D.G. Henshaw, R.H. March, K.R. Rao, M. Sakamoto, R.N. Sinclair, A.T. Stewart and H. Watanabe. Mr. E.A. Glaser and many others have given invaluable technical assistance.

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DISCUSSION

B. BURAS: In your paper you show dispersion curves for lead which include "kicks" that are supposed to be responsible for the Kohn effect. Does this mean that the "kicks" are found at places where they would be expected to occur, e.g. on the basis of calculations of the Fermi surface?

A.D.B. WOODS: This depends on what you believe to be the right place. The "kicks" are consistent with and sometimes complementary to data available from other experiments, such as Gold's measurements using the de Haas-van Alphen effect.

N.A. TCHERNOPLEKOV: I would like to ask how much justification there is for making a dispersion curve analysis by Fourier's method. As you know, this problem should be considered as a non-linear one, owing to electron-phonon interaction. However, the Fourier analysis is an analysis in linear approximation. The appearance of anomalies of the Kohn type in the present case doubtless means that we should take a very large number of Fourier components in order to plot a dispersion curve.

A.D.B. WOODS: That is quite correct. I might mention that the curves for sodium were based on calculations done by Toya which took direct account of the electron-phonon interaction. The Fourier analysis is just one way of expressing the results. You can analyse any curve you like in a series of this sort. Whether you believe that these coefficients have physical significance in terms of interatomic force constants is a matter of interpretation. In the case of sodium, oddly enough, the electron-phonon interaction is very small, so that the effects you are talking about will not make very much difference. In lead, however, the interatomic forces are of very long-range nature and we do not have the data to solve for them.

N.A. TCHERNOPLEKOV: It seems to me that where we are dealing with a linear problem, the Fourier coefficient has a definite physical meaning, but where the problem is non-linear, it is difficult to give it such a meaning. Secondly, I would like to draw the attention of the author and all those interested in this question to the fact that in the Soviet Union Kagan has considered this problem of phonon-electron interaction for the general type of Fermi surface. He has obtained interesting results showing that the nature of the singularities depend considerably on the nature of the surface, e.g. whether the surface is cylindrical or flat. Altogether, the appearance of open Fermi surfaces leads to different types of these singularities. Sometimes they may be such that a considerable increase in the resolving power of our experimental equipment is necessary in order to be able to observe them. So in cases where we do not observe them we cannot yet state firmly that this is due to the fact that they are absent; perhaps we have not discovered them yet.

A.D.B. WOODS: We are not saying that they are absent in sodium but merely that they are smaller than we are able to observe at the moment.

J.J.J. KOKKEDEE: For the same reason that there are singularities in the dispersion curve for phonons in metals (Kohn effect), there should also be a broadening of the one-phonon peaks due to electron-phonon coupling. One would in fact expect an abrupt change in the line width for those values of the phonon wave vector $\underline{q}$ which satisfies $|\underline{q} + 2\underline{\pi} \underline{\tau}| = 2K_F$, where $\underline{\tau}$ is any reciprocal lattice vector and K_F is the Fermi momentum. Have you found any indication of this effect in your experiments?

A.D.B. WOODS: We have seen no abrupt changes in peak width.

DETERMINATION OF POLARIZATION VECTORS FROM NEUTRON GROUP INTENSITIES

B. N. BROCKHOUSE*, L. N. BECKA**, K. R. RAO*** AND A. D. B. WOODS
ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

DETERMINATION OF POLARIZATION VECTORS FROM NEUTRON GROUP INTENSITIES. The constant Q method for measuring the neutron groups produced in one-phonon scattering offers promise of obtaining intensities sufficiently accurate to permit experimental determination of the polarization vectors of the normal modes and hence the interatomic forces in the crystal. Experiments on sodium have been carried out to determine the polarization vector of modes at several off-symmetry positions in a (110) plane. The directions, good to about 3° , were in satisfactory agreement with vectors calculated from a force constant model deduced from the results in symmetry directions. Experiments have been carried out on germanium in which the line intensities of 25 selected neutron groups, corresponding to modes for which the polarization vectors are fixed by symmetry, were studied. When corrected for the various specific factors (frequency, wave vector transfer Q , population factor etc.) involved, the intensities showed a residual disagreement (R-factor) of 7.3%. Measurements at simple non-symmetry positions showed apparent differences from inelastic structure factors calculated on a first neighbour model. The results to date are still not sufficiently accurate, but offer promise. Accurate determination of the backgrounds under the peaks seems to be the major experimental difficulty.

DÉTERMINATION DES VECTEURS DE POLARISATION A PARTIR DES INTENSITÉS DE GROUPES DE NEUTRONS. La méthode du Q constant employée pour la mesure des groupes de neutrons produits dans une diffusion à un phonon semble devoir permettre d'obtenir des valeurs suffisamment précises des intensités et de déterminer expérimentalement les vecteurs de polarisation des modes normaux ainsi que, par conséquent, les forces interatomiques du cristal. Des expériences ont été faites dans le sodium pour déterminer les vecteurs de polarisation de modes pour plusieurs positions asymétriques dans un plan (110). Les directions, bonnes jusqu'à 3° environ concordent assez bien avec les vecteurs calculés à partir d'un modèle à constante de force déduit des résultats relatifs aux directions symétriques. Des expériences ont été faites avec du germanium dans lequel les intensités des raies de 25 groupes de neutrons choisis correspondant aux modes pour lesquels les vecteurs de polarisation sont fixés par symétrie, ont été étudiées. Après la correction due aux divers facteurs spécifiques (fréquence, transfert de vecteurs d'onde Q , facteur de polarisation, etc.) les intensités présentent un écart résiduel (facteur R) de 7,3%. Les mesures faites pour des positions asymétriques simples montrent des différences évidentes par rapport aux facteurs de structure inélastique calculés en se fondant sur le modèle des forces limitées à deux atomes voisins. Les résultats ne sont pas encore suffisamment précis à ce jour, mais ils paraissent prometteurs. La détermination précise du bruit de fond sous les pics semble constituer la difficulté expérimentale essentielle.

ОПРЕДЕЛЕНИЕ ВЕКТОРОВ ПОЛЯРИЗАЦИИ ПО ГРУППОВОЙ ПЛОТНОСТИ НЕЙТРОНОВ. Метод постоянной Q для измерений нейтронных групп, образовавшихся при одно-фононном рассеянии, предоставляет возможность получения плотности с достаточной точностью в целях экспериментального определения векторов поляризации нормальных видов и, следовательно, межатомных сил в кристалле. Эксперименты на натрии были проведены для определения вектора поляризации видов для нескольких внесимметричных положений в плоскости 110. Направления в пределах около 3° были в удовлетворительном согласии с векторами, вычисленными на основании постоянной силовой модели, выведенной из данных по симметрическим направлениям. Были изучены результаты экспериментов, проведенных на германии, в котором имелась линия плотности 25 отобранных нейтронных групп, соответствующих тем видам, для которых

* Now at Physics Department, McMaster University, Hamilton, Ontario, Canada.

** National Research Council (Canada) Fellow. Now at University of Buenos Aires.

*** Visiting scientist from Atomic Energy Establishment, Trombay, Bombay, India, now returned.

векторы поляризации определяются симметрией. Когда были внесены поправки согласно различным специфическим коэффициентам (частота, волновой вектор передачи Q , коэффициент популяции и т.д.), плотности продемонстрировали остаточную несогласованность (R -коэффициент) порядка 7,3%. Измерения простых несимметричных положений показали явные отличия от неупругих структурных коэффициентов, вычисленных на первой соседней модели. Полученные данные являются не очень точными, но перспективными. Точное определение фонов ниже внешних точек представляет большие экспериментальные трудности.

DETERMINACIÓN DE LOS VECTORES DE POLARIZACIÓN A PARTIR DE LA INTENSIDAD DE GRUPOS NEUTRÓNICOS. El método de Q constante para medir los grupos de neutrones producidos en la dispersión de un fonón parece ofrecer la posibilidad de obtener intensidades lo suficientemente precisas para poder determinar experimentalmente los vectores de polarización de los modos normales y, en consecuencia, las fuerzas interatómicas de un cristal. Se han realizado experimentos con sodio para determinar el vector de polarización de modos correspondientes a varias posiciones asimétricas del plano (110). Las direcciones, determinadas con una precisión de 3', concuerdan satisfactoriamente con los vectores calculados en función de un modelo de fuerza constante, deducido de los resultados obtenidos en las direcciones de simetría. Se han efectuado experimentos con germanio en el curso de los cuales se ha estudiado la intensidad de las líneas de 25 grupos neutrónicos seleccionados, correspondientes a los modos cuyos vectores de polarización están determinados por la simetría. Después de introducir las correcciones correspondientes a los diferentes factores específicos que intervienen (frecuencia, factor Q de transferencia del vector de onda, factor de población, etc.), las intensidades presentan una discrepancia residual (factor R) de 7,3%. Las mediciones efectuadas en posiciones asimétricas simples acusan diferencias aparentes debidas a los factores de estructura inelástica calculados según el modelo de los átomos más próximos. Los resultados obtenidos hasta ahora no son suficientemente exactos, pero parecen prometedores. La determinación precisa del efecto de fondo debajo de los picos parece constituir la mayor dificultad experimental.

I. INTRODUCTION

The current methods of studying crystal dynamics by neutron inelastic scattering utilize only part of the information contained in the neutron energy distributions. The frequency (ν) and wave vector (q) of a normal mode is determined from the energy of a neutron group in the distribution by applying the conservation equations

$$\underline{Q} \equiv \underline{k}_0 - \underline{k}' = 2\pi \underline{\tau} - \underline{q} \quad (1a)$$

$$E_0 - E' = \pm h\nu \quad (1b)$$

where E_0 , E' , $\underline{k}_0$ and $\underline{k}'$ are, respectively, the incoming and outgoing neutron energies and wave vectors, and $\underline{\tau}$ is a vector of the reciprocal lattice. The interatomic forces are determined by fitting the force constants to the measured frequencies. In general, the theoretical expressions for the squares of the frequencies are $3n \times 3n$ determinantal equations, where n is the number of atoms in the primitive unit cell; only in special cases for very simple crystals are the expressions linear in the squares of the frequencies. Consequently, the analysis involves non-linear, least squares fitting, and this introduces serious uncertainty in the results. By studying the intensities of the neutron groups, it should be possible to determine the polarization vectors of the normal modes (ξ_{jk} , the polarization vector of the j -th normal mode for the K -th atom in the primitive unit cell). When both the frequency and polarization vectors of a particular normal mode are known, the theoretical expressions for the "equations of motion in q -space" are linear in

the interatomic force constants, and can be used to determine them. Since the equations are linear, the force constants can be determined unambiguously, without necessity for prior knowledge of their approximate values. Aspects of this subject are discussed in more detail elsewhere [1, 2]. In this paper we present the first measurements of polarization vectors for a few especially simple cases.

II. THEORY OF THE METHOD

The partial differential cross-section [3, 4] (per steradian, per unit energy) of a crystal for production or annihilation of one phonon of the j -th normal mode, can be written

$$G_1^j = \frac{4\pi^2 \hbar}{B} \left\{ \frac{N_j}{N_j + 1} \right\} \frac{k'}{k_0} |g_j(\underline{q}, \underline{\tau})|^2 \delta(\underline{Q} - 2\pi \underline{\tau} + \underline{q}) \delta(E_0 - E' \pm \hbar \nu) \quad (2)$$

where the "structure factor" g is defined as

$$g_j(\underline{q}, \underline{\tau}) = \sum_K^{\text{unit cell}} \frac{b_K \underline{Q} \cdot \underline{\xi}_{jK}}{(M_K \nu)^{1/2}} \exp(-W_K) \times \exp(i \underline{Q} \cdot \underline{R}_K) \quad (2a)$$

and the population factor is defined as

$$N_j(\underline{q}) = \left[\exp(\hbar \nu / k_B T) - 1 \right]^{-1}. \quad (2b)$$

For phonon annihilation the sign in the delta function is positive and N_j is the population factor; for phonon creation a negative sign and $\{N_j + 1\}$ are used. In this expression B is the volume per unit cell, and M_K is the mass, b_K the scattering length, $\exp(-W_K)$ the Debye-Waller amplitude factor, and $\underline{R}_K$ the position vector of the K -th atom in the unit cell. The suitably normalized [5, 6] and possibly complex polarization vectors $\underline{\xi}_{jK}$ give the direction of the motion of the K -th atom, and its phase relative to that of the origin of the unit cell.

In conventional methods a fixed incoming energy is used, and the outgoing energy distribution is measured. The intensity of a neutron group is determined by integrating Eq. (2) over the outgoing neutron energy E' . However, since $E = (\hbar K)^2 / 2m$ and $\nu = \nu_j(\underline{q})$, the two delta functions are not independent and a transformation must be first applied. WALLER and FROMAN [4] have carried out the integration, to first order in the resolution, with the result that the cross-section (per steradian per unit cell) for production of a single neutron group is given by the expression

$$\sigma_j(\underline{k} \rightarrow \underline{k}') = \frac{\hbar^4 k}{4\pi k_0} \left\{ \frac{N_j}{N_j + 1} \right\} \frac{|g_j(\underline{q}, \underline{\tau})|^2}{|J_j|}, \quad (3)$$

where the Jacobian of the transformation is

$$J_j = 1 + \frac{\epsilon h}{2E} (\underline{k}' \cdot \text{grad}_{\underline{q}} \nu)$$

with $\epsilon = +1$ for neutron energy loss (phonon creation) and $\epsilon = -1$ for neutron energy gain, and where the variables now take on the mean values for the neutron groups and Eqs.(1) are satisfied for these mean values. From Eq.(3) it will be seen that the gradient of the dispersion relation $\nu = \nu_j(\underline{q})$ must be known as well as the values ν and $\underline{q}$ themselves, if the intensities are to be utilized.

The constant momentum transfer or "Constant Q" method [2] evades these difficulties. In this method, the angle of scattering ϕ , the crystal orientation ψ , and one of the energies E_0 or E' , are varied simultaneously and non-linearly, in such a way as to keep $Q \equiv k'_0 - k$ at a fixed, desired value. The intensity of a neutron group is then given by the integral over the variable energy of Eq.(2), with $\delta(Q - 2\pi\tau + q)$ now having a constant argument. Thus the integral is easily evaluated, and no transformation is required.

The usual experimental procedure is to use a fixed outgoing energy E , and a variable incoming energy E_0 . If the same fixed E' is used for a series of experiments, and if, in each experiment, the duration of counting at each E_0 is determined by means of a thin monitor counter (having an inverse velocity characteristic) in the incoming beam, then the relative intensities of the neutron groups are independent of the efficiencies of the analysing spectrometer and of the monochromator. To first order in the resolution, the cross-section for production of a single neutron group is given by the simple expression

$$\sigma_j(\underline{k}_0 \rightarrow \underline{k}') = \frac{h}{4\pi} \left\{ \frac{N_j}{N_j + 1} \right\} |g_j(\underline{q}, \tau)|^2. \quad (4)$$

The factor $1/k_0$ in Eq.(2) is cancelled by the inverse velocity dependence of the monitor counter, while the factor k' is merely a constant which is included in the (constant) instrumental efficiency. Because of this independence of instrumental efficiency, the possible accuracy should be greatly enhanced.

By measuring intensities, we obtain the quantity $|g|^2$. It is, however, the polarization vectors $\underline{\xi}_{jk}$ in which we are interested. To obtain them from the measured structure factors $|g|$, we must carry out an analysis somewhat similar to that involved in determining an antiferromagnetic structure. We are assisted by the fact that the $\underline{\xi}$'s satisfy orthonormality relations [5] and sometimes symmetry conditions. Correspondingly, symmetry conditions and "sum rules" apply to the structure factors.

The use of the polarization vectors in determining the interatomic forces has already been discussed elsewhere [1, 2] in a general way. Some specific points will be discussed in the following sections.

III. POLARIZATION VECTORS IN SODIUM

Sodium is body-centred cubic with one atom per primitive unit cell. For any particular $\underline{q}$ the three polarization vectors $\underline{\xi}_j(\underline{q})$ are orthogonal unit

vectors. For $\underline{q}$ in a mirror plane, one of the polarization vectors is normal to the plane and the other two lie in the plane. The mode with its vector normal to the mirror plane does not contribute to scattering at values of $\underline{Q}$ which lie in the plane.

Measurements were made using the "constant $\underline{Q}$ " method with fixed analyser, at several values of $\underline{Q}$ in non-symmetric positions (and at one in a symmetry position) in the (1,1,0) plane. At each value of $\underline{Q}$ two neutron groups, corresponding to the two polarizations, were obtained. One such pattern is shown in Fig.1. Fast neutron background (obtained with the analysing crystal rotated out of the Bragg position) has been subtracted point-by-point from the measurements.

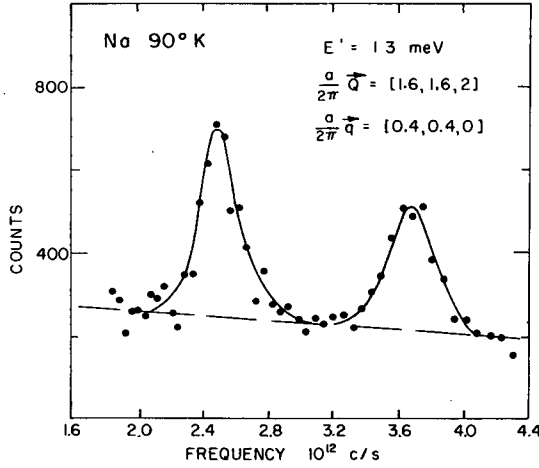


Fig. 1

Neutron groups corresponding to longitudinal and transverse phonons in the symmetric $[\zeta, \zeta, 0]$ directions of the reduced zone ($\zeta = 0.4$), taken using the "constant $\underline{Q}$ " method with fixed analyser. This is a better than average pattern.

From Eq.(4) the ratio of the integrated intensities of the neutron groups is given by the expression

$$\frac{I_1}{I_2} = \left\{ \frac{N_1 + 1}{N_2 + 1} \right\} \frac{(\underline{Q} \cdot \underline{\xi}_1)^2}{(\underline{Q} \cdot \underline{\xi}_2)^2} \frac{\nu_2}{\nu_1}, \quad (5)$$

all other factors in Eq.(4) being constant. If β is the angle between $\underline{Q}$ and a coordinate axis, and α is the angle between $\underline{\xi}_1$ and the same coordinate axis, then α can be determined from the equation

$$\tan^2(\beta - \alpha) = \left\{ \frac{N_1 + 1}{N_2 + 1} \right\} \frac{\nu_2 I_2}{\nu_1 I_1}, \quad (6)$$

where we have used the fact that $\underline{\xi}_1$ and $\underline{\xi}_2$ are orthogonal. The correct one

of the two possible solutions can be determined (a) by making measurements at two or more points, $\underline{Q}$, in reciprocal space corresponding to the same reduced wave vector, $\underline{q}$, or (b) by continuity from known polarization vectors. The results for the measured polarization vectors are given in Fig. 2 and Table I.

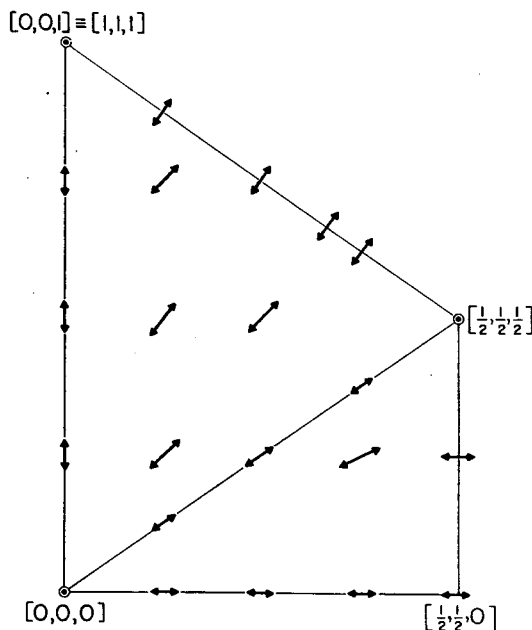


Fig. 2

Polarization vectors in the (110) plane of the reduced zone of sodium,
for the highest frequency mode at the particular $\underline{q}$.

From an extensive series of measurements of the lattice frequencies in sodium, a force constant model was deduced [7]. The model includes forces out to fifth neighbour atoms, and is believed to be a reasonably accurate representation of the harmonic forces in sodium. Using the parameters of this model we have computed the polarization vectors for the modes in Table I and the results are given in the last column. The agreement is within the probable experimental error of two or three degrees.

Sodium is a relatively unfavourable material for these experiments because of the large incoherent scattering background under the neutron groups, and because the appreciable mosaic width of the crystal makes possible multiple scattering effects [8]. The specimen also did not have the cylindrical symmetry desirable. Nevertheless, the results are good enough to make it evident that, with some additional effort, the polarization vectors could be determined with sufficient accuracy for use in the analysis.

IV. POLARIZATION VECTORS IN GERMANIUM

In sodium it has turned out [7] that sufficient information is contained in the symmetry directions alone, to enable the main features of the inter-

atomic force system to be deduced. The frequencies and polarization vectors for other wave vectors were needed only as a check on the validity of the model. Sodium is a rather special case in this respect, however. Usually the symmetric directions alone do not contain nearly enough information to enable the force system to be deduced. Thus in germanium, a rather

TABLE I

THE MEASURED AND CALCULATED ANGLES (α) BETWEEN THE POLARIZATION VECTOR OF THE HIGHEST FREQUENCY MODE AND THE [001] DIRECTION, FOR A FEW WAVE VECTORS

$\frac{\mathbf{a}}{2\pi} \mathbf{q}$	$\frac{\mathbf{a}}{2\pi} \mathbf{Q}$	Measured α	Calculated α
0.4, 0.4, 0	1.6, 1.6, 2	90.0°	90.0°*
1/8, 1/8, 1/4	-1/8, -1/8, 2-1/4	45.2°	45.6°
1/8, 1/8, 3/4	1/8, 1/8, 2-3/4	40.7°	40.2°
1/4, 1/4, 1/2	$\left\{ \begin{array}{l} 1/4, 1/4, 2-1/2 \\ 1-1/4, 1-1/4, 1/2 \end{array} \right.$	$\left\{ \begin{array}{l} 40.6^\circ \\ 47.6^\circ \end{array} \right.$	$\left. \right\} 42.6^\circ$
3/8, 3/8, 1/4	$\left\{ \begin{array}{l} 1-5/8, 1-5/8, 1/4 \\ 3/8, 3/8, 2-1/4 \end{array} \right.$	$\left\{ \begin{array}{l} 69.7^\circ \\ 63.3^\circ \end{array} \right.$	$\left. \right\} 68^\circ$
1/8, 1/8, 1/2	1/8, 1/8, 2-1/2	36.1°	41.4°

* Fixed by symmetry (longitudinal mode).

symmetric crystal, which has the diamond structure with only two atoms per primitive unit cell, there are only two branches (the longitudinal branches in the $[\frac{1}{2}, 0, 0]$ direction) and six other special frequencies which can be used to obtain force constants by linear least squares fitting. However, it is known from previous work [9] that the forces certainly extend beyond fifth neighbours, and thus involve at least nineteen force constants (and probably many more).

The theory of the lattice dynamics of the diamond structure has been given in some detail by H. SMITH [10], and more recently by HERMANN [9], and the relation of the theory to the neutron scattering problem has been discussed [6].

For the symmetry directions, it is convenient to define a reduced structure factor g_0^2 , related to g^2 by the equation

$$g^2 = \frac{b^2(\mathbf{Q} \cdot \mathbf{E}_j)^2}{2M_\nu} \exp(-2W) g_0^2 \quad (7)$$

$$g_0^2 = |\exp(i\delta_{12}(\mathbf{q})) + \exp(i\mathbf{Q} \cdot \mathbf{R}_{12})|^2.$$

In these equations $\mathbf{E}_j$ is a unit vector in the direction of polarization of the vibration, the same for both atoms (1,2) in the primitive unit cell, $\mathbf{R}_{12}$ is the vector distance from atom 2 to atom 1, and δ_{12} is the phase of atom 2 relative to atom 1. It should be noted that δ does not have the full symmetry*

* If, say, $\mathbf{R} = a/4[1,1,1]$, then δ is different for $[q_1, q_1, q_1]$ and $[q_1, q_1, -q_1]$.

of the reciprocal lattice, though g_0^2 does, and care must be taken to maintain consistency.

From a technical point of view germanium is a good subject material for experiments to measure intensities: it has little incoherent scattering, the crystals are almost perfect and therefore no multiple scattering effects will complicate matters, and the frequencies are in a convenient range for measurement.

1. Preliminary experiments

Measurements were made on an approximately cylindrical boule of germanium about 3 cm in diameter. The results for the first set of experiments are shown in Fig. 3. These neutron groups correspond to $L[0, 0, \xi]$

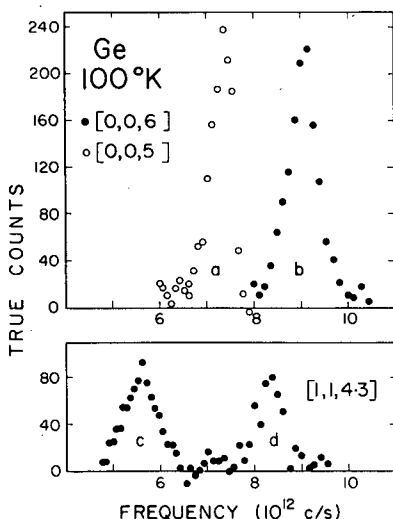


Fig. 3

Neutron groups ($E^* = 0.0202$ eV) for longitudinal phonons propagating in the $[0, 0, \xi]$ direction of the reduced zone of germanium. The groups represent (a) the doubly degenerate longitudinal mode at the zone boundary, (b) the triply degenerate optical mode at $\underline{q} = 0$, and (c) the longitudinal acoustic and (d) the longitudinal optic modes at $\underline{q} = 2\pi/a [0, 0, 0.7]$.

modes, for which the polarization vectors, and therefore the intensities, are known by symmetry. For groups along the line $2\pi/a[0, 0, Q_3]$, the reduced structure factor has the value 4; for groups along the line $2\pi/a[1, 1, Q_3]$ it is 2. The ratios of the measured intensities of Fig. 3 are consistent with these values to about 10%.

Several other experiments were performed to test the accuracy with which structure factors could be determined:

(a) Seventeen phonons belonging to the symmetric $[0, 0, \xi]$ L branch* were measured along a line in reciprocal space from $[0, 0, 4.3]$ to $[0, 0, 5.9]$,

* The $[0, 0, \xi]$ LA and LO branches are continuous in reciprocal space and can be considered as a single branch in a reduced zone of twice the usual size.

for which the frequencies (10^{12} c/sec) ranged from 2.7 to 9.0. When corrected according to Eqs. (4) and (7), the measured reduced structure factors showed a residual disagreement (from their expected equal values) of 7.3% about the mean. This mean value was defined as $g_0^2 = 4$ and used as a calibration in the two succeeding experiments.

(b) The structure factors corresponding to five optical phonons for symmetric modes at different Q 's were determined. The mean of these five structure factors differed from the theoretical value 4 by -2.4%. The Root Mean Square deviation about the theoretical value was $5 \frac{1}{2}\%$.

(c) Neutron groups at four positions in reciprocal space, $[1.75, 1.75, 3.75]$, $[2.25, 2.25, 4.25]$, $[3.75, 3.75, 0.25]$, $[2.25, 2.25, 0.25]$, which corresponded to the LA $[1/4, 1/4, 1/4]$ mode, gave an average frequency $\nu = 4.03 \pm 0.08 \times 10^{12}$ c/sec and an average reduced structure factor $g_0^2 = 3.73 \pm 0.1$. [The errors are the internal standard deviations for the means.] The structure factor for this mode is not determined by symmetry; a first neighbour model [6] gives $g_0^2 = 3.65$.

A number of other scattered experiments were made. These experiments were not sufficiently compatible for a good statistical analysis to be carried out; qualitatively, deviations of the order of 10% were observed. In all the experiments many broad, overlapping, or otherwise defective neutron groups were discarded at the outset; only about half of the measurements made were used.

2. The structure factor for the TA[1,1,1] branch

A series of experiments was carried out to determine the structure factors for the TA[1,1,1] branch. Measurements were made along the line $[0,0,4]$ to $[2,2,2]$ in reciprocal space with $E = 13.7$ meV. The results are shown in Fig. 4. The structure factors were put on an absolute basis by means of a symmetry property: The reduced structure factor is symmetric about the value 2 at the point $[1,1,3]$; thus the sum of the structure factors for any two symmetrically related positions (Eq. [0.6, 0.6, 3.4] and $[1.4, 1.4, 2.6]$) is 4. The average value of the sum for the experiments had a statistical error of 1.6% and an internal error of 1.3%. Thus an accurate normalization could be made. The error bars in Fig. 4 are standard deviations, computed from the counting statistics.

The reduced structure factor at the zone boundary, indicated by dashed straight lines in Fig. 4, is fixed by symmetry at the values 0.5858 or 3.4142.

Fig. 4 shows also structure factors computed on two simple models: (a) the first neighbour model used in [6], and (b) a model in which the two atoms in an appropriately chosen unit cell move in exact phase (e.g. $\underline{q} = [q_1, q_1, -q_1]$ and $\underline{R}_{12} = a/4[1,1,1]$). For model (a) the calculated frequencies are considerably higher than the measured frequencies [6]; for model (b) the calculated frequencies are zero. As might be expected, the structure factors tend to lie between the two extremes.

From the structure factors and Eq. (7), the phase angle δ has been computed and is given in Table II. It is seen to be very small; the two atoms move substantially in phase. Correspondingly, by symmetry, the two atoms move almost 180° out of phase in the TO mode. Thus, to good approxi-

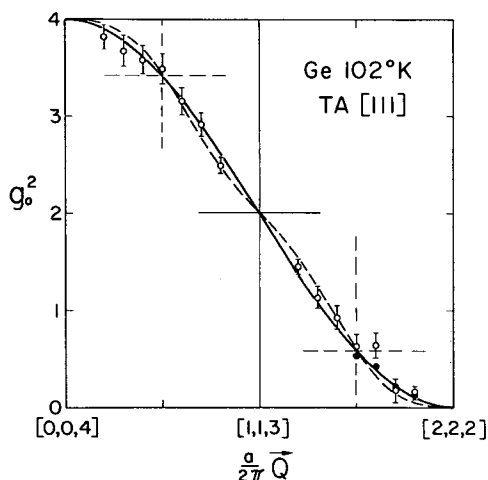


Fig. 4

The reduced structure factor g_0^2 for transverse acoustic modes propagating in a $[\zeta\zeta\zeta]$ direction of the reduced zone. The solid points were actually measured at the equivalent positions $(2.2, 2.2, 2.2)$ to $(2.5, 2.5, 2.5)$. The dashed line shows structure factors calculated from the elastic constants on a first neighbour model [6]. The solid line shows structure factors calculated on the assumption that the two atoms in an appropriately chosen primitive unit cell move in phase together.

TABLE II

MEASURED PHASES BETWEEN ATOMS AT
 $(1/4, 1/4, 1/4)a$ AND $(1/2, 1/2, 0)a$ FOR
 TA $[111]$ MODES OF GERMANIUM

$\frac{a}{2\pi} \mathbf{q}$	Phase angle (degrees)
$[0.2, 0.2, 0.2]$	1.9 ± 2
$[0.3, 0.3, 0.3]$	1.5 ± 2.5
$[0.4, 0.4, 0.4]$	-0.8 ± 3
$[0.5, 0.5, 0.5]$	$-0.3 \pm 3^*$

* Zero by symmetry.

mation, the transverse modes in the $[1,1,1]$ direction (and probably also in the $[1,0,0]$ direction) have fixed phases, and the squared frequencies for these branches must be almost linear in the force constants.

3. An attempted measurement at a general position

Patterns were taken at various points in reciprocal space corresponding to the corner of the reduced zone, $[1/4, 1/4, 1]$ or $[3/4, 3/4, 0]$. Instead of the four groups expected only three were observed, at frequencies 10^{12}

c/sec) of 3.70 ± 0.14 (six observations), 6.42 ± 0.08 (eight observations) and 3.5 ± 0.15 (three observations). (The quoted errors are internal standard deviations of a single observation.) Because only three groups were observed, no analysis could be performed. Since the experiments were carried out, DOLLING [11] has found a near degeneracy for similar modes in silicon, and the 6.42×10^{12} c/sec mode is presumably an extremely close doublet.

V. GENERAL DISCUSSION

The preceding sections have demonstrated that, in reasonably favourable cases, it is possible to measure the intensities of one-phonon neutron groups to a useful degree of accuracy. From an experimental point of view the requirements are:

(a) The crystal should have a narrow mosaic width and suitable geometric form.

(b) The atoms composing the crystal should not have too much incoherent scattering, and the temperature of the specimen should be low.

(c) The neutron groups should be sharp and well separated from each other in frequency.

(d) The incident neutron beam should be reasonably free from contamination by higher orders, etc. since even if the observed neutron groups are well defined and unaffected by the contamination, the monitor response on which the method depends will be altered by the contamination. (This, however, can be corrected.) The greatest difficulty (aside from the usual one of getting sufficient intensity at the necessary resolution) is in determining the background under the peaks. As in ordinary crystallography, it may be hoped that the errors produced are usually in the same direction, and that they may be partially taken up in the normalization and in the Debye-Waller factor.

For the cases considered in this paper the structure factors obtained were only a little less accurate than the squares of the frequencies. If regions of reciprocal space are chosen for which the structure factors are sensitive to the polarization vectors, the polarization vectors obtained should be of equivalent accuracy to the squared frequencies, and directly useable in the analysis. For cases in which the polarization vectors are less accurate, an analysis involving successive approximation could be carried out as follows. The measured frequencies and the best estimate of the polarization vectors are used in the linear "equations of motion in q -space" (the set of linear equations which determine ν and $\xi_{jk}(q)$). This over-determined set of linear equations is solved by least squares for a set of force constants, in a chosen model. This model is then used to compute a new set of estimated polarization vectors, which are in turn used with the measured frequencies in a new least squares fit for a new set of force constants and so on. By this means the hazard of non-linear least squares fitting can be avoided, even where a complete set of accurate polarization vectors are not obtainable.

ACKNOWLEDGEMENTS

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DISCUSSION

P. K. IYENGAR: Do you think the variation in physical size of the crystal which intercepts the beam for different values of ψ contributes to the error in intensity?

B. N. BROCKHOUSE: The shape of the specimen, where it is a thick one, is indeed of importance and there is some discussion of this matter in the paper. The sodium crystals represented an unfavourable case owing to their somewhat asymmetrical shape and incoherent scattering background. They also showed a multiple scattering effect. Our results in this case are therefore less accurate. For germanium we had cylindrical symmetry and therefore I do not think any correction would be necessary.

P. K. IYENGAR: Does this mean that there is a problem similar to that of extinction in single-crystal structure analysis?

B. N. BROCKHOUSE: There is no problem of extinction at all; in fact, the more nearly perfect the crystal the better, since then no appreciable one-phonon elastic double scattering can occur.

W. COCHRAN: The idea of determining the polarization vectors by experiment is a good one. However, measurements at one point in reciprocal space give only the reciprocal-space analogue of force constants - the "coefficients". These have to be known throughout the Brillouin zone before they can be Fourier-transformed to give the usual force constants of the Born-von Kármán theory. In a general case, therefore, many measurements throughout the Brillouin zone would appear to be required.

B. N. BROCKHOUSE: It is not necessary, however, to use a Fourier transformation. One can select points in the Brillouin zone which are sufficiently "orthogonal" to permit force constants to be determined for some

particular range of forces by least squares fitting. In this way, the number of measurements need not be very much greater than the number of force constants required.

N. A. TCHERNOPLEKOV: I would like to support Dr. Brockhouse.

LATTICE VIBRATIONS IN CRYSTALS WITH THE DIAMOND STRUCTURE

G. DOLLING

ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

LATTICE VIBRATIONS IN CRYSTAL WITH THE DIAMOND STRUCTURE. The triple axis crystal spectrometer at the NRU reactor has been used to obtain dispersion relations in the $\{\xi 00\}$, $\{\xi \xi \xi\}$, and $\{0\xi\xi\}$ directions in a single crystal of silicon, at room temperature. The frequencies for certain $\{\xi 00\}$ direction modes are slightly higher than previous measurements, probably because of the improved resolution and calibration of the present experiments. Typical frequencies (units of 10^{12} counts/s) are : TA $(1/2 \ 1/2 \ 1/2)$, 3,43 ; TA $(1/2 \ 1/2 \ 1/2)$, 14,7 ; O ($q = 0$), 15,5 ; AI $(1/2 \ 1/2 \ 0)$, 6,10 ; AII $(1/2 \ 1/2 \ 0)$, 8,6. Modes AI and AII are neither longitudinal nor transverse, but they are related, respectively, to TA and LA-type modes.

The results are analysed in terms of modified versions of the "shell" model, proposed originally by Cochran to describe the dispersion relations in the $\{\xi 00\}$ and $\{\xi \xi \xi\}$ directions in germanium. A substantial improvement between theory and experiment is obtained by the introduction of short range interactions between second nearest neighbour atoms. The shell model analyses for silicon and germanium are extremely similar, and only the results for silicon are presented in detail.

VIBRATIONS DE RÉSEAUX DANS DES CRISTAUX AYANT LA STRUCTURE DU DIAMANT. L'auteur a utilisé le spectromètre à cristal triaxial du réacteur NRU pour déterminer des relations de dispersion dans les directions $\{\xi 00\}$, $\{\xi \xi \xi\}$ et $\{0\xi\xi\}$ d'un monocristal de silicium à température ambiante. Les fréquences caractérisant certains modes de direction $\{\xi 00\}$ sont légèrement supérieures aux fréquences mesurées précédemment; ces différences sont dues sans doute à une résolution améliorée et un meilleur étalonnage dans les expériences présentes. Voici quelques fréquences caractéristiques (en unités de 10^{12} cps) : TA $(1/2 \ 1/2 \ 1/2)$, 3,43 ; TO $(1/2 \ 1/2 \ 1/2)$, 14,7 ; O ($q = 0$), 15,5 ; AI $(1/2 \ 1/2 \ 0)$, 6,10 ; AII $(1/2 \ 1/2 \ 0)$, 8,6. Les modes AI et AII ne sont ni longitudinaux ni transversaux, mais ils sont liés respectivement aux modes TA et LA.

L'auteur analyse les résultats en se fondant sur des versions modifiées du modèle en couches, que Cochran a proposées le premier pour décrire les relations de dispersion dans les directions $\{\xi 00\}$ et $\{\xi \xi \xi\}$ à l'intérieur du germanium. On obtient une amélioration sensible de l'accord entre les résultats théoriques et les résultats expérimentaux en introduisant des interactions à portée courte entre deux atomes séparés par un troisième. Les analyses du modèle en couches pour le silicium et le germanium sont extrêmement semblables, et seuls les résultats relatifs au silicium sont exposés en détail.

КОЛЕБАНИЯ РЕШЕТКИ В КРИСТАЛЛАХ С РОМБИЧЕСКОЙ СТРУКТУРОЙ. Трехосевой кристаллический спектрометр в реакторе NRU использовался для изучения дисперсионных соотношений в $\xi 00$, $\xi \xi \xi$ и $0\xi\xi$ направлениях в монокристалле силикона при комнатной температуре. Обнаружены несколько более высокие частоты для некоторых направлений колебаний $\xi 00$, возможно, вследствие улучшенной разрешающей способности и калибровки в настоящем опыте. Типичными частотами (единица 10^{12} отсчетов в секунду) были: TA $(1/2 \ 1/2 \ 1/2)$; 3,43; TO $(1/2 \ 1/2 \ 1/2)$; 14,7; O ($q=0$); 15,5; AI $(1/2 \ 1/2 \ 0)$; 6,10; AII $(1/2 \ 1/2 \ 0)$; 8,6. Колебания AI и AII не были ни продольными ни поперечными, но зависели, соответственно, от колебаний типа TA и LA.

Анализ результатов производился в форме видоизмененной модели "оболочки, предложенной первоначально Кохреном для описания дисперсионных соотношений в $\xi 00$ и $\xi \xi \xi$ направлениях в германии. Значительное приближение теории к эксперименту было достигнуто за счет использования взаимодействия между вторичными ближайшими соседними атомами. Результаты анализа модели "оболочки" для силикона и германия очень похожи, но подробные данные приводятся только для силикона.

VIBRACIONES RETICULARES EN CRISTAL DE ESTRUCTURA ROMBOIDAL. El autor utilizó el espectrómetro de cristal triaxial del reactor NRU a fin de determinar las relaciones de dispersión en las direcciones

[$\xi 00$], [$\xi \xi \xi$] y [$0\xi\xi$], en un monocristal de silicio a temperatura ambiente. Para ciertos modos de dirección [$\xi 00$], las frecuencias son algo superiores a las obtenidas en mediciones anteriores, lo que se debe probablemente al mayor poder de resolución y a la calibración más precisa de dichos experimentos. Las frecuencias típicas (siendo la unidad 10^{12} Hz) son: TA ($1/2 \ 1/2 \ 1/2$), 3,43; TO ($1/2 \ 1/2 \ 1/2$), 14,7; O ($q=0$), 15,5; AI ($1/2 \ 1/2 \ 0$), 6,10; AII ($1/2 \ 1/2 \ 0$), 8,6. Los modos AI y AII no son ni longitudinales ni transversales, pero están relacionados con los tipo TA y LA, respectivamente.

El autor analiza los resultados en función de varias versiones modificadas del modelo de capas, propuesto originariamente por Cochran para describir las relaciones de dispersión en las direcciones [$\xi 00$] y [$\xi \xi \xi$], en el germanio. Se aumenta considerablemente la concordancia entre los resultados teóricos y los experimentales admitiendo la existencia de interacciones de corto alcance entre los segundos átomos más próximos. Los análisis del modelo de capas para el silicio y el germanio son muy análogos; en la memoria sólo se presentan en detalle los resultados correspondientes al silicio.

I. INTRODUCTION

A considerable literature, both experimental and theoretical, has accumulated in recent years on the subject of lattice vibrations in crystals having the diamond structure. On the experimental side, to mention just one example, there is the work by BROCKHOUSE and IYENGAR [1] on germanium, while the papers of HERMAN [2] and of COCHRAN [3] may be cited from the theoretical literature. HERMAN [2] analysed the experimental data for germanium [1] on the basis of the Born-von Kármán theory, and was obliged to postulate at least fifth nearest neighbour interatomic forces in order to obtain satisfactory agreement with experiment. The surprisingly long range of these interatomic forces has been shown by COCHRAN [3] to be of electrostatic origin, arising from the polarizability of the (neutral) germanium atoms. A brief outline of the Cochran model is given in Section II, together with details of various modifications to it, which have been made in efforts to fit experimentally measured dispersion relations for silicon. These experimental measurements are presented in Section III, and compared with theoretical computations for specific force models in Section IV. Similar computations, for the analogous case of germanium, are also discussed. Finally (Section V) we consider the present status of the shell model for the diamond structure in the light of these results.

II. SHELL MODELS

The mathematics underlying the shell model was first proposed by MASHKEVITCH and TOLPYGO [4]. According to these authors, the effective potential function for the nuclei in a crystal, apart from a constant term, should be expressed as a quadratic function of the nuclear displacements and of the atomic dipole moments. (The adiabatic and harmonic approximations are assumed.) The effects, if any, of higher order electric multipoles are neglected, and so we may regard this as a "dipole approximation". One of the achievements of Cochran in this field was to develop a model of the crystal, the shell model, which, while mathematically identical with the dipole approximation, provided both a physical picture of the processes involved, and also a relatively simple method of calculating dispersion curves from the potential function. The shell model was originally proposed by

DICK and OVERHAUSER [5] in a paper dealing with the theory of the dielectric constants of alkali halides. In this model, an atom is supposed to consist of a core, the nucleus and inner electrons, and a spherical shell of outer electrons, assumed to be of zero mass, bound to its parent core by an isotropic force constant. Short range forces are postulated between neighbouring cores and shells, representing the effects of overlap repulsion, Van der Waal's attraction, and so on. During a lattice vibration, the cores and shells become relatively displaced, and the resultant dipoles exert long range electrostatic forces on each other.

In the original COCHRAN model for germanium [3], short range forces between first nearest neighbour cores and shells only were postulated. This "first neighbour" model will be referred to as model I. The model has seven independent parameters, of which three are certain ratios of force constants for the "core-core", "core-shell", and "shell-shell" interactions (γ_R , γ_T and γ_S , respectively, in the notation of [3]). The values of γ_R and γ_T are fixed by the elastic constants. Since the latter, in the case of germanium, obey closely the Born relation

$$4C_{11}(C_{11} - C_{44}) = (C_{11} + C_{12})^2$$

it was possible to assume (as Cochran did) that $\gamma_R = \gamma_T$. A simplification of the mathematics was achieved by making the further assumption that $\gamma_S = \gamma_R$, and the resulting simple shell model was found to provide a fairly good fit to the experimental data then available.

There is, however, no particular physical reason why the three γ -parameters should be equal, either for germanium or silicon; it is in any case not possible to fit the elastic constants of silicon on the basis of model I unless unequal γ parameters are assumed. It has been suggested [6, 7] that a better fit to experiment may be obtained by an extension of the shell model to include short range forces between second nearest neighbour atoms. The difficulty with such an extension is that, in the general case, there are 12 additional parameters to be specified, viz. 4 force constants (μ , λ , ν , and δ , in the notation of [2]) for each of the "core-core", "core-shell", and "shell-shell" interactions. This is an embarrassingly large number of disposable parameters, particularly since we shall find that most of these second neighbour forces are only a few percent of the first neighbour forces. A variety of "second neighbour" shell models (type II) can thus be constructed, depending on what assumptions are made in order to reduce this number to manageable proportions. Attempts have been made to obtain a satisfactory fit to the experimental data for silicon by means of three such models II, in addition to model I in which second neighbour interactions are neglected. Similar fitting processes have also been carried out for germanium, using the recent dispersion relation measurements of BROCKHOUSE *et al.* [8] .

In the description of these models, the force constant notation of [2] will be employed, with subscripts R, T or S to denote the three types of force mentioned above. Thus the force constant matrices for the first and second neighbour "shell-shell" interactions are, respectively,

$$\alpha_S \quad \beta_S \quad \beta_S \quad \text{and} \quad \mu_S \quad \nu_S \quad \delta_S$$

$$\begin{array}{ccc}
 \beta_S & \alpha_S & \beta_S \\
 \beta_S & \beta_S & \alpha_S
 \end{array}
 \qquad
 \begin{array}{ccc}
 \nu_S & \mu_S & \delta_S \\
 \delta_S & \delta_S & \lambda_S
 \end{array}$$

In terms of COCHRAN'S notation [3] , we have $S_0 = 4\alpha_S$, and $\gamma_S = (\beta_S/\alpha_S)$, and similar expressions involving R and T. (Note: Cochran uses the symbols α and β to refer to the atomic polarizability: we replace his symbol β by π_0 .)

We make a simplifying assumption common to all three models of type II, which is very similar to the assumption of equal γ parameters invoked by COCHRAN [3] for the first neighbour forces: the ratio of any given second neighbour force constant, for example λ , to the first neighbour force constant α , is the same for all subscripts R, T and S:

$$\lambda_R/\alpha_R = \lambda_T/\alpha_T = \lambda_S/\alpha_S = \gamma_\lambda$$

and similar relations for μ , ν , and δ . For the cases we consider, this assumption implies that the second neighbour short range forces are transmitted very largely through the shells, a not unreasonable restriction. No further assumptions are made for the most complex model we consider, model II(c). This has eleven disposable parameters, of which four refer to the second neighbour forces. One of these four ($\gamma_\delta = \delta/\alpha$) is antisymmetric and does not appear in the expressions for the dispersion relations in the high-symmetry directions [$\xi 00$] and [$\xi \xi \xi$]. A non-linear least squares fitting programme has been written* in order to find the ten parameters (γ_δ is excluded) giving the best fit to the elastic and dielectric constants and to 40 phonon frequencies for the two high-symmetry directions. The initial parameter values required for this programme were obtained as a by-product of the computations for the two other models II(a) and II(b). The additional assumptions made for the latter models were such as to allow semi-analytic methods for the determination of the required parameters.

For model II(a), the additional assumption is that the three γ parameters for the first neighbour forces are equal:

$$\beta_R/\alpha_R = \beta_T/\alpha_T = \beta_S/\alpha_S.$$

The second neighbour forces are still specified by four parameters, and the model therefore has nine disposable parameters in all, of which one is inoperative in the two high-symmetry directions.

In contrast to model II(a), which places a restriction upon the first neighbour forces, the additional assumption for model II(b) is that the second neighbour forces are derivable from a central potential: this implies that $\gamma_\delta = 0$ and $\gamma_\lambda = (1 - \gamma_\nu)$, a reduction in the number of second neighbour parameters from four to two. With nine parameters involved in the calculation of symmetry direction frequencies, this model is slightly more complex than model II(a).

The characteristics of the four models discussed above are summarized in Table I. It should be mentioned, in passing, that a certain discretion is

* This programme was written for the Bendix G-20 computer by Mr. G.J. Luste.

TABLE I

SUMMARY OF SHELL MODEL CHARACTERISTICS

The figure in parentheses in the fourth column is the number of disposable parameters operative in the two high-symmetry directions.

The remarks for model II(c) apply also to II(a) and II(b)

Model	First neighbour interactions	Second neighbour interactions	Number of parameters	Remarks
I	$\gamma_R \neq \gamma_T \neq \gamma_S$		7(7)	
II(a)	$\gamma_R = \gamma_T = \gamma_S$	$\mu, \lambda, \nu, \delta$	9(8)	δ is antisymmetric
II(b)	$\gamma_R \neq \gamma_T \neq \gamma_S$	μ, λ	9(9)	$\delta = 0; \nu = \mu - \gamma$
II(c)	$\gamma_R \neq \gamma_T \neq \gamma_S$	$\mu, \lambda, \nu, \delta$	11(10)	$\frac{\mu_R}{\alpha_R} = \frac{\mu_T}{\alpha_T} = \frac{\mu_S}{\alpha_S}$, etc.

necessary in carrying out these fitting processes, in order to avoid physically unreasonable sets of parameters, which nonetheless produce apparently acceptable dispersion curves.

III. EXPERIMENTAL RESULTS

The experiments were performed on a single crystal of pure silicon at room temperature (296°K), by means of the triple axis crystal spectrometer at the NRU reactor, Chalk River. Fairly complete dispersion curves for the three directions $[\xi 00]$, $[\xi \xi \xi]$ and $[0\xi\xi]$, as shown in Fig. 1, were

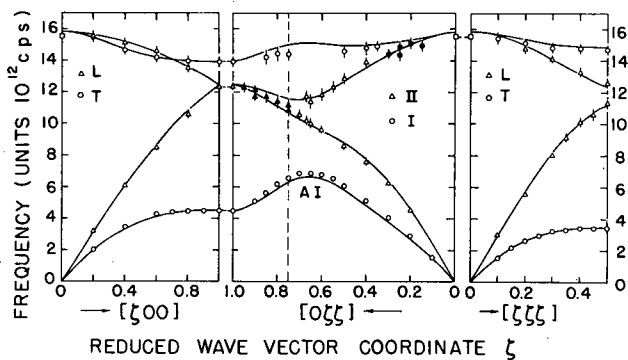


Fig. 1

Phonon dispersion relation for the directions $[\xi 00]$, $[0\xi\xi]$ and $[\xi\xi\xi]$ in a single crystal of silicon at 296°K. The solid curves are computed from shell model II(c). The vertical dashed line at $\xi = 0.75$ in the $[0\xi\xi]$ direction marks the position of the zone boundary.

Code: Open circles - transverse (T) or type I $[0\xi\xi]$ modes;
 Open triangles - longitudinal (L) or type II $[0\xi\xi]$ modes;
 Solid points - undetermined polarization.

measured for those modes with polarization vectors in a (011)-type mirror plane of the crystal. All the results shown in Fig. 1 were obtained by means of the "constant-Q" technique [9], in which the energy distribution of initially monoenergetic neutrons, scattered from the crystals, is observed for a predetermined fixed point in reciprocal space, that is to say, for a fixed value of the neutron momentum transfer vector, $\underline{Q}$. The solid curves shown in Fig. 1 represent the best least-squares fit to the data on the basis of model II(c) (see Section IV).

For the two high symmetry directions $[\bar{1}00]$ and $[\bar{1}\bar{1}\bar{1}]$, the modes are strictly longitudinal or transverse. In the $[0\bar{1}\bar{1}]$ direction, however, complete factorization of the dynamical matrix does not occur, and the only symmetry restriction on the observed modes is that their polarization vectors must lie in the (011) mirror plane. Thus the curves for this direction have been labelled I and II rather than T and L. The general level of experimental error is around 2% to 2.5% in frequency, and certain frequencies of particular theoretical interest were measured to an accuracy of about 1.5%. A list of selected phonon frequencies, including all those employed in the fitting processes, is given in Table II. These results are in generally good agreement with previous data for silicon [6, 10], and it seems probable (though this is not definitely proven) that the minor discrepancies which do exist can be explained in terms of the higher resolution and improved instrumental calibration of the present experiments.

TABLE II

SELECTION OF PHONON FREQUENCIES IN SILICON AT 296° K

Wave vector coordinates	Optic		Acoustic	
	T, I	L, II	T, I	L, II
0.0 0 0	15.53±0.23		----	
0.2 0 0	15.40±0.36	15.55±0.38	2.00±0.08	3.20±0.12
0.4 0 0	14.65±0.33	15.15±0.35	3.45±0.06	6.10±0.15
0.6 0 0	14.18±0.35	14.60±0.35	4.27±0.10	8.50±0.20
0.8 0 0	13.95±0.34	13.60±0.27	4.46±0.07	10.60±0.20
1.0 0 0	13.90±0.30	12.32±0.20 ⁽¹⁾	4.49±0.06	12.32±0.20 ⁽¹⁾
0.1 0.1 0.1	15.40±0.37	15.45±0.35	1.53±0.03	3.0 ±0.13
0.2 0.2 0.2	15.10±0.30	14.78±0.30	2.62±0.05	5.60±0.15
0.3 0.3 0.3	14.83±0.30	14.13±0.30	3.22±0.05	8.03±0.15
0.4 0.4 0.4	13.78±0.27	13.30±0.22	3.41±0.05	10.12±0.20
0.5 0.5 0.5	14.68±0.30	12.60±0.32	3.43±0.05	11.35±0.30
0 0.2 0.2	15.10±0.35 ⁽³⁾		2.91±0.07	4.55±0.10
0 0.4 0.4	14.8 ±0.4	13.87±0.28	5.11±0.09	7.60±0.20
0 0.5 0.5	14.55±0.38	12.83±0.27	6.06±0.12	8.60±0.18
0 0.75 0.75 ⁽²⁾	14.40±0.38	11.15±0.30 ⁽³⁾	6.56±0.14	10.85±0.30 ⁽³⁾
0 0.85 0.85	14.20±0.34	11.7 ±0.30 ⁽³⁾	5.60±0.11	11.7 ±0.30 ⁽³⁾

Frequencies are quoted in units of 10^{12} c/sec.

(1) Degenerate mode.

(2) Zone boundary in $[0\bar{1}\bar{1}]$ direction.

(3) Undetermined polarization.

IV. THEORETICAL DISPERSION CURVES

Computations have been performed (i) for silicon at 296° K, on the basis of models I, II(a), II(b), and II(c), and (ii) for germanium at 90° K, on the basis of models I, II(a), and II(c). The results for germanium are rather similar to those for silicon, except that it is generally possible, for any given model, to obtain a slightly better fit to the available data for germanium than it is for silicon. In view of this similarity, and also of the relatively small amount of $[0\zeta\zeta]$ direction data available for germanium, we shall restrict the following detailed discussion to the case of silicon.

Fig. 2 shows the experimental results for the two high-symmetry directions, together with theoretical curves computed from models I (dashed

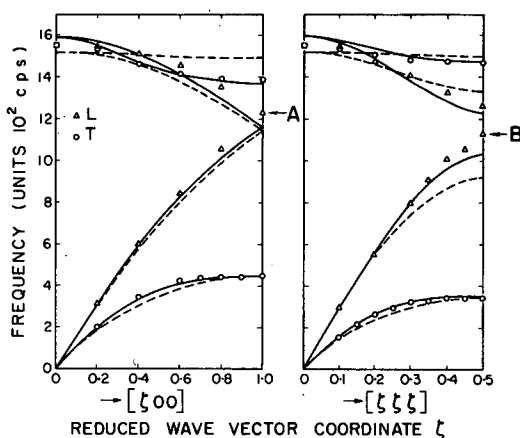


Fig. 2

Comparison of shell models I (dashed curves) and II(a) (solid curves) for the two high-symmetry directions in silicon.

lines) and II(a) (solid lines). Both sets of curves have been fitted by a semi-analytic method, to the three elastic constants, the dielectric constant, and to 8 special phonon frequencies - those at the zone boundaries and at zero wave vector - for which the theoretical expressions are relatively simple. (Application of the non-linear least squares fitting programme for these two models produces barely perceptible changes in the fits.)

The dashed curves provide a good qualitative fit to the experimental data, a result rather similar to that obtained by COCHRAN [3] for the case of germanium. The chief merit of model I is the close fit achieved for the transverse acoustic modes in these two directions, which are quite impossible to fit (to within 50%) on the basis of a simple Born-von Kármán model involving only first and second neighbour interatomic forces (and neglecting the long range electrostatic forces). The addition of second neighbour interactions to shell model I, even simultaneously with the restrictions on first neighbour forces imposed in model II(a), produces a marked improvement in the fit to experiment. The improvement achieved by model II(a) is especially noticeable in the shapes of the dispersion curves for the transverse

modes, and in the longitudinal mode frequencies at the zone boundary points, A and B.

Nevertheless, the model II(a) curves cannot be regarded as entirely satisfactory. In particular, it seems to be very difficult to eliminate the remaining discrepancies at the points A and B, without significantly worsening the agreement elsewhere. Rather similar conclusions are obtained from the analysis of model II(b) for the two high-symmetry directions, in spite of the fact that an extra parameter is available. For reasons of space, this model will not be discussed in detail.

Further evidence of the inadequacy of model II(a) is furnished in Fig. 3, which shows the experimental results and associated theoretical curves* for the $[0\zeta\zeta]$ direction. The treatment of these results separately from those

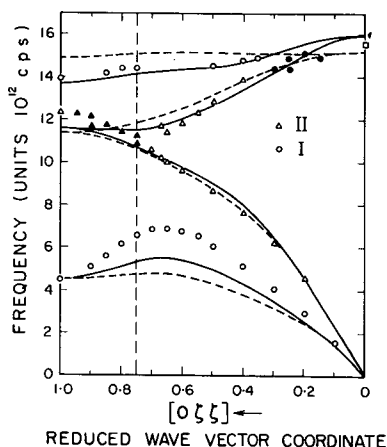


Fig. 3

Comparison of shell models I (dashed curves) and II(a) with $\delta = 0$ (solid curves) for the off-symmetry direction $[0\zeta\zeta]$ in silicon.

in the high-symmetry directions is a reflection of the increased difficulty, both experimental and theoretical, of dealing with such off-symmetry directions in the crystal. As in Fig. 2, the dashed and solid curves represent models I and II(a) respectively. The most significant feature is the poor fit displayed by both models to the acoustic type I(AI) modes. In the case of model II(a), some improvement in the fit may be obtained by varying the antisymmetric parameter δ . (Since the parameters for the model II(a) curves in Fig. 3 are obtained from symmetry direction data only, δ is undetermined, and has been put equal to zero as a first approximation.) The overall improvement for $\delta \neq 0$ is, however, rather small, since an improvement in one branch tends to be counterbalanced by a worsening fit for another branch. The dispersion curves for the $[0\zeta\zeta]$ direction computed from model II(b) provide a fit to experiment of roughly similar quality to those of model II(a) with $\delta = 0$, and do not warrant further discussion.

* These curves were obtained with the aid of a programme written for the Burroughs 205 computer by Mr. R. A. Cowley.

The general conclusion to be drawn from these computations for 8- and 9-parameter models, is that although they represent a substantial advance over the 7-parameter model I, they do not provide a completely satisfactory fit to the available experimental data.

Finally, we consider model II(c); as mentioned in Section II, the set of 10 "best fit" parameters (operative in the high-symmetry directions) for this model, is determined by means of a non-linear least-squares fitting programme, which utilizes the known values of the dielectric constant [11] and elastic constants [12], together with 20 phonon frequencies at evenly spaced wave vectors along each of the two high-symmetry directions. Having obtained values for the 10 parameters from these 44 observations, the value of the 11th parameter δ is adjusted by trial and error to give a (rather approximate) "best" fit to the $[0\bar{1}1]$ direction data. The resulting dispersion curves are shown in Fig. 1, and the values of the parameters employed are listed in Table III. The agreement between theory and experiment for this 11-parameter model is extremely good, except perhaps for the AI $[0\bar{1}1]$ branch. It is considered that this last remaining imperfection could be removed by a proper "least squares" determination of δ (though this is not a trivial problem!). The parameter errors shown in Table III are computed as part of the least squares fitting programme on the assumption of independent parameters. This assumption is, however, not completely valid for all the parameters used, and the calculated error values should therefore be treated with some caution.

TABLE III

BEST FIT PARAMETERS FOR SHELL MODEL II(c)
(Results for silicon at 296° K)

Parameter	Value (error)		Equivalent notation of [3]
α_R	21.42	(1.28)	$0.25 R_0 (v/e^2)$
γ_R	0.214	(0.011)	γ_R
γ_T	-0.009	(0.071)	γ_T
γ_S	-0.328	(0.026)	γ_S
B_1	83.54	(16.30)	$[B_1 = T_0^2/(k+F_0)] (v/e^2)$
B_2	1.330	(0.157)	$B_2 = S_0/(k+F_0)$
π_0	0.09339	(0.00006)	β
μ_R	-0.725	(0.124)	
λ_R	-2.199	(0.485)	
ν_R	+0.818	(0.270)	
δ_R	+6.0	--	

The values of all force constants are given in units of (e^2/v) where e is the electronic charge and v the volume of the unit cell.

V. CONCLUSION

(i) Dispersion curves for both silicon and germanium calculated on the basis of the 7-parameter shell model I display good qualitative agreement with the experimental data, and constitute a considerable advance from simple Born-von Kármán Force models for the diamond structure [13, 14].

(ii) A substantial improvement upon model I may be achieved by extending it to include the effects of second neighbour short range forces, though it seems that a fairly complex model with 10 or 11 disposable parameters is required for an entirely satisfactory fit to experiment. This kind of statement has also been made in connection with shell models for alkali halides [15]. The necessity for such a complicated model for silicon and germanium may well be quite reasonable in view of their complex electronic configurations.

Another possible cause of this proliferation of parameters is the neglect, in shell models, of quadrupole interactions. The distortion of the electronic configuration consequent upon a lattice vibration may in principle be expressed as a series of electric multipoles - dipoles, quadrupoles, etc. All electrostatic interactions, except those between dipoles, are neglected in the shell models we have considered. The electrostatic forces between the higher order multipoles are mostly of short range, and can probably be taken into account by the short range force parameters. Electrostatic forces involving quadrupole moments may, however, constitute an exception to this statement, and it is possible that such forces could, with advantage, be represented explicitly in some future force model for the diamond structure. For the present purposes, however, we continue to express the effective potential function for the atomic motions in terms of the dipole approximation.

(iii) An interesting feature of the model II(c) parameters listed in Table III is the large value of the antisymmetric force constant δ . This constant is associated with modes of vibration in which the angles between nearest neighbour bonds are distorted. δ would be zero if the second neighbour forces were derivable from a central potential. The present neutron scattering experiments for the $[0\bar{1}1]$ direction may perhaps be regarded as the first determination of such an antisymmetric force constant.

(iv) The symmetric second neighbour force constant λ, μ and ν are quite small in comparison with the first neighbour constant α ; this provides some justification for the arbitrary assumption (Eq. (1)) mentioned in Section II. There is less justification, however, for such an assumption in respect of the force constant δ , and it would perhaps be more reasonable to treat δ_R , δ_T , and δ_S independently. The calculation of "best fit" values for these additional parameters would, however, be very laborious, and in view of the excellent agreement between theory and experiment provided by model II(c) as it stands, such a calculation has not been attempted.

(v) The values of some of the parameters, obtained from the "best fit" analyses of the simpler shell models, differ considerably from those listed in Table III for model II(c). For example, to cite an extreme case, the "best" value for γ_R , determined on the basis of model I, is 0.693, as compared with 0.214 for model II(c). While such large differences are not necessarily

unreasonable, we cannot, at the present time, be certain of the precise physical meanings of these shell model parameters.

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DISCUSSION

H. HAHN: My remarks also apply to the papers by Woods and Brockhouse et al. In computing "harmonic" coupling parameters from the (temperature-dependent) frequencies measured, one is in fact getting only a sort of phenomenological description. In order to know what one is really doing in determining the force constants from the measured frequencies and to get the actual harmonic coupling parameter that would be found if all the anharmonicities (including thermal expansion effect) were absent, one would have to extrapolate to absolute zero the linear dependence on temperature shown by the experimental frequencies above the Debye temperature and then perform the calculations reported by Dr. Dolling on the harmonic frequencies thus obtained. To obtain a description of the temperature dependence of the frequencies, one could then try to use the anharmonic force constants. This would have the advantage that all the constants used for the description were independent of temperature.

G. DOLLING: In the experiments on which I am reporting, however, the operational temperature was quite low compared with the Debye temperature and certainly very low by comparison with the melting temperature. They therefore represent one of those cases where you would expect the anharmonic effect not to be too large.

H. HAHN: Yes, but even at zero temperature there may well be a considerable anharmonicity effect owing to zero-point effects.

G. DOLLING: Do you have any figures to support this?

H. HAHN: I'm afraid not. However, one case where we can see that the zero-temperature anharmonic effects are quite considerable is in the elastic constants of many crystals. It can also be seen from the deviation of the 0°K value from the value extrapolated by the procedure which gives the harmonic value.

B.N. BROCKHOUSE: This is probably an effect that is just on the edge of observability, with the accuracy now available. My impression of these effects is that they amount to 1-2%. To some extent, they will be homogeneous with the frequencies. What happens is that you simply change the scale of things a bit. All the elastic constants behave in the same way on nearly all the frequencies. We did find frequencies in lead that rose, but this is an abnormal case anyway. One other point is that, as Dr. Dolling mentioned, the cases described were favourable ones, as far as this trouble is concerned. The germanium-silicon family shows rather small anharmonic effects. We have attempted, but without success, to see line broadening in germanium at about half the melting point, although we did see frequencies shifts.

THE DISTRIBUTION OF HIGHER ENERGY NORMAL MODES IN DIAMOND

E. W. J. MITCHELL AND J. R. HARDY*

READING UNIVERSITY

AND

D. H. SAUNDERSON

NUCLEAR PHYSICS DIVISION, AERE, HARWELL, DIDCOT, BERKS.

UNITED KINGDOM

Abstract — Résumé — Аннотация — Resumen

THE DISTRIBUTION OF HIGHER ENERGY NORMAL MODES IN DIAMOND. The beryllium detector method was used to measure the spectrum of neutrons scattered inelastically by polycrystalline sample of diamond at room temperature. The results are used to derive the phonon frequency distribution in the modes between 0.11 and 0.17 eV by a method based on the analysis described by Egelstaff and Cocking. Peaks in the distribution are compared with the results of previous measurements of the 2-phonon spectrum by I-R spectroscopy.

DISTRIBUTION DES MODES NORMAUX D'ÉNERGIE ÉLEVÉE DANS LE DIAMANT. Les auteurs ont employé la méthode du détecteur au béryllium pour mesurer le spectre de neutrons diffusés inélastiquement par un échantillon polycristallin de diamant à la température ambiante. Ils utilisent les résultats pour déterminer la distribution de fréquence des phonons pour les modes compris entre 0,11 et 0,17 eV, par une méthode fondée sur l'analyse décrite par Egelstaff et Cocking. Ils comparent les pics de la distribution avec les résultats de mesures antérieures du spectre à 2-phonons effectuées par la méthode spectroscopique I-R.

РАСПРЕДЕЛЕНИЕ НОРМАЛЬНЫХ КОЛЕБАТЕЛЬНЫХ УРОВНЕЙ ВЫСОКОЙ ЭНЕРГИИ В АЛМАЗЕ. При помощи метода бериллиевого детектора был измерен спектр неупругого рассеяния нейтронов поликристаллическим образцом алмаза при комнатной температуре. Результаты измерений были использованы для вывода относительно распределения частот фононов в пределах между 0,11 и 0,17 эв по методу, основанному на анализе, описанном Эгелстаффом и Коккингем. Положение пиков в распределении частот сопоставляется с результатами более ранних измерений двухфононного спектра при помощи инфракрасной спектроскопии.

DISTRIBUCIÓN DE MODOS NORMALES DE ENERGÍA ELEVADA EN EL DIAMANTE. Los autores han aplicado el método del detector de berilio para medir a temperatura ambiente el espectro de los neutrones dispersados inélasticamente por una muestra de diamante policristalino. Utilizan los resultados para deducir la distribución de frecuencias de los fonones en los modos comprendidos entre 0,11 y 0,17 eV por un método basado en el análisis descrito por Egelstaff y Cocking. Comparan los picos en la distribución con los resultados de mediciones anteriores del espectro de dos fonones determinado por espectroscopia infrarroja.

INTRODUCTION

Measurements of the coherent inelastic scattering of neutrons by the diamond-structure materials germanium and silicon [1] have yielded considerable information on phonon dispersion curves in these materials. However, PHILLIPS [2] has demonstrated that the normal mode distribution function is by no means uniquely defined by even such detailed measurements of dispersion curves as those made on germanium, since this

* AEI Research Fellow.

information alone does not reproduce the specific heat data measured by DESNOYERS and MORRISON [3] when used to interpolate a distribution function $\rho(\omega)$. Evidently $\rho(\omega)$ contains additional information about the inter-atomic forces and is thus worth measuring in its own right. Moreover, the energies of the VAN HOVE [4] singularities in $\rho(\omega)$ may, by the converse of Phillips' analysis, be assigned to phonons at various symmetry points and, in the case of a crystal for which dispersion curves are unknown, can be used to test particular force constant models. Such a test is almost as stringent as the requirement that the model reproduce given dispersion curves for a few symmetry directions.

In the present work this approach has been applied to diamond, since large single crystals are not required as they are for measuring dispersion curves, which are consequently unknown for diamond. Also the phonon energies at symmetry points have been inferred previously [5] from the two-phonon infra-red lattice absorption.

One is particularly interested in the higher frequency end of $\rho(\omega)$ and the momentum transfer involved in single phonon creation by a neutron is such that one may use an approach, similar to that of EGELSTAFF and COCKING [6] in their work on graphite which enables a direct determination of $\rho(\omega)$ to be made from observations on the inelastic scattering by polycrystal or powder.

EXPERIMENTAL

The measurements were made in the energy transfer range $0.11 < -\epsilon < 0.18$ eV on the Dido High Intensity Crystal Spectrometer by the beryllium detector technique described in the accompanying paper [7].

The sample consisted of 60 g of micron diamond power dried and packed into a pure aluminium can with a thin (0.02 in) window for scattering in reflection. All components around the diamond sample were sheaved in cadmium metal to minimize background scattering.

A relatively thick sample (transmission $\sim 50\%$) was necessary because of the adverse count to background ratio in the 0.10 - 0.20 eV region. The effects of multiple scattering processes must therefore be considered carefully. Diamond is predominantly a coherent scatterer so that elastic scattering processes have a strong directional dependence. To check that features in the observed spectra were not due to strong primary or multiple Bragg reflections reduced by the large but finite attenuation of the filter above the cutoff energy of 0.005 eV, the filter was replaced by a simple collimator and the unfiltered diffraction patterns compared with the original distributions. No correlation was found between peaks in the two distributions.

Of the properly filtered neutrons entering the detector ($0 < E' < 0.005$ eV) the majority arise from a single inelastic collision in which energy $-\epsilon = E_0 - E'$ and momentum $-\mathbf{K} = \mathbf{k}_0 - \mathbf{k}'$ have been transferred to the diamond lattice where E and $\mathbf{k}$ are the neutron energy and wave vector suffixed 0 for incident and primed for scattered.

The less probable process in which the neutron first suffers an elastic collision and then an inelastic collision with an energy transfer $-\epsilon$ will also be detected. In this case there is an uncertainty in the direction, but not

the magnitude of $\underline{k}_0$ with respect to $\underline{k}'$, the maximum possible effect on $\underline{K}$ at $\epsilon = -0.15$ eV being $\pm 15\%$.

The similarity of the Bragg cut-off energies in beryllium and diamond excludes the possibility of detecting an inelastic followed by an elastic multiple process. For a sample of this thickness the probability of multiple inelastic processes is negligible in comparison with the processes involving a single inelastic collision.

Measurements were made at two scattering angles, 90° and 120° . Between these angles the magnitude of $\underline{K}$ for inelastic scattering changes by about 8% while the corresponding scattering wave vector for elastic (Bragg) scattering changes by 23%.

Apart from a difference in intensity the two distributions were identical within the accuracy of the measurements except for one point at $\epsilon = -0.17$ eV which appeared consistently high (by $4\times$ standard deviation) with respect to its immediate neighbours in the 90° results only. This point has been ignored in the final analysis.

The results of several experimental runs have been averaged, after applying a normalizing scaling factor of 1.15 to the 120° results, and are shown in Fig. 1 in the form of counts per output pulse from a $(1/\nu)$ monitor

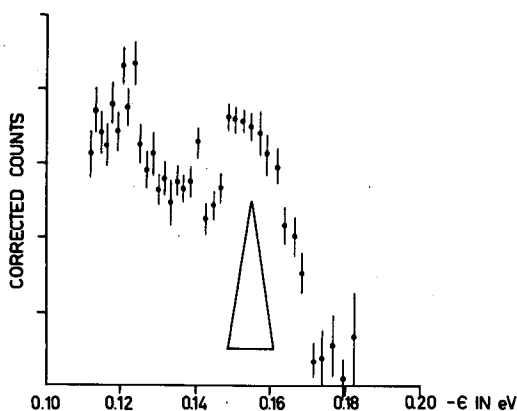


Fig. 1

Counting rate, corrected for background, as a function of energy transfer.

in the incident beam and multiplied by $\exp(\epsilon/2k_B T)$ where $k_B T$ is the sample temperature in energy units. The error bars include statistical counting errors. The corrected counts are plotted against energy transfer where $\langle E \rangle$ the mean detected energy has been calculated to be 0.0034 eV for this apparatus.

Fig. 2 shows these results multiplied by a factor $(\epsilon/|\underline{K}|^2) \sinh(\epsilon/2k_B T)$ to give a curve proportional to the phonon frequency distribution $\rho(\omega)$.

EGELSTAFF [8] has shown that, provided one is observing inelastic scattering processes involving large momentum transfers, the coherent cross-section is governed by the "self" part of the scattering law, i.e. in

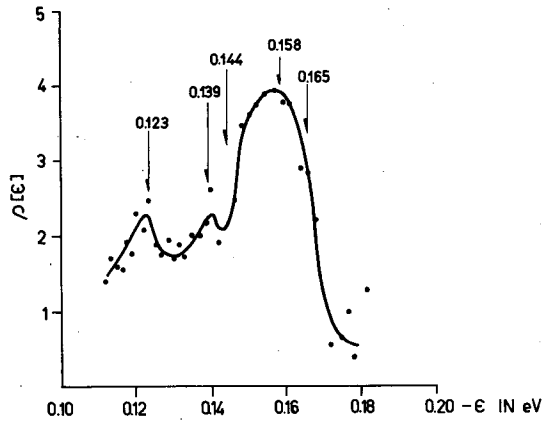


Fig. 2

Frequency distribution derived from result shown in Fig. 1.

the summation over pairs of lattice sites (n, m) the terms $n = m$ are dominant, and therefore has the same form as the incoherent cross-section. In this limit the coherent cross-section of a crystal composed of R . Bravais sub-lattices with a cross-section of $4\pi\hbar^2$ per site of the r 'th sub-lattice, is:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \epsilon} = \sum_{qj} \frac{k'}{k_0} \delta(\epsilon \pm \hbar\omega) \frac{\hbar(\bar{n} + 1/2 \pm 1/2)}{2\omega} \sum_r \frac{e^{-2W_r} b_r^2}{M_r} |\underline{K} \cdot \underline{V}_j|^2 \quad (1)$$

where $j = 1, 2, \dots, 3R$. $\bar{n}$, ω , $\underline{V}_j$ refer to the occupation number, frequency and polarization vector of the normal mode wave vector $\underline{q}$ of branch ' j '; M_r and W_r are the mass and Debye-Waller factor for atoms on the sub-lattice ' r '. Eq. (1) may be written as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \epsilon} = 3N \frac{k'}{k_0} \frac{\rho(\omega)}{\omega} \hbar(\bar{n} + 1/2 \pm 1/2) \sum_r \left[\frac{b_r^2 e^{-2W_r}}{M_r} |\underline{K} \cdot \underline{V}_j|^2 \right] \quad (2)$$

where the bars denote averages over a surface of constant energy, $\rho(\omega)$ is the distribution function for the whole lattice normalized to unity, and N the number of atoms per sub-lattice.

For a cubic crystal the averages in Eq. (2) can be performed exactly, but it is only for a Bravais lattice that the polarization vectors $\underline{V}$ can be eliminated and a direct relationship between cross-section and $\rho(\omega)$ obtained. In general for two, or more, sub-lattices occupied by different atoms the relationship also involves the polarization vectors and the cross-section does not then provide a means of deriving $\rho(\omega)$.

However, in diamond the two face-centred cubic sub-lattices are both occupied by carbon atoms and one finds, using the normalization condition, (for any given branch)

$$|\underline{V}|^2 + |\underline{V}^2| = 1$$

$$\rho(\omega) = \frac{\omega k_0 e^{2WM}}{3 N k^1 b^2 K^2 \hbar (\bar{n} + 1/2 \pm 1/2)} \frac{\partial^2 \sigma}{\partial \Omega \partial E} \quad (3)$$

where "b", W and M refer to carbon. Eq. (3) is independent of the $\underline{V}$'s and of the same form as the cross-section for a cubic Bravais lattice.

Thus we may once again derive $\rho(\omega)$ directly from the measured cross-section provided we neglect any change in W, which is a good approximation for our results. There is one additional factor which must be considered namely that the present theory only applies when $\underline{K}$ is large, and, in this limit, multiphonon scattering is likely to be significant. We have not, at present, attempted to correct for these effects since the cross-section above 0.165 eV, which is due entirely to these processes, is small and almost constant and it is reasonable to extrapolate this into the single-phonon region when the resultant correction is not significant. Even if this assumption is false it seems likely that any background variation will be smooth [9] and that the distinctive features below 0.165 eV are characteristic of the single phonon cross-section.

DISCUSSION

In Fig. 2 we show $\rho(\hbar\omega) = \rho(-\epsilon)$ in arbitrary units, and, on the same scale, the energies of the singular points as inferred from the two-phonon infrared absorption data [3]. It is evident that the two sets of results are entirely consistent in that the energy of every definite feature in the present results can be assigned to one of the singular point phonon energies derived from the infra-red data. In particular, the existence of a strong peak in $\rho(\hbar, \omega)$ near 0.16 eV is now confirmed. The present data does not establish the existence of a 0.144 eV singularity, but this does not preclude its existence, since, if the associated discontinuous change in slope is small, the present data would not reveal its presence.

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DISCUSSION

P. SCHOFIELD: In the diamond results you are working with large values of the momentum transfer, so you might expect quite a large multi-phonon contribution from the lower energy modes. Is any correction made for this in your results?

P. EGELSTAFF: A correction has been calculated and has been found to be a smooth function of energy, so that it does not materially affect the shape of the peaks. It was not subtracted from the data shown in Fig. 2.

G. DOLLING: Why were no measurements made for energies lower than about 0.1 eV?

P. EGELSTAFF: The reason is that interference terms in the scattering begin to be important at those lower energies because the type of momentum transfer involved is then lower. This would have necessitated a substantial interference correction.

G. DOLLING: I understand that maximum frequencies of the order of $40 - 45 \times 10^{12}$ c/sec are observed for diamond. Is Dr. J. Hardy satisfied with these figures?

P. EGELSTAFF: Yes, the energies are in fact ≈ 0.16 eV, and Dr. Hardy is very pleased with this value.

THE FREQUENCIES OF THE NORMAL MODES OF ALUMINIUM*

G. L. SQUIRES
CAVENDISH LABORATORY, CAMBRIDGE
UNITED KINGDOM

Abstract — Résumé — Аннотация — Resumen

FREQUENCIES OF THE NORMAL MODES OF ALUMINUM. The results of Larsson, Dahlborg and Holmryd, who have measured the frequencies of about 300 normal modes of aluminum in the 001 symmetry plane, have been analysed on the basis of the Born-von Kármán theory of lattice vibrations.

The calculation shows that at least seventh neighbour forces are necessary in order to fit the data. Each time the model is extended to take account of forces due to the next set of neighbours, the values of the previously determined force constants change appreciably. The values finally obtained are therefore of doubtful significance.

LES FRÉQUENCES DES MODES NORMAUX DE L'ALUMINIUM. Les résultats obtenus par Larsson, Dahlborg et Holmryd qui ont mesuré les fréquences d'environ 300 modes normaux de l'aluminium dans le plan de symétrie [001], ont été analysés en partant de la théorie de Born-von Karman sur les vibrations de réseaux.

Les calculs montrent que, pour expliquer ces données, il faut tenir compte pour le moins des forces exercées par le septième atome voisin. Or, chaque fois que l'on étend le modèle pour prendre en considération les forces exercées par la série suivante d'atomes voisins, les valeurs des constantes relatives à la force déterminée auparavant sont modifiées de façon appréciable. Il s'ensuit que les valeurs finalement obtenues sont d'une utilité douteuse.

КОЛЕБАТЕЛЬНЫЕ ЧАСТОТЫ НОРМАЛЬНЫХ УРОВНЕЙ АЛЮМИНИЯ. Результаты, полученные Ларссоном, Дальборгом и Хольмридом, которые измерили частоты приблизительно 300 нормальных уровней алюминия в плоскости симметрии 001, были проанализированы на основании теории вибраций решетки Борифон Кармана.

Подсчеты показывают, что для получения этих данных необходимо учитывать по меньшей мере силы взаимодействия между 7 соседними атомами. Каждый раз, когда модель выходит за пределы учитываемых сил взаимодействия со следующими соседними атомами, определения ранее силовых констант значительно изменяются. Поэтому окончательные значения имеют малую достоверность.

FRECUENCIAS DE LOS MODOS NORMALES DEL ALUMINIO. El autor analiza según la teoría de Born-von Karman relativa a las vibraciones reticulares, los valores medidos por Larsson, Dahlborg y Holmryd de las frecuencias de unos 300 modos normales del aluminio en el plano de simetría 001.

Los cálculos demuestran que para ajustar los datos es preciso recurrir a fuerzas que alcancen hasta el séptimo átomo por lo menos. Cada vez que el modelo se ha ampliado para tomar en consideración fuerzas debidas al grupo siguiente de átomos vecinos, los valores de las constantes de fuerzas determinadas anteriormente han cambiado de modo apreciable. Por tanto, los valores obtenidos en definitiva son de significación dudosa.

1. INTRODUCTION

Several sets of measurements of the frequencies of the normal vibrations of aluminium have been made by the inelastic scattering of X-rays [1]

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and neutrons [2, 3]. The results have been analysed in terms of the interatomic force constants of the Born-von Kármán theory, which is based essentially on the assumption of static harmonic forces. The question of the validity of the theory for metals and the interpretation of frequency data have been discussed by FOREMAN and LOMER [4].

In 1960, LARSSON, DAHLBORG and HOLMRYD [5] published some further neutron results for aluminium, which appeared sufficiently numerous and accurate to permit a useful test of the theory. An analysis of these results is described in the present paper.

2. BORN-VON KÁRMÁN THEORY

The structure of aluminium is face-centred cubic with cube side denoted by "a". The reciprocal lattice is body-centred cubic with cube side of length $2/a$.

Consider a normal mode whose wave vector $\underline{q}$ has components q_1, q_2, q_3 along the three tetrad axes. On the Born-von Kármán theory the three values of ω , the angular frequency, are the square roots of the eigenvalues of the 3×3 symmetric matrix A , whose elements are given by

$$A_{ii} = \frac{8}{M} \sum_s \frac{n^s}{48} \sum_j \alpha_j^s \{ 2 - C_{j,i}^s (C_{j+1,i+1}^s C_{j+2,i+2}^s + C_{j+2,i+1}^s C_{j+1,i+2}^s) \},$$

$$A_{i,i+1} = \frac{8}{M} \sum_s \frac{n^s}{48} \sum_j \beta_j^s C_{j,i+2}^s (S_{j+1,i}^s S_{j+2,i+1}^s + S_{j+2,i}^s S_{j+1,i+1}^s),$$

$$C_{j,i}^s = \cos \pi a h_j^s q_i \quad S_{j,i}^s = \sin \pi a h_j^s q_i. \quad (1)$$

In these and the other equations of this section, "i" takes values 1, 2, 3. Subscripts of the form $i+1$ and $i+2$ whose values are greater than 3 are to be interpreted as $i-2$ and $i-1$ respectively; similarly for $j+1$ and $j+2$. The superscripts "s" stands for the s^{th} set of neighbours, i.e. the set of n^s lattice points represented by the trio of integers h_1^s, h_2^s, h_3^s , of which either one or all three are even and $h_1^s \geq h_2^s \geq h_3^s$. The interatomic force constants α_i^s, β_i^s , for the lattice point h_1^s, h_2^s, h_3^s form the matrix

$$\begin{array}{ccc} \alpha_1^s & \beta_3^s & \beta_2^s \\ \beta_3^s & \alpha_2^s & \beta_1^s \\ \beta_2^s & \beta_1^s & \alpha_3^s \end{array}$$

M is the mass of an aluminium atom. The notation is explained more fully in an accompanying paper [6], references to which are denoted by I.

A list of the force constants for the first few sets of neighbours is given in Table I.

TABLE I

INTERATOMIC FORCE CONSTANTS FOR FACE-CENTRED CUBIC CRYSTAL

s	$h_1 h_2 h_3$	Interatomic force constants
1	110	$\alpha_1 \quad \alpha_3 \quad \beta_3$
2	200	$\alpha_1 \quad \alpha_2$
3	211	$\alpha_1 \quad \alpha_2 \quad (\beta_1) \quad \beta_2$
4	220	$\alpha_1 \quad (\alpha_3) \quad \beta_3$
5	310	$\alpha_1 \quad \alpha_2 \quad \alpha_3 \quad \beta_3$
6	222	$(\alpha_1) \quad (\beta_1)$
7	321	$\alpha_1 \quad \alpha_2 \quad (\alpha_3) \quad (\beta_1) \quad (\beta_2) \quad \beta_3$
8	400	$\alpha_1 \quad \alpha_2$
9	411	$\alpha_1 \quad \alpha_2 \quad (\beta_1) \quad \beta_2$

We shall require the quantities $\partial g / \partial \alpha$, and $\partial g / \partial \beta$, where "g" is an eigenvalue of the matrix A. Put $A_{ii} = A_i$ and $A_{i,i+1} = B_{i+2}$. By writing the eigenvalues as the roots of a cubic equation, it is readily shown that

$$\frac{\partial g}{\partial \alpha} = \frac{1}{D} \sum_i [g^2 - g(A_{i+1} + A_{i+2}) + A_{i+1} A_{i+2} - B_i^2] \frac{\partial A_i}{\partial \alpha},$$

$$\frac{\partial g}{\partial \beta} = \frac{2}{D} \sum_i [g B_i - A_i B_i + B_{i+1} B_{i+2}] \frac{\partial B_i}{\partial \beta},$$

$$D = \sum_i (g^2 - 2gA_i + A_{i+1} A_{i+2} - B_i^2). \quad (2)$$

The quantities $\partial A_i / \partial \alpha$ and $\partial B_i / \partial \beta$ are obtained immediately from Eqs. (1).

3. METHOD OF ANALYSIS

The wave vectors and the polarization vectors of the phonon measured by Larsson *et al.* lie in the plane perpendicular to the 001 axis. For such phonons the values of ω^2 are the eigenvalues of the matrix

$$\begin{array}{cc} A_{11} & A_{12} \\ A_{21} & A_{22} \end{array}$$

whose elements are obtained from Eqs. 1 with $q_3 = 0$.

The coordinates of the wave vector may be expressed as θ, q , where θ is the angle between the wave vector and the 100 axis, and q/a is its com-

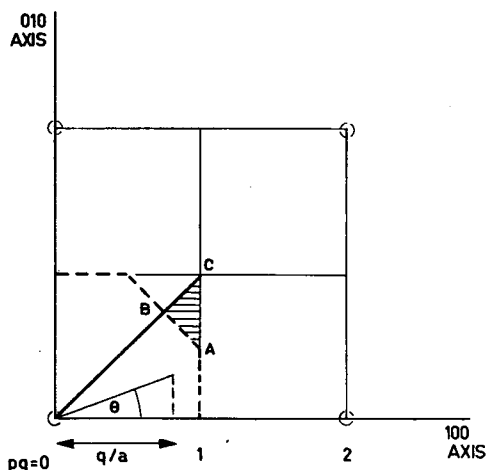


Fig. 1

Plane perpendicular to 001 axis in reciprocal lattice.

○ reciprocal lattice point
 ---- boundary of 1st Brillouin zone

ponent along the 100 axis (Fig. 1). For each phonon, the quantities θ , q , ω and also δq and $\delta\omega$, the respective errors in q and ω , are given.

It simplifies the analysis if the errors are only in ω .

An effective error $\delta\omega'$ is therefore defined by the equation

$$(\delta\omega')^2 = (\delta\omega)^2 + [(\partial\omega/\partial q)_\theta \delta q]^2. \quad (3)$$

This ignores the error in θ , but the quantity $(\partial\omega/\partial\theta)_q$ is usually fairly small. The quantity $(\partial\omega/\partial q)_\theta$ was obtained with sufficient accuracy by plotting the experimental values of ω against q for constant θ , and measuring the slopes graphically.

A least squares method was used to find a set of force constants that are the best fit to the data. We start with a set of force constants S_0 . Let the measured values of θ , q , ω and $\delta\omega'$ for the i^{th} phonon be θ_i , q_i , ω_i and $\delta\omega'_i$. The quantities θ_i , q_i and the force constants S_0 give g_i , the square of the theoretical value of the frequency. Put

$$f_i = \frac{g_i}{2\omega_i \delta\omega'_i} \quad \text{and} \quad e_i = \frac{\omega_i^2}{2\omega_i \delta\omega'_i}.$$

The root mean square deviation ξ is given by

$$\xi^2 = \frac{1}{N} \sum_{i=1}^N (f_i - e_i)^2. \quad (4)$$

where N is the total number of phonons. For a given set of data, ξ is a function of the force constants, and for a particular force model, i. e. forces

up to a specified number of neighbours, the best fit is obtained by finding the set of force constants for which ξ is a minimum.

Let the set S_0 consist of "n" parameters (force constants) with values $x_1, x_2, \dots, x_n$. We require a set of parameters such that $\partial \xi / \partial x_j = 0$ for $j = 1, 2, \dots, n$. Suppose that f_i can be expressed as

$$f_i \approx f_{i0} + \sum_k \frac{\partial f_i}{\partial x_k} \Delta x_k \quad (5)$$

where f_{i0} is the value of f_i for the set S_0 . Then

$$\begin{aligned} \frac{\partial \xi}{\partial x_j} &= \frac{1}{N\xi} \sum_i (f_i - e_i) \frac{\partial f_i}{\partial x_j} \\ &= \frac{1}{N\xi} \sum_i (f_{i0} - e_i) + \sum_k \frac{\partial f_i}{\partial x_k} \Delta x_k \frac{\partial f_i}{\partial x_j} = 0 \end{aligned}$$

if

$$\sum_k \left(\sum_i \frac{\partial f_i}{\partial x_j} \frac{\partial f_i}{\partial x_k} \right) \Delta x_k = \sum_i (e_i - f_{i0}) \frac{\partial f_i}{\partial x_j} \quad (6)$$

(The zero has been dropped from the subscript of f on the right hand side of Eq. 6.)

The expressions for $\partial f_i / \partial x_j = (1/2\omega_i \delta\omega_i^2)(\partial g_i / \partial x_j)$ are obtained from section 2. We thus have n equations, obtained by allowing j to take values $1, 2, \dots, n$, for n unknown Δx_k . On solving them we obtain a new set S_1 consisting of the parameters $x_1 + \Delta x_1, x_2 + \Delta x_2, \dots, x_n + \Delta x_n$. The cycle may be repeated.

It has been found that the method works very rapidly for $n \leq 11$. For $n = 2$, the set S reaches a limiting set L , for which the values of $\partial \xi / \partial x$ are very small after one iteration. The number of iterations needed increases gradually with "n", but for $n = 11$ only about 4 or 5 are necessary.

As "n" increases above 11, the method works less often, though with the present data it has often been successful for "n" up to 19. When it does not work, the values of the set S do not tend to a limit but vary erratically. Of course even when the method works and a minimum is found, there is no certainty that a lower minimum does not exist for a completely different set of force constants.

The analysis may be carried out under various conditions. We may for example impose the condition that the force constants satisfy the values of the elastic constants and/or that they satisfy certain values of the interplanar constants [6]. These conditions have the common property that the values of certain linear combinations of the force constants are fixed.

Suppose there are $(n_x + n_y)$ parameters with n_y linear relations between them. These relations may be used to eliminate n_y of the parameters, which may be selected arbitrarily. Denote them by y_k ($k = 1, 2, \dots, n_y$) and the others by x_j ($j = 1, 2, \dots, n_x$).

Let the n_y relations be of the form

$$\sum_{j=1}^{n_x} X_{ij} x_j + \sum_{k=1}^{n_y} Y_{ik} y_k = R_i \quad i = 1, 2, \dots, n_y \quad (7)$$

where X_{ij} , Y_{ik} are numerical constants, and R_i is the value of an elastic or interplanar constant. Let t be any function of the "x" and "y" parameters. Denote the derivative of t with respect to x_j , when no account is taken of the relations linking the "x" and "y" parameters, by $\partial t / \partial x_j$, and the same derivative, when the y parameters have been eliminated by means of Eqs. 7, by dt/dx_j . Then it is readily shown that

$$\frac{dt}{dx_j} = \frac{\partial t}{\partial x_j} - \sum_{k=1}^{n_y} \frac{\partial t}{\partial y_k} \sum_{m=1}^{n_y} Y_{km}^{-1} X_{mj} \quad (8)$$

Y^{-1} is the inverse matrix of Y .

Thus to minimize ξ subject to conditions of the type specified in Eq. 7, the "y" parameters are eliminated in the calculation of the matrix elements A_{ij} , and the quantities $\partial f_i / \partial x_j$ in Eq. 6 replaced by df_i / dx_j according to Eq. 8.

The calculations were carried out subject to the condition that the interatomic force constants fit the elastic constants. The equations relating the two sets of quantities are given in I. The three force constants that were eliminated by the relations were chosen to be those of the nearest neighbour, α_1^{110} , α_3^{110} , β_3^{110} .

The procedure adopted was to start with these constants fixed by the elastic constants, all the other force constants or parameters being zero. Call this set L_1 . The minimum value of ξ , when the five parameters of the first and second neighbours were varied subject to their satisfying the three elastic constants, was then found by the method described above. This optimum or limiting set is denoted by L_2 .

The calculation was then carried out with the inclusion of third neighbour forces, the initial set of parameters being provided by L_2 . In this way the set L_3 was found and formed the initial set of the calculation for fourth neighbour forces, and so on.

It is pointed out in I that phonons, whose wave and polarization vectors lie in the plane perpendicular to the 001 axis, give essentially quantities, denoted by μ and ν , which may be regarded as force constants between lines of atoms parallel to this axis. By considering the relations between these interline force constants and the interatomic force constants, it is shown that if the forces extend beyond the second neighbour the interatomic force constants cannot all be determined. In the present calculation we have arbitrarily put certain of the interatomic constants equal to zero. (They are indicated by brackets in Table I.) The remaining constants may then be determined, but the set obtained is one of an infinite number, each of which corresponds to the same set of interline force constants and gives the same frequencies throughout the symmetry plane.

The relations between μ , ν , α and β are given in Table II.

TABLE II

RELATIONS BETWEEN INTERLINE AND INTERATOMIC FORCE CONSTANTS

		110	200	211	220	310	222	321	400	411
		$a_1 \ a_3 \ \beta_3$	$a_1 \ a_2$	$a_1 \ a_2 \ \beta_1 \ \beta_2$	$a_1 \ a_3 \ \beta_3$	$a_1 \ a_2 \ a_3 \ \beta_3$	$a_1 \ \beta_1$	$a_1 \ a_2 \ a_3 \ \beta_1 \ \beta_2 \ \beta_3$	$a_1 \ a_2$	$a_1 \ a_2 \ \beta_1 \ \beta_2$
10	μ_1 μ_2	2 2				2 2				
11	μ_1 ν	1 1		2 2						2 2
20	μ_1 μ_2		1 1		2 2					
21	μ_1 μ_2 ν			2 2 2				2 2 2		
22	μ_1 ν				1 1		2 2			
30	μ_1 μ_2					2 2				
31	μ_1 μ_2 ν					1 1 1		2 2 2		
32	μ_1 μ_2 ν							2 2 2		
40	μ_1 μ_2								1 1	
41	μ_1 μ_2 ν									2 2 2

This table is to be interpreted according to the following example: $\mu_1^{10} = 2\alpha_1^{110} + 2\alpha_2^{310}$.

4. RESULTS AND DISCUSSION

The experimental results consist of 307 phonons, 159 longitudinal and 148 transverse. The 11 least accurate longitudinal phonons were rejected. The root mean square value of $\delta\omega'/\omega$ for the remaining 296 was 4.8%.

These data were analysed by the method described in the last section. The values of L_s , the set of interatomic force constants that are the best fit for forces up to s neighbours, are given in Table III. For each set the corresponding values of the interline force constants were calculated and are given in Table IV.

TABLE III

VALUES OF THE INTERATOMIC FORCE CONSTANTS
THAT ARE BEST FIT TO THE DATA

No. of Neighbours	1	2	3	4	5	7	8	9
No. of Parameters	0	2	5	7	11	14	16	19
ξ	2.33	1.60	1.27	1.14	1.09	0.97	0.97	0.95
110 a_1	11.0	10.5	10.9	10.2	10.6	10.0	10.0	10.4
a_3	-5.3	-2.7	-2.2	-2.4	-3.1	-3.1	-3.0	-3.4
β_3	9.3	9.3	11.3	12.3	11.3	10.6	10.7	10.0
200 a_1		0.5	2.0	4.7	4.2	1.6	1.6	1.9
a_2		-1.0	2.6	2.4	2.0	2.2	2.2	1.9
211 a_1			-0.1	0.1	0.7	1.5	1.5	1.6
a_2			-0.8	-0.3	-0.6	-0.7	-0.7	-0.8
β_2			-0.2	-0.2	-0.2	0.0	0.0	0.1
220 a_1				-0.9	-0.5	0.1	0.1	0.1
β_3				-0.3	0.5	2.0	1.9	2.8
310 a_1					-0.4	0.1	0.1	-0.1
a_2					-0.1	1.0	1.0	0.8
a_3					0.2	0.1	0.1	0.4
β_3					-0.4	-0.3	-0.2	-0.4
321 a_1						-0.2	-0.2	0.0
a_2						-0.5	-0.5	-0.5
β_3						-0.3	-0.3	-0.3
400 a_1							0.1	0.2
a_2							-0.1	0.8
411 a_1								-0.2
a_2								-0.2
β_2								-0.0

The forces are in units of 10^3 dyne/cm.

TABLE IV

VALUES OF THE INTERLINE FORCE CONSTANTS CORRESPONDING TO
VALUES OF THE INTERATOMIC FORCE CONSTANTS IN TABLE III

No. of Neighbours	1	2	3	4	5	7	8	9
10 μ_1	20.1	21.1	21.8	20.5	21.1	22.0	21.9	22.4
μ_2	-10.6	-5.4	-4.3	-4.9	-5.8	-5.8	-5.7	-6.0
11 μ_1	11.0	10.5	9.3	9.6	9.3	8.6	8.6	8.3
20 μ_1		0.5	2.0	2.9	3.3	1.9	1.8	2.0
21 μ_1			-0.1	0.2	1.5	2.0	1.9	2.2
30 μ_1					-0.8	0.1	0.2	-0.3
31 μ_1					-0.4	-0.3	-0.3	-0.1
40 μ_1							0.3	0.3

The forces are in units of 10^3 dyne/cm.

Interline force constants which are simply multiples of the interatomic force constants of Table III are not included, e. g. $\nu^{11} = \beta_3^{110}$ (since β_1^{211} has been set equal to zero), $\mu_1^{30} = 2 a_1^{310}$.

The values of the elastic constants used in analysis were (in units of 10^{11} dyne/cm²)

$$\begin{aligned} c_{11} &= 10.92 \\ c_{12} &= 6.40 \\ c_{44} &= 3.04 \end{aligned}$$

They are obtained from measurements of the velocity of sound [7].

The best criterion for deciding when a set of forces fits the data is based on the scatter of the experimental points about the theoretical values. Plots have been made of the quantity $(f_i - e_i)$ as a function of the position of the wave vector, and these indicate that the set of force constants L_7 give an approximate fit. Another criterion is $\xi = 1$. Either criterion gives the same result here, which indicates that the experimental estimates of the error are roughly correct.

In Figs. 2-4, the experimental values of ω as a function of q , together with two theoretical curves, are given for $\theta = 0, 20^\circ$ and 40° . The theoretical curves correspond to (1) first neighbour forces only, i. e. the set L_1 with no variable parameters, and (2) forces up to the seventh neighbour, i. e. the set L_7 with 14 variable parameters. Several points may be noted.

The curves for L_1 follow the experimental points qualitatively, although they clearly do not fit them. In their paper, Larsson et al. compared their results with the predictions of a model suggested by DE LAUNAY [8], which attempts to take into account the effect of the conduction electrons on the motion of the atoms. They found the same qualitative agreement. The quantity ξ for de Launay's theory has been computed and found to have the value 2.32 compared with 2.33 for the set L_1 . (The same values of the elastic constants were used in the two calculations.) In this case then, the model

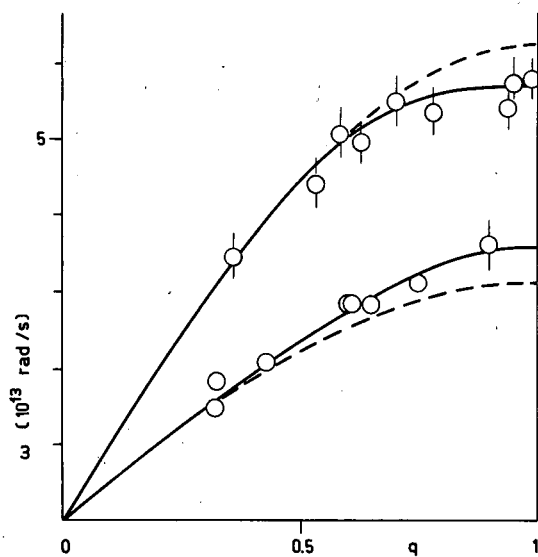


Fig. 2

Dispersion curve ω v q for $\theta = 0$.

--- theoretical curve for forces to 1st neighbour
 — theoretical curve for forces to 7th neighbour

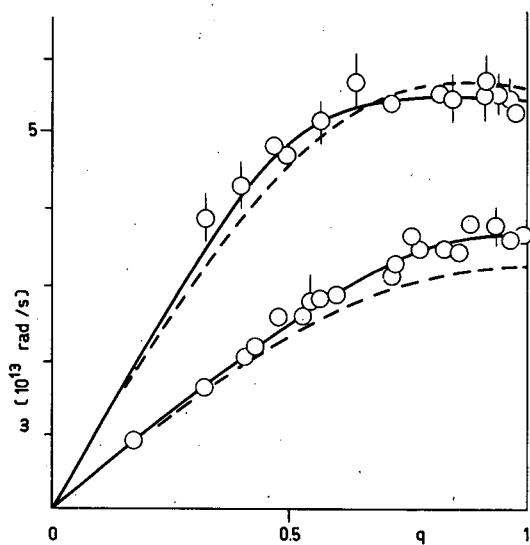


Fig. 3

Dispersion curve ω v q for $\theta = 20^\circ$.

--- theoretical curve for forces to 1st neighbour
 — theoretical curve for forces to 7th neighbour

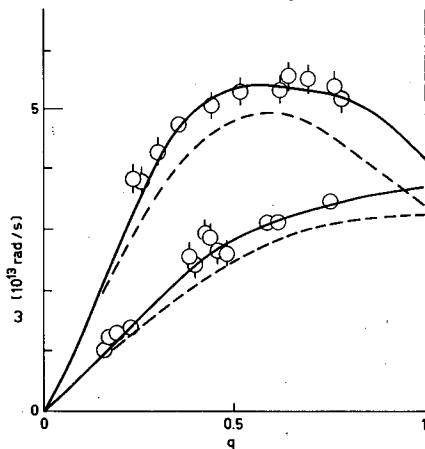


Fig. 4

Dispersion curve ω v q for $\theta = 40^\circ$.
 ---- theoretical curve for forces to 1st neighbour
 ——— theoretical curve for forces to 7th neighbour

of de Launay is not significantly better than a simple model with nearest neighbour forces only.

The improvement obtained as more and more distant forces are admitted is very gradual. Almost certainly, forces of shorter range than seventh neighbour do not fit the data. In fact the set L_7 may not quite fit them. It can be seen that for $\theta = 40^\circ$, the experimental points for the longitudinal branch are slightly high for $q \approx 0.25$ and slightly low for $q \approx 0.5$. This is not significant for the $\theta = 40^\circ$ results alone, but there is a similar trend in the results at other values of θ greater than 25° .

The analysis was carried out for values of the elastic constants other than those given above. A change of 3% was made in each constant in turn. Very little difference was found in the value of ξ for forces beyond the second neighbour.

A feature of Tables III and IV is the marked change in the values of the parameters in going from s to $s+1$ neighbour forces. The absolute values of the change appear to be of the same order of magnitude for the smaller as for the large force constants. This characteristic of changing values of the parameters is probably due to the non-linear relation between ω^2 and the force constants.

The situation may be contrasted with the case of phonons lying along a symmetry axis, when the relation between ω^2 and ' q ' can be expressed as a Fourier series whose coefficients are the interplanar force constants. BROCKHOUSE *et al.* [9] have analysed measurements for such phonons in lead and find that the values of the force constants deduced from the data vary very little as successive terms in the series are calculated.

The wave vectors of the present data lie within the first Brillouin zone. Thus there are no experimental points in the area ABC in Fig. 1. The possibility that this lack of coverage was responsible for the changing behaviour

of the force constants was investigated. (In the case of phonons along a symmetry axis the absence of data over a range of q gives rise to similar behaviour.) Some results for the region ABC were manufactured and added to the genuine data. However, the behaviour persisted.

YARNELL, WARREN and KOENIG [10] have made some accurate neutron measurements of the frequencies along the symmetry axis 100 and 110. The data of Larsson *et al.* along the symmetry axes are fairly consistent with these results. It may be remarked that a Fourier analysis of the latter shows that the forces definitely extend to the fourth neighbour plane, that is, to at least the 400 lattice point (eighth neighbour). Indeed, there is some evidence that they extend to the fifth neighbour plane, that is, to at least the 510 lattice point (fourteenth neighbour).

An attempt was made to analyse the Larsson data subject to the condition that the force constants satisfy not only the elastic constants but also some of the interplanar force constants obtained from the Yarnell data. This was not successful. Forces up to seventh neighbour no longer gave a fit and beyond the seventh neighbour the least squares method failed to give a converging set of constants.

Of the earlier results, those of BROCKHOUSE and STEWART [2] may be mentioned. Though somewhat less accurate than those of Larsson *et al.*, they have the advantage of containing phonons in both the symmetry planes, which means that in principle they are capable of determining all the force constants up to a fairly large number of neighbours (see I). Only the results in the plane perpendicular to the 001 axis may be compared directly with those of Larsson *et al.* and they prove to be slightly lower. The results from both planes have been analysed and it is found that only forces up to second neighbours are needed to fit them, a conclusion reached by the experimenters themselves.

Anharmonic effects have been ignored in the calculation. The results we have analysed were obtained at room temperature. Larsson *et al.* also made measurements at higher temperatures but it is difficult to draw any conclusions about the range of the forces from them. Systematic measurements at low temperature are highly desirable.

Another phenomenon which might complicate the observations is the Kohn effect, in which the conduction electrons give rise to kinks in the dispersion curves at values of the wave vector that are related to the Fermi surface of the metal. This has not so far been found in aluminium, and WOLL and KOHN [11] have given theoretical reasons for believing it to be small.

In summarizing we may say that, on the basis of the conventional Born-von Kármán theory, it is difficult to extract a significant set of values for the force constants from frequency measurements in a symmetry plane.

It is easy to obtain a qualitative fit with forces extending to one or two neighbours only, and this involves a small number of parameters. But as the forces due to more and more distant neighbours are included in the calculation, the rapid increase in the number of adjustable parameters produces only a gradual improvement in the fit.

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DISCUSSION

D. T. GOLDMAN: Have you examined the problem, alluded to earlier in the Symposium, of minima in multiparameter space? We have run into this problem in nuclear physics calculations where we are concerned with an analogous feature, i. e. how we can set limits on parameter variation on the basis of theoretical models. Perhaps an appropriate model for the crystal could be built into the programme, thus restricting the automatic variation routine.

G. SQUIRES: As noted in the paper, there is always the possibility that other minima exist in this multidimensional space. In the present calculation I did not encounter any situation where more than one minimum was found.

I. WALLER: Do you have any idea as to the relation between the empirical force constants method which you have described and the set of force constants calculated by Toya for sodium?

G. SQUIRES: No, I'm afraid not.

W. COCHRAN: I think that Toya's work is relevant, although not immediately applicable to aluminium because his calculations show the presence of Kohn anomalies in the case of sodium. While these anomalies are very small, they are nevertheless there and hence Toya's calculations could not be duplicated exactly by a force-constant model, which cannot produce Kohn anomalies.

B. N. BROCKHOUSE: This is true, but a comparison of theoretical and experimental force constants might be a useful way of finding out where improvements in the theory are needed.

S. H. VOSKO: Aluminium is quite different from sodium as can be shown by reference to the experimental values, without regard to the theory. The importance of the electrons in aluminium in relation to the situation which is to be found in sodium can be seen by comparing one measured transverse frequency modes with the calculated values of the uniform background model. In sodium, the values agree to within a few per cent, indicating that the electron response for large wave number q is very small, while in aluminium the measured values are less by a factor of 2 than the frequencies given by the uniform model. The reason for the Toya formulae not being applicable to aluminium lies in the Bardeen matrix element used by Toya for the electron-phonon interaction. This element was derived from monovalent metals and is not applicable to polyvalent ones. At present, we are using a more appropriate electron-phonon interaction and the results appear promising.

K. E. LARSSON: I just want to mention one thing about the anharmonic effect that might be present. The temperature variation of the phonon frequencies that we observed in aluminium was quite large - of the order of 20% over the temperature region from 300 - 600° K. Therefore the anharmonic effects at room temperature might be very large and be responsible for the large number of constants necessary for fitting the data.

G. SQUIRES: Let me emphasize that all I was interested in was how this variation varied over the symmetry plane. If it was a constant variation, this would not matter, but if it varied itself then it would affect the conclusion.

B. N. BROCKHOUSE: With reference to the comment of Dr. Larsson, the point is this: how much do the frequencies that you actually measure differ from the extrapolated frequencies? In Dr. Wood's paper on crystal dynamics from neutron spectrometry* everything is measured at a fairly low temperature. Now, as far as aluminium is concerned, room temperature is not a very low temperature. The figure quoted by Dr. Larsson is of course correct, the frequencies do change by this amount, but this is not the amount you would have to apply a correction for, even in the case of room-temperature data. A further consideration is that Dr. Larsson's measurements show that the frequencies for aluminium behave very isotropically as a function of temperature. And while this is not peculiar to aluminium, it is nevertheless a fact and, this being the case, all that happens in a force-constant analysis is that you change the scale of the force constants. If the anharmonic effects are the same for all the frequencies, then correction for the anharmonic effects will not alter the force constants except for the scale.

H. HAHN: In reply to Dr. Brockhouse, may I say that I think that the anharmonic effects would probably be greater at large frequencies and perhaps greatly reduce the number of neighbours that would have to be taken into account in the harmonic approximation. It seems to me that these small discrepancies between the first-neighbour model and the experimental values would be due to anharmonicities rather than to higher-order neighbours (up to tenth), I would like to re-emphasize that one can really get the harmonic part by extrapolating the temperature dependence above the Debye temperature to absolute zero. The fact that the frequencies do not vary with temperature below the Debye temperature tells us nothing about the influence of anharmonicity as long as the Debye temperature is high.

* See these proceedings.

B. N. BROCKHOUSE: I agree fully with everything you have said, but my point was that Dr. Larsson's measurements show that all the frequencies change with temperature in almost the same way. This applies to the elastic constants as well, so that there are no longer anharmonic effects for high frequencies, or for large wave vectors compared with small.

K. E. LARSSON: What you say is correct for the frequency region which we studied, which was somewhere in the medium frequencies, but I cannot say anything about the very high frequencies or the lower ones.

A. SJOELANDER: The use of the Born-von Kármán model introduces uncertainties not only by reason of anharmonic effects but also to the fact that the adiabatic assumptions inherent in this model are not exactly true. At least in principle, the phonon frequency (expressed in terms of wave vectors and force constants) should appear in rather complicated form, not in such a simple way as that described. As long as these uncertainties have not been eliminated I therefore question the justification of trying to fit the experimental data to a Born-von Kármán model with a high degree of accuracy. To the best of my understanding the fact that the Kohn effect is very small does not prove anything about the effect of non-adiabatic behaviour.

G. SQUIRES: It is true that the analysis described is based on the adiabatic approximation, but I believe this is now thought to hold reasonably well for metals. I think that the Born-von Kármán theory may be regarded as a phenomenological approach. In undertaking this calculation, we hoped that we might be able to explain the experimental values with a few sets of, if you like, empirical parameters. The amount of computer work involved is not really any greater when you go up to ten neighbours than if you limit yourself to two or three. It is true, of course, that the Born-von Kármán theory proved much less useful to us than we had thought.

THE RELATION BETWEEN THE INTERATOMIC FORCES AND THE FREQUENCIES OF SYMMETRY PHONONS IN CUBIC CRYSTALS *

G. L. SQUIRES
CAVENDISH LABORATORY, CAMBRIDGE
UNITED KINGDOM

Abstract — Résumé — Аннотация — Resumen

THE RELATION BETWEEN THE INTERATOMIC FORCES AND THE FREQUENCIES OF SYMMETRY PHONONS IN CUBIC CRYSTALS. Measurements of the frequencies of normal modes in a crystal are often made for phonons whose wave vectors have some special symmetry position in the reciprocal lattice. The extent to which the interatomic force constants can be determined from such measurements has been investigated for face-centred and body-centred cubic crystals.

RELATIONS ENTRE LES FORCES INTERATOMIQUES ET LES FRÉQUENCES DES PHONONS DE SYMÉTRIE DANS LES CRISTAUX CUBIQUES. Les fréquences des modes normaux d'un cristal sont souvent mesurées pour les phonons dont les vecteurs d'onde occupent une position symétrique particulière dans le réseau réciproque. La question de savoir à quel point il est possible de déterminer les constantes des forces interatomiques au moyen de telles mesures a été étudiée pour des cristaux à faces centrées et pour des cristaux cubiques centrés.

СОТНОШЕНИЕ МЕЖДУ МЕЖАТОМНЫМИ СИЛАМИ И ЧАСТОТАМИ СИММЕТРИЧНЫХ ФОНОНОВ В КУБИЧЕСКИХ КРИСТАЛЛАХ. Измерение частот нормальных уровней колебаний в кристалле часто производится для фононов, волновые векторы которых занимают особое симметричное положение во взаимной решетке. Было исследовано, в какой мере могут быть определены константы межатомных сил для гранецентрированных и объемно-центрированных кубических кристаллов.

RELACIÓN ENTRE LAS FUERZAS INTERATÓMICAS Y LAS FRECUENCIAS DE FONONES DE SIMETRÍA EN CRISTALES CÚBICOS. En muchos casos se miden las frecuencias de modos normales de un cristal para fonones cuyos vectores de onda ocupan una posición simétrica especial en la red recíproca. El autor investigó la medida en que estas constantes de fuerzas interatómicas pueden determinarse basándose en mediciones para cristales cúbicos centrados en las caras y cristales cúbicos centrados en el cuerpo.

1. INTRODUCTION

Much work has been done in the past decade on the measurement of the frequencies of the normal modes of a crystal by the inelastic scattering of neutrons and X-rays. The results are usually interpreted in terms of the interatomic force constants of the Born-von Kármán theory. In the majority of experiments that have been reported, the phonons measured have wave vectors lying in symmetry planes or along symmetry axes in the reciprocal lattice. It is therefore of interest to investigate the extent to which the interatomic force constants can be deduced from such measurements.

The frequencies of phonons in symmetry planes give certain linear combinations of the force constants which may be identified as force constants between lines of atoms; those of phonons along symmetry axes give other linear combinations which may be identified as force constants between

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planes of atoms. It is necessary to consider the relations between the inter-line and interplanar force constants on the one hand and the interatomic force constants on the other. The discussion is restricted to face-centred and body-centred cubic crystals.

2. PHONONS IN GENERAL RECIPROCAL SPACE

The equations of motion leading to the values of the angular frequency ω as a function of the wave vector $\mathbf{q}$ for the normal modes of a crystal have been derived by several authors [1]. We give here only the results for a cubic crystal with general n^{th} neighbour forces.

Consider a cubic crystal of identical atoms of mass M , with cube side of length a . Take coordinate axes x_1, x_2, x_3 along the three tetrad axes (Fig. 1).

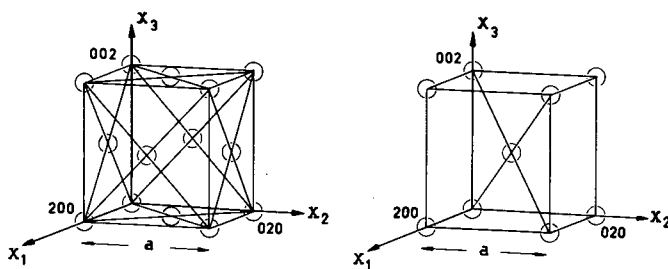


Fig. 1

Face-centred and body-centred cubic lattices.

Consider a lattice point "p" with coordinates $h_1 a/2, h_2 a/2, h_3 a/2$, where h_1, h_2, h_3 are three non-negative integers with $h_1 \geq h_2 \geq h_3$. The inter-atomic force constant ϕ_{ij}^p is defined to be the force on the origin atom in the "i" direction when the atom "p" moves unit distance in the "j" direction. The force matrix ϕ^p is symmetric and we denote its elements by

$$\alpha_1 \quad \beta_3 \quad \beta_2,$$

$$\beta_3 \quad \alpha_2 \quad \beta_1,$$

$$\beta_2 \quad \beta_1 \quad \alpha_3.$$

The point "p" is one of a set of points demanded by the symmetry of the lattice. The force matrices of the other members of the set consist of rearrangements of the same set of force constants. Denote the set by $s = 1, 2, 3$ etc., corresponding to the nearest neighbours, second nearest, third nearest, etc. The indices h_i and the force constants α_i, β_i for different sets are distinguished by the superscript "s". A list of the first few sets for face and body-centred cubic lattices is given in Table I.

TABLE I

LIST OF NEIGHBOURS FOR FACE-CENTRED AND BODY-CENTRED CUBIC CRYSTALS

s	Face-centred		Body-centred	
	$h_1 h_2 h_3$	n	$h_1 h_2 h_3$	n
1	110	12	111	8
2	200	6	200	6
3	211	24	220	12
4	220	12	311	24
5	310	24	222	8
6	222	8	400	6
7	321	48	331	24
8	400	6	420	24
9	330	12	422	24
10	411	24	333	8
11	420	24	511	24
12	332	24	440	12

The angular frequencies of the three phonons with wave vector q are equal to the square roots of the eigenvalues of the 3×3 symmetric A , whose elements are given by

$$A_{ii} = \frac{3}{M} \sum_s \frac{n^s}{48} \sum_j \alpha_j^s \{ 2 - C_{j,i}^s [C_{j+1,i+1}^s C_{j+2,i+2}^s + C_{j+2,i+1}^s C_{j+1,i+2}^s] \}$$

$$A_{i,i+1} = \frac{8}{M} \sum_s \frac{n^s}{48} \sum_j \beta_j^s C_{j,i+2}^s [S_{j+1,i}^s S_{j+2,i+1}^s + S_{j+2,i}^s S_{j+1,i+1}^s]$$

$$C_{j,i}^s = \cos \pi a h_j^s q_i \quad S_{j,i}^s = \sin \pi a h_j^s q_i. \quad (1)$$

In these equations "i" takes values 1, 2, 3. Subscripts of the form $i+1$ and $i+2$, whose values are greater than 3, are to be interpreted as $i-2$ and $i-1$ respectively; similarly for $j+1$ and $j+2$. n^s is the number of lattice points in the set "s", and q_1 , and q_2 , q_3 are the coordinates of the wave vector q .

The relations between the interatomic force constants and the elastic constants c_{11} , c_{44} and c_{12} are obtained by allowing $|q|$ to tend to zero and

comparing the matrix A with the corresponding matrix for elastic waves in a continuum. For face-centred cubic crystals the relations are

$$\begin{aligned} ac_{11} &= 8 \sum_s \frac{n^s}{48} \sum_j (h_j^s) \alpha_j^s \\ ac_{44} &= 4 \sum_s \frac{n^s}{48} \sum_j [(h_{j+1}^s)^2 + (h_{j+2}^s)^2] \alpha_j^s \\ a(c_{12} + c_{44}) &= 16 \sum_s \frac{n^s}{48} \sum_j h_{j+1}^s h_{j+2}^s \beta_j^s \end{aligned} \quad (2)$$

The same equations hold for body-centred cubic crystals when the right hand sides are divided by 2.

The first few terms for the elements of the matrix A are given in Table II and for the right hand sides of Eqs. 2 in Table III.

3. PHONONS IN SYMMETRY PLANES

$$q_3 = 0$$

Consider a normal mode whose wave vector lies in the plane $q_3 = 0$. The matrix A becomes

$$\begin{array}{ccc} A_{11} & A_{12} & 0, \\ A_{12} & A_{22} & 0, \\ 0 & 0 & A_{33} \end{array}$$

and clearly has one eigenvector along the axis 001 and two in the plane perpendicular to that axis.

The motion involved for such a mode is one in which lines of atoms parallel to the 001 axis vibrate as a whole, and it may be regarded as the motion of a two-dimensional lattice, each point of which represents a line of N_1 atoms in the three-dimensional lattice (Fig. 2).

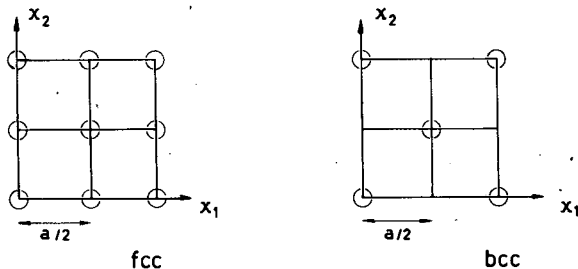


Fig. 2

Two dimensional lattice corresponding to phonons with $q_3 = 0$.

TABLE II
ELEMENTS OF MATRIX A

Face-centred cubic	
$M A_{11}$	$= 4a_1^{110} \{ 2 - \cos\theta_1 (\cos\theta_2 + \cos\theta_3) \} + 2a_3^{110} (2 - \cos\theta_2 \cos\theta_3)$ $+ 2a_1^{200} (1 - \cos 2\theta_1) + 2a_2^{200} \{ 2 - (\cos 2\theta_2 + \cos 2\theta_3) \}$ $+ 8a_1^{211} (1 - \cos 2\theta_1 \cos\theta_2 \cos\theta_3)$ $+ 8a_2^{211} \{ 2 - \cos\theta_1 (\cos 2\theta_2 \cos\theta_3 + \cos\theta_2 \cos 2\theta_3) \}$ $+ 4a_1^{220} \{ 2 - \cos 2\theta_1 (\cos 2\theta_2 + \cos 2\theta_3) \}$ $+ 2a_3^{220} (2 - \cos 2\theta_2 \cos 2\theta_3)$ $+ \dots$
$M A_{12}$	$= 4\beta_3^{110} \sin\theta_1 \sin\theta_2$ $+ 8\beta_1^{211} \cos\theta_3 \sin\theta_1 \sin\theta_2 + 8\beta_2^{211} \cos\theta_3 (\sin\theta_1 \sin 2\theta_2 + \sin 2\theta_1 \sin\theta_2)$ $+ 4\beta_3^{220} \sin 2\theta_1 \sin 2\theta_2$ $+ \dots$
Body-centred cubic	
$M A_{11}$	$= 2a_1^{111} (1 - \cos\theta_1 \cos\theta_2 \cos\theta_3)$ $+ 2a_1^{200} (1 - \cos 2\theta_1) + 2a_2^{200} \{ 2 - (\cos 2\theta_2 + \cos 2\theta_3) \}$ $+ 4a_1^{220} \{ 2 - \cos 2\theta_1 (\cos 2\theta_2 + \cos 2\theta_3) \} + 2a_3^{220} (2 - \cos 2\theta_2 \cos 2\theta_3)$ $+ 8a_1^{311} (1 - \cos 3\theta_1 \cos\theta_2 \cos\theta_3)$ $+ 8a_2^{311} \{ 2 - \cos\theta_1 (\cos 3\theta_2 \cos\theta_3 + \cos\theta_2 \cos 3\theta_3) \}$ $+ \dots$
$M A_{12}$	$= 8\beta_1^{111} \cos\theta_3 \sin\theta_1 \sin\theta_2 + 4\beta_3^{220} \sin 2\theta_1 \sin 2\theta_2$ $+ 8\beta_1^{311} \cos 3\theta_3 \sin\theta_1 \sin\theta_2$ $+ 8\beta_1^{311} \cos\theta_3 (\sin\theta_1 \sin 3\theta_2 + \sin 3\theta_1 \sin\theta_2)$ $+ \dots$
$\theta_1 = \pi a q_1$	$\theta_2 = \pi a q_2$
$\theta_3 = \pi a q_3$	
A_{22} is obtained from A_{11} by replacing θ_1 by θ_2 , θ_2 by θ_3 and θ_3 by θ_1 .	
A_{23} is obtained from A_{12} in the same way. Similarly for A_{33} and A_{31} .	

The force matrices for the two-dimensional lattice are readily derived. Consider a point "p" with coordinates $ua/2, va/2$, where "u" and "v" are non-negative integers with $u \geq v$. (For a body-centred cubic crystal, the sum of "u" and "v" must be even.) We define an interline force constant χ_{ij}^p so that $N_1 \chi_{ij}^p$ is the force on the origin point in the "i" direction due to the point "p" moving unit distance in the "j" direction. Only four elements of χ need to be considered. They are the 11, 22, 33 and 12 elements and we denote them by μ_1, μ_2, μ_3 and ν respectively.

TABLE III

RELATIONS BETWEEN THE ELASTIC CONSTANTS AND THE INTERATOMIC FORCE CONSTANTS FOR CUBIC CRYSTALS

Face-centred	110			200		211				220			310			
	α_1	α_3	β_3	α_1	α_2	α_1	α_2	β_1	β_2	α_1	α_3	β_3	α_1	α_2	α_3	β_3
$ac_{11} =$	4			4		16	8			16			36	4		
$ac_{44} =$	2	2			4	4	20			8	8		2	18	20	
$a(c_{12} + c_{44}) =$			4					8	32			16				24

Body-centred	111		200		220			311				222		400	
	α_1	β_1	α_1	α_2	α_1	α_3	β_3	α_1	α_2	β_1	β_2	α_1	β_1	α_1	α_2
$ac_{11} =$	2		2		8			18	2			8		8	
$ac_{44} =$	2		2	4	4			2	20			8			8
$a(c_{12} + c_{44}) =$		4					8			4	24		16		

This Table and Tables IV - VI are to be interpreted according to the following example:

$$\text{Face-centred cubic} \quad ac_{11} = 4a_1^{110} + 4a_1^{200} + 16a_1^{211} + \dots$$

The relation between the interline force constants χ and the interatomic force constants ϕ is given at once by

$$\chi_{ij}^{uv} = \sum_w \phi_{ij}^{uvw} \quad (3)$$

where the integers "u", "v", "w" represent a point in the three-dimensional lattice. For given "u" and "v", "w" takes all values, positive and negative, consistent with the lattice [2].

It is convenient to rearrange the terms in Eq. 3 to express them in terms of the α 's and β 's of successive sets. We write

$$\mu_1^{uv} = \sum_s m^s \alpha_1^s,$$

$$\mu_2^{uv} = \sum_s m^s \alpha_j^s,$$

$$\mu_3^{uv} = \sum_s m^s \alpha_k^s,$$

$$\nu^{uv} = \sum m^s \beta_k^s. \quad (4)$$

In these equations m^s is zero unless two of the integers h_1^s, h_2^s, h_3^s for the set "s" are equal to "u" and "v". In that case put $u = h_i^s, v = h_j^s$ and $|w| = h_k^s$. Since $h_1^s \geq h_2^s \geq h_3^s$, the subscripts "i", "j", "k" are the integers 1, 2, 3 in some order that depends on the relative magnitudes of "u", "v", "w". When $h_k^s = 0$, only one point from the set "s" contributes to the interline force and $m^s = 1$; when $h_k^s \neq 0$, two points contribute and $m^s = 2$.

TABLE IV

RELATIONS BETWEEN THE INTERLINE FORCE CONSTANTS
(LINES PARALLEL TO 001 AXIS) AND THE INTERATOMIC
FORCE CONSTANTS

		110	111	200	211	220	310
		$a_1 \ a_3 \ \beta_3$	$a_1 \ \beta_1$	$a_1 \ a_2$	$a_1 \ a_2 \ \beta_1 \ \beta_2$	$a_1 \ a_3 \ \beta_3$	$a_1 \ a_2 \ a_3 \ \beta_3$
10	μ_1	2					2
	μ_2	2					2
	μ_3	2					2
11	μ_1	1	2		2		
	μ_3	1			2		
	ν	1	2		2		
20	μ_1			1		2	
	μ_2			1		2	
	μ_3			1		2	
21	μ_1				2		
	μ_2				2		
	μ_3				2		
	ν				2		
22	μ_1					1	
	μ_3					1	
	ν					1	
30	μ_1						2
	μ_2						2
	μ_3						2
31	μ_1						1
	μ_2						1
	μ_3						1
	ν						1

The relations expressed in Eqs. (4) are given for the first few "uv" terms and the first few sets "s" in Table IV.

$$q_1 = q_2$$

For normal modes whose wave vectors lie in the symmetry plane perpendicular to the 110 axis we have a similar situation. Lines of atoms parallel to that axis move as a whole. The effective two-dimensional lattices for face and body-centred cubic crystals are shown in Fig. 3.

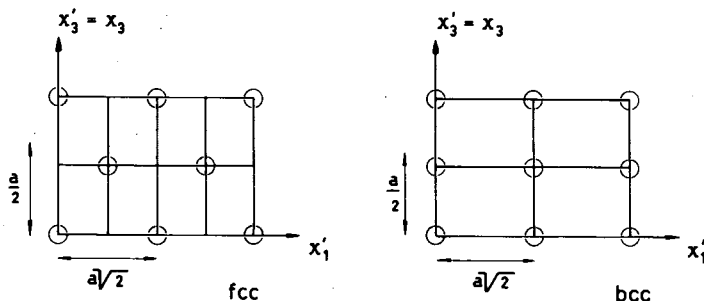


Fig. 3

Two dimensional lattice corresponding to phonons with $q_1 = q_2$.

We take new coordinate axes x'_1, x'_2, x'_3 obtained by rotating the old axes $\pi/4$ about the 001 axis so that the x'_1 axis lies along the 110 direction. The interline force constants ψ'_{ij} are defined with respect to the new axes in a manner similar to χ_{ij} , and the 11, 22, 33 and 13 elements denoted by $\kappa_1, \kappa_2, \kappa_3$ and λ respectively.

The coordinates of a point in the two-dimensional lattice may be expressed as $x'_1 = ua/2\sqrt{2}$ and $x'_3 = va/2$, where "u", "v" is a pair of integers. The sum of "u" and "v" is even for a face-centred, and "u" is even for a body-centred cubic lattice.

The relation between the constants ψ' and ϕ' is given by

$$(\psi'_{ij})^{uv} = \sum_w (\phi'_{ij})^{w, u-w, v} \quad (5)$$

where "w" takes integral values, positive or negative, consistent with the three-dimensional lattice. Dropping superscripts for the moment, we have for the relations between ϕ' and ϕ

$$\begin{aligned} \phi'_{11} &= 1/2(\phi_{11} + \phi_{22}) + \phi_{12}, \\ \phi'_{22} &= 1/2(\phi_{11} + \phi_{22}) - \phi_{12}, \\ \phi'_{33} &= \phi_{33}, \\ \phi'_{13} &= (\phi_{23} + \phi_{31})/\sqrt{2}. \end{aligned} \quad (6)$$

The constants ϕ_{ij} are eliminated between Eqs. 5 and 6, and the ϕ_{ij} rearranged to correspond to contributions from successive sets. We then have

$$\begin{aligned}\kappa_1^{uv} &= \sum_s m^s \left\{ \frac{1}{2} (\alpha_i^s + \alpha_j^s) \pm \beta_k^s \right\} \\ \kappa_2^{uv} &= \sum_s m^s \left\{ \frac{1}{2} (\alpha_i^s + \alpha_j^s) \mp \beta_k^s \right\} \\ \kappa_3^{uv} &= \sum_s m^s \alpha_k^s \\ \lambda^{uv} &= \sum_s m^s \left\{ \pm \beta_i^s + \beta_j^s \right\} / \sqrt{2}\end{aligned}\quad (7)$$

In these equations the coefficient m^s is zero unless one of the integers h_1^s, h_2^s, h_3^s is equal to "v" and the remaining pair add or subtract to "u". In that case put $v = h_k^s$. This gives "k", one of the integers 1, 2, 3; "i" and "j" are the remaining pair with $i > j$. The upper or lower sign is to be taken according to whether h_i^s and h_j^s add or subtract to "u". If $h_i^s = h_j^s = 1/2u$, $m_s = 1$; otherwise $m_s = 2$. It may be noted that if "u" or "v" is zero, $\lambda^{uv} = 0$.

The relations for the first few "uv" terms and first few sets "s" are given explicitly in Table V.

4. PHONONS ALONG SYMMETRY AXES

If the wave vector of a phonon lies along one of the symmetry axes 100, 110 or 111, either the matrix A is diagonal, or it can be made so by an appropriate rotation of axes. Such phonons correspond to displacements in the lattice in which all the atoms in a plane perpendicular to the symmetry axis move as a whole. The motion is therefore equivalent to that of a one-dimensional lattice in which each point represents a plane of atoms in the three-dimensional lattice.

For these phonons, one polarization vector lies along the direction of $\underline{q}$, corresponding to a pure longitudinal mode. If $\underline{q}$ lies along the 100 or 111 direction, the frequencies of the two transverse modes are equal and hence the polarization vectors lie anywhere in the plane perpendicular to $\underline{q}$. If $\underline{q}$ lies along the 110 direction, the frequencies of the two transverse modes are not in general equal, and the polarization vectors lie along $\bar{1}10$ and 001 .

100 axis

Consider a phonon with "q" lying along the 100 axis. Label the origin point in the one-dimensional lattice zero, and successive points 1, 2, 3...n. A longitudinal interplanar force constant π_1^n is defined so that when the point "n" moves unit distance along the 100 axis, the force on the origin point in the same direction is $N_2 \pi_1^n$, where N_2 is the number of atoms in the plane in the three-dimensional lattice. The transverse interplanar force constant π_t^n is defined similarly.

TABLE V

RELATIONS BETWEEN THE INTERLINE FORCE CONSTANTS
(LINES PARALLEL TO $1\bar{1}0$ AXIS) AND THE INTERATOMIC
FORCE CONSTANTS

	110	111	200	211	220	310
	a_1 a_2 β_3	a_1 β_1	a_1 a_2	a_1 a_2 β_1 β_2	a_1 a_2 β_3	a_1 a_2 a_3 β_3
01 κ_1 κ_2 κ_3		2 $\bar{2}$ 2 2 2				
11 κ_1 κ_2 κ_3 $\lambda/\sqrt{2}$	1 1 2 1 1 1			1 1 $\bar{2}$ 2 1 1 2 $\bar{1}$ 1		
20 κ_1 κ_2 κ_3	1 1 1 1 $\bar{1}$		1 1 2 1 1			1 1 $\bar{2}$ 2 1 1 2
21 κ_1 κ_2 κ_3 $\lambda/\sqrt{2}$		1 1 1 1 $\bar{1}$ 1				
02 κ_1 κ_2 κ_3		1	1	2 $\bar{2}$ 2 2 2		
31 κ_1 κ_2 κ_3 $\lambda/\sqrt{2}$				1 1 2 2 1 1 $\bar{2}$ 1 1		1 1 2 1 1 1
22 κ_1 κ_2 κ_3 $\lambda/\sqrt{2}$				1 1 1 1 $\bar{1}$ 1	1 1 2 1 1 1	
40 κ_1 κ_2 κ_3					1 1 1 1 $\bar{1}$	1 1 2 2 1 1 $\bar{2}$

These two force constants are related to the interatomic force constants by

$$\begin{aligned}\pi_1^n &= \sum_v \sum_w \phi_{11}^{nvw} \\ \pi_1^n &= \sum_v \sum_w \phi_{22}^{nvw} = \sum_v \sum_w \phi_{33}^{nvw}.\end{aligned}\quad (8)$$

The sums over the integers "v" and "w" are for positive and negative values that correspond to points in the three-dimensional lattice.

As usual the terms on the right hand side are rearranged to correspond to contributions from successive sets.

$$\begin{aligned}\pi_1^n &= \sum_s m^s \alpha_i^s \\ \pi_t^n &= \frac{1}{2} \sum_s m^s (\alpha_j^s + \alpha_k^s).\end{aligned}\quad (9)$$

The coefficient m^s is zero unless one of the integers h_1^s, h_2^s, h_3^s is equal to "n". In that case put $n = h_i^s$. This gives the value of "i" equal to 1, 2 or 3; "j" and "k" are the remaining pair. If $h_j^s = h_k^s = 0$, $m^s = 1$; if one of h_j^s, h_k^s is zero and the other not zero, $m^s = 4$; if $h_j^s = h_k^s \neq 0$, $m^s = 4$. In all other cases $m^s = 8$.

The relations are given explicitly for the first few values of "n" and "s" in Table VI.

We include here the case of phonons in a face-centred cubic crystal whose wave vectors have coordinates $q_1, 1/a, 0$. Such phonons do not correspond to motions in which planes of atoms move as a whole. However, the matrix A is diagonal for them, and we may define a set of constants τ analogous to the interplanar force constants π .

The polarization vectors of these phonons lie along the 100, 010 and 001 axes. Denote the corresponding angular frequencies by ω_1, ω_2 and ω_3 . The constants τ are defined by the equations

$$\begin{aligned}M\omega_1^2 &= 2\tau_1^0 + 2 \sum_{n=1}^{\infty} \tau_1^n (1 - \cos \pi n q_1), \\ M\omega_2^2 &= 2\tau_2^0 + 2 \sum_{n=1}^{\infty} \tau_2^n (1 - \cos \pi n q_1).\end{aligned}\quad (10)$$

Since ω_3 for the wave vector $q_1, 1/a, 0$ is equal to ω_2 for the wave vector $1/a - q_1, 1/a, 0$, this frequency need not be considered.

The equations defining τ may be compared with the equations relating the frequencies ω_l and ω_t of the longitudinal and transverse modes to the wave number q_1 for phonons lying along the 100 axis. They are

TABLE VI

RELATIONS BETWEEN THE INTERPLANAR FORCE CONSTANTS
AND THE INTERATOMIC FORCE CONSTANTS

Axis	n	Poln.	110	111	200	211	220	310
			$a_1 \ a_3 \ \beta_3$	$a_1 \ \beta_1$	$a_1 \ a_2$	$a_1 \ a_2 \ \beta_1 \ \beta_2$	$a_1 \ a_3 \ \beta_3$	$a_1 \ a_2 \ a_3 \ \beta_3$
100 π	1	l t	4 2 2	4 4		8 4 4		4 2 2
	2	l t			1 1	4 4	4 2 2	
	3	l t						4 2 2
110 ρ	1	l t ₂ t ₄	2 2 2 2 4			2 2 2 2 4		2 2 2 2 4
	2	l t ₂ t ₄	1 1 1 1 1	2 2 2 2 2	1 1 1 1 2	2 2 2 2 2	2 2 2 2 4	1 1 1 1 2
	3	l t ₂ t ₄				2 2 2 2 4		2 2 2 2 4
	4	l t ₂ t ₄					1 1 1 1 1	1 1 1 1 2
111 σ	1	l t		1 2 1 1				
	2	l t	2 1 2 2 1 1		1 2 1 2	2 4 4 2 4 2		2 2 2 4 2 2 2 2
	3	l t		1 2 1 1				
	4	l t				1 2 2 4 1 2 1 2	2 1 2 2 1 1	2 2 2 4 2 2 2 2
q10 τ	0	1 2	4 4 8			8 8 16		4 4 8 8 8
	1	1 2	zero 2 2			4 4		2 2
	2	1 2			1 1	4 4 4 4	4 2 2	
	3	1 2	zero					2 2

$$\begin{aligned}
 M\omega_l^2 &= 2 \sum_{n=1}^{\infty} \pi_l^n (1 - \cos \pi a n q_1), \\
 M\omega_t^2 &= 2 \sum_{n=1}^{\infty} \pi_t^n (1 - \cos \pi a n q_1).
 \end{aligned} \tag{11}$$

The expressions for the τ 's in terms of the interatomic force constants are readily obtained from the matrix A by putting $q_2 = 1/a$, $q_3 = 0$. The results are included in Table VI.

110 axis

The frequencies of phonons with q lying along the 110 axis may be expressed in terms of three sets of force constants defined in a manner similar to that of the π 's. The force constants for longitudinal motion are denoted by ρ_l^n , for transverse motion parallel to a two-fold axis of symmetry by ρ_{t2}^n and for transverse motion parallel to a four-fold axis of symmetry by ρ_{t4}^n .

We simply give the results for the relations between the ρ 's and the interatomic force constants. They are

$$\begin{aligned}
 \rho_l^n &= \sum_s m^s \left\{ \frac{1}{2} (\alpha_i^s + \alpha_j^s) \pm \beta_k^s \right\} \\
 \rho_{t2}^n &= \sum_s m^s \left\{ \frac{1}{2} (\alpha_i^s + \alpha_j^s) \mp \beta_k^s \right\} \\
 \rho_{t4}^n &= \sum_s m^s \alpha_k^s.
 \end{aligned} \tag{12}$$

The coefficient m^s is zero unless two of the integers h_1^s, h_2^s, h_3^s add or subtract to "n". In that case denote the third integer by h_k^s . This gives the integer $k = 1, 2$ or 3 ; "i" and "j" are the remaining pair. The upper or lower sign is to be taken according to whether the two integers h_i^s and h_j^s add or subtract to "n". If $h_i^s = h_j^s$, m^s is 1 or 2 depending on whether the third integer h_k^s is zero or not. If $h_i^s \neq h_j^s$, m^s is 2 or 4 depending on whether h_k^s is zero or not.

The relations for the first few values of "n" and "s" are given in Table VI.

111 axis

The interplanar force constants are denoted by σ_l^n and σ_t^n . They are given in terms of the interatomic force constants by

$$\begin{aligned}
 \sigma_l^n &= \sum_s m^s (\alpha_1^s + \alpha_2^s + \alpha_3^s \pm \beta_1^s \pm \beta_2^s \pm \beta_3^s), \\
 \sigma_t^n &= \sum_s m^s (\alpha_1^s + \alpha_2^s + \alpha_3^s \mp \beta_1^s \mp \beta_2^s \mp \beta_3^s).
 \end{aligned} \tag{13}$$

The coefficient m^s is zero unless the three integers h_1^s, h_2^s, h_3^s satisfy the equation

$$\pm h_1^s \pm h_2^s \pm h_3^s = n \quad (14)$$

for some combination of the + and - signs. If the three signs in Eq. (14) are the same, take the upper signs in Eqs. (13). If the sign of h_1^s is opposite to that of the other two integers, take the upper sign for β_1^s and the lower sign for the other two β^s . If all three integers are equal and add to "n", $m^s = 1$; if two of them are equal and have the same sign in Eq. (14), $m^s = 3$; in all other cases $m^s = 6$.

The relations for the first few values of "n" and "s" are given in Table VI.

5. INFORMATION TO BE OBTAINED FROM PHONON FREQUENCIES

The results in the last two sections enable us to determine which interatomic force constants may be deduced, at least in principle, from a given set of frequency measurements.

It is assumed for the present purpose that the set contains an arbitrarily large number of very accurate measurements. Whether a meaningful set of force constants can be deduced from a given set of measurements in practice is another matter. For measurements along a symmetry axis, ω^2 is a linear function of the force constants and the process is fairly straightforward [3]. However, for measurements in a symmetry plane or in more general parts of reciprocal space ω^2 is not a linear function of the force constants and the latter are not readily extracted from the data [4]. We are not here concerned with these difficulties but only with the maximum number of force constants that can be deduced theoretically.

If the wave vectors are scattered throughout the first Brillouin zone, then, provided the forces do not extend to a large number of neighbours, all the interatomic force constants may in principle be determined. FOREMAN and LOMER [5] have pointed out that in order to determine all the interatomic force constants, it is necessary to know not only the frequency but also the polarization of all the phonons in the first Brillouin zone. This is true for general forces. However, if the forces are effectively zero for distant neighbours, the interatomic force constants may be determined from frequency measurements alone.

If the wave vectors of the phonons lie in symmetry planes or along symmetry axes, the frequencies give essentially certain interline or interplanar force constants. These are not all independent. There are relations between them which depend on the range of the forces. Only if the number of independent interline or interplanar force constants is equal to the number of interatomic force constants can the latter be determined individually.

Symmetry planes

Measurements are often made for phonons whose wave vectors and polarization vectors lie in the same symmetry plane [6, 7, 8]. Consider the specific case of a face-centred cubic crystal in which the symmetry plane is perpendicular to the 001 axis.

Suppose that the forces extend to the second neighbour (200). Table IV shows that there are six non-zero interline force constants, μ_1^{10} , μ_2^{10} , μ_1^{11} , ν^{11} , μ_1^{20} and μ_2^{20} , with one relation between them, namely $2\mu_1^{11} = \mu_1^{10}$. The number of interatomic force constants is five and therefore they can all be determined.

If the forces extend to the third neighbour (211), there are nine interline constants with one relation between them, namely $2\mu_1^{11} = \mu_1^{10} + 2\mu_2^{21}$. Since there are nine interatomic constants, they cannot all be determined. Inspection of Table IV shows that seven out of the nine can be determined but for the remaining two, β_3^{110} and β_1^{211} , only the combination $(\beta_3^{110} + 2\beta_1^{211})$ is known.

The situation is similar for body-centred cubic crystals. Only if the forces do not extend beyond the second neighbour (200), do measurements on phonons, whose wave vectors and polarization vectors lie in the 001 plane, give all the interatomic force constants.

We may also consider similar measurements in which the symmetry plane is perpendicular to the 110 axis. Here the situation is that for a face-centred cubic crystal, such measurements determine all the interatomic constants, provided the forces do not extend beyond the third neighbour. If they extend to the fourth neighbour (220), there are 15 interline constants but four relations between them. From the 11 independent constants, three of the 12 interatomic constants may be deduced; the remaining nine satisfy eight relations.

For body-centred cubic crystals, measurements in this plane give all the interatomic constants, provided the forces do not extend beyond the tenth sets of neighbours (511) and (333). But if they extend to the twelfth set (440), there are 36 interatomic constants of which 27 may be determined. The remaining nine are related to eight values of the interline constants.

If measurements from both symmetry planes are combined, then for both face-centred and body-centred cubic crystals, all the interatomic force constants can be determined, at least up to sixteenth neighbour forces.

Symmetry axes

Another common set of measurements are those in which the wave vectors lie along the three symmetry axes [3, 9]. These measurements give the seven sets of interplanar constants π_1^n , π_2^n , ρ_1^n , ρ_2^n , ρ_{14}^n , σ_1^n , σ_2^n .

FOREMAN and LOMER [5] have considered the case of a face-centred cubic crystal and point out that there are always at least seven relations between the interplanar force constants. Of these, four arise because the seven values of $d\omega/dq$ at $q=0$ are fixed by three elastic constants. The remaining three come from the fact that the points $1/a$, $1/a$, 0 and $1/a$, 0 , 0 represent equivalent waves. Five dispersion curves end at these points but there are only two values of the frequency. The authors have shown that for forces up to the fourth neighbour (220), all twelve interatomic forces may be deduced from the measurements.

If the forces extend to the fifth neighbour (310), there are 22 interplanar constants with eight relations between them. Thus there are 14 independent quantities which are insufficient to determine the 16 interatomic constants. The addition of data with wave vector q_1 , $1/a$, 0 (see Section 4) gives six further constants but only one of them is independent. It is still true therefore that all the interatomic force constants cannot be determined.

For a body-centred cubic crystal, there are also at least seven relations between the interplanar force constants. Four arise as before from the slopes of the dispersion curves at the origin, and three from the fact that the points $1/a$, $1/a$, $1/a$ and $1/a$, 0 , 0 represent equivalent waves. Four dispersion curves end at these points but there is only one value of the frequency. It may be shown that measurements along the three symmetry axes determine all the force constants if the forces do not extend beyond the seventh neighbour (331), but not if they have a longer range.

Other combinations of measurements are of course possible. For example, measurements in the plane 001 may be combined with measurements along the 111 axis. Nor have we considered measurements in which the wave vector lies in a symmetry plane and the polarization vector is perpendicular to the plane. In each specific case the information that can be derived may be determined from the results of Sections 2 and 3.

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$$\sum_{\text{all } p} \chi_{ij}^p = 0$$

This equation gives χ_{ij}^0 in terms of all the other χ_{ij}^p . The same relations hold for the other interline and interplanar force constants.

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DISCUSSION

G. DOLLING: I would just like to point out that all the results quoted in this paper apply only to the face-centred cubic and body-centred cubic simple cubic lattices, because sometimes you imply a more general application than this.

G. SQUIRES: Yes, this is correct.

NEUTRON-PHONON INTERACTION STUDIES IN COPPER, ZINC AND MAGNESIUM SINGLE CRYSTALS

E. MALISZEWSKI, J. SOSNOWSKI, K. BLINOWSKI,
J. KOZUBOWSKI, L. PADLO AND D. ŚLEDZIEWSKA
INSTITUTE OF NUCLEAR RESEARCH, WARSAW
POLAND

Abstract — Résumé — Аннотация — Resumen

NEUTRON-PHONON INTERACTION STUDIES IN COPPER, ZINC AND MAGNESIUM SINGLE CRYSTALS. The phonon dispersion relations in copper single crystals has been studied by means of a triple-axis crystal neutron spectrometer. In the [100] direction the transversal branch, not reported in the papers of Cribier and Jacrot, has been found. This branch fits well to the recent data of sound velocity; however, it differs partly from the X-ray results of Jacobsen. For the longitudinal branch in the [100] direction the dispersion curve obtained by Cribier and Jacrot is lying well above the Jacobsen's curve, and the experimental points reported in the present paper support the results of Cribier and Jacrot.

The phonon dispersion relations in zinc and magnesium single crystals has been studied using the cold neutron method and by means of a triple-axis crystal neutron spectrometer as well. The scattering surfaces in the [1010] plane were traced, the AT and AL branches found and the phonon dispersion relations in the [001] and [010] directions obtained. The results have been compared with those obtained by Johnson with X-rays. In the [001] direction the present results fit well to Johnson's for the AL branch. In the [010] direction for the AT branch a large discrepancy has been found between Johnson's and the present results. Some explanation of this discrepancy is given. Similar measurements in the same directions in magnesium single crystals are under way and will be reported.

ÉTUDE DES INTERACTIONS NEUTRON-PHONON DANS DES MONOCRISTAUX DE CUIVRE, DE ZINC ET DE MAGNÉSIUM. Les auteurs ont étudié les relations de dispersion des phonons dans des monocristaux de cuivre, au moyen d'un spectromètre neutronique à cristal triaxe. Ils ont trouvé, dans la direction [100], la branche transversale que n'ont pas signalée Cribier et Jacrot dans leurs travaux. Cette branche s'adapte bien aux données récentes relatives à la vitesse du son, mais elle diffère partiellement de celles qui ont été obtenues par Jacobsen pour les rayons X. En ce qui concerne la branche longitudinale dans la direction [100], la courbe de dispersion obtenue par Cribier et Jacrot se trouve nettement au-dessus de la courbe de Jacobsen et les points expérimentaux signalés dans le présent mémoire confirment les résultats de Cribier et de Jacrot.

Les relations de dispersion des phonons dans des monocristaux de zinc et de magnésium ont été étudiées à l'aide de la méthode des neutrons froids et d'un spectromètre neutronique à cristal triaxe. Les auteurs ont tracé les surfaces de diffusion dans le plan [1010], trouvé les branches AT et AL ainsi que les relations de dispersion des phonons dans les directions [001] et [010]. Ils ont comparé ces résultats à ceux qu'a obtenus Johnson avec des rayons X. Dans la direction [001], les résultats s'adaptent bien à la courbe de Johnson en ce qui concerne la branche AL. Dans la direction [010], pour la branche AT, les auteurs observent un grand écart entre leurs résultats et ceux de Johnson. Ils en donnent une explication. Ils décrivent des mesures semblables faites à l'heure actuelle dans les mêmes directions, dans des monocristaux de magnésium.

ИЗУЧЕНИЕ ВЗАИМОДЕЙСТВИЯ НЕЙТРОНОВ И ФОНОНОВ В МОНОКРИСТАЛЛАХ МЕДИ, ЦИНКИ И МАГНИЯ. Сотношения для рассеяния фононов в монокристаллах меди были изучены при помощи трехосевого кристаллического спектрометра нейтронов. В направлении оси 100 была обнаружена поперечная ветвь, о которой не сообщалось в докладах Крийе и Жакро. Ее характеристики совпадают с последними данными относительно скорости звука, однако частично отличаются от результатов Якобсена для рентгеновских лучей. Для продольной ветви в направлении си 100 кривая рассеяния, полученная Крийе и Жакро, расположена значительно выше кривой Якобсена, и сообщаемые в настоящем докладе экспериментальные данные подтверждают результаты Крийе и Жакро.

* At present with the Warsaw University.

Выражения для рассеяния фононов в монокристаллах цинка и магния были изучены при использовании метода рассеяния холодных нейтронов и также при помощи трехосевого кристаллического спектрометра нейтронов. Были вычерчены поверхности рассеяния в плоскости 1010, что позволило найти ветви AT и AL и получить выражения для рассеяния фононов в направлениях 001 и 010. Эти результаты были сравнены с результатами, полученными Джойнсоном для рентгеновских лучей. Полученные в настоящее время результаты для направления 001 хорошо совпадают с данными Джойсона для ветви AL. В направлении 010 для ветви AT наблюдается значительное расхождение между данными Джойсона и полученными теперь результатами. Даются некоторые объяснения этого расхождения. В настоящее время производятся аналогичные измерения в тех же направлениях в монокристаллах магния. Результаты будут сообщены дополнительно.

ESTUDIO DE LAS INTERACCIONES NEUTRÓN-FONÓN EN MONOCRISTALES DE COBRE, CINCO Y MAGNESIO. Los autores han estudiado las relaciones de dispersión de fonones en monocristales de cobre con ayuda de un espectrómetro neutrónico triaxial. En la dirección 100 han observado la rama transversal, no mencionada en las memorias de Cribier y Jacrot. Esta rama concuerda satisfactoriamente con los datos recientes relativos a la velocidad del sonido, pero difiere en parte de los resultados roentgenográficos obtenidos por Jacobsen. En cuanto a la rama longitudinal en la dirección 100, la curva de dispersión obtenida por Cribier y Jacrot se encuentra netamente por encima de la curva de Jacobsen y los puntos experimentales a que se refiere la presente memoria confirman los resultados de Cribier y Jacrot.

Los autores han estudiado las relaciones de dispersión de fonones en monocristales de cinc y magnesio por el procedimiento de los neutrones fríos, utilizando además un espectrómetro neutrónico triaxial. Han determinado las superficies de dispersión en el plano 1010, observado las ramas AT y AL y obtenido las relaciones de dispersión de fonones en las direcciones 001 y 010. Han comparado esos resultados con los datos roentgenográficos por Johnson. En la dirección 001, los resultados de los autores concuerdan satisfactoriamente con los obtenidos por Johnson para la rama AL. En la dirección 010 han observado en el caso de la rama AT una discrepancia considerable entre los resultados de Johnson y los propios. Los autores explican parcialmente dicha discrepancia; en la actualidad están efectuando mediciones análogas en las mismas direcciones en monocristales de magnesio, y presentarán datos al respecto.

I. INTRODUCTION

The measurement of the coherent inelastic scattering of slow neutrons from a single crystal gives information on the frequency wave number relation for the phonons in the crystal lattices. For a crystal with N atoms per primitive unit cell the dispersion relation is

$$\nu = \nu_j(\underline{g}) \quad (1)$$

where j refers to a particular phonon branch. The energy exchange of neutrons with lattice vibrations and the phonon wave number are determined from an energy-momentum law:

$$[(\hbar^2/2m)(K^2 - K_0^2)] = \pm \hbar \nu_j(\underline{q}) \quad (2)$$

$$\underline{K} - \underline{K}_0 = \underline{q} + \underline{z} \quad (3)$$

where $\underline{K}_0$ and $\underline{K}$ are the wave vectors of the incident and scattered neutrons, respectively, ν_j and $\underline{q}$ are the frequency and propagation vector of the normal mode, and $\underline{z}$ is the appropriate reciprocal lattice vector. When the energy-momentum law is satisfied, neutrons are scattered with an intensity given by the WALLER and FROMAN equation [1, 2]. As follows from this

equation the scattering intensity is large for small ν (intensity varies as ν^{-1}). The cross-section is proportional to a structure factor [3] g^2 (an analogue of the structure factor for elastic scattering) which includes the factor $[(\underline{K}_0 - \underline{K}) \cdot \underline{e}_{j\ell}]^2$ ($\underline{e}_{j\ell}$) are the polarization vectors, and a sum over all atoms in the unit cell in the case when $N > 1$. The factor $[(\underline{K}_0 - \underline{K}) \cdot \underline{e}_{j\ell}]^2$ makes it possible to distinguish the polarization directions of phonons by intensity measurements under different experimental conditions. The factor

$$[1 + \epsilon (\underline{n} \cdot \underline{C}_j / v)]^{-1}$$

from the Waller and Froman equation (where $\underline{n}$ is the unit vector along the scattering direction, v is the velocity of the scattered neutrons, $\underline{C}_j = \text{grad } \nu_j(q)$ is the group velocity and ϵ is equal ± 1). It is a measure of the number of normal modes, satisfying the energy-momentum law and it can also strongly affect the intensity. Its significance is large, particularly when the final neutron velocity is smaller than the velocity of phonons or when $\underline{k}$ is a tangent of the scattering surface. In this latter case broad neutron groups are observed. The above mentioned factors must be taken into account in the intensity measurements along any one of the dispersion relation branches.

Taking this all into consideration and using the experimental methods described in Section II the phonon dispersion relations in copper, zinc and magnesium single crystals have been studied as described in Section III.

II. EXPERIMENTAL METHODS

The two different techniques were used in the present investigation performed at the EWA reactor in Warsaw. In one method the measurements were carried out on the triple-axis crystal spectrometer described elsewhere [4]. The monochromator and the analyser were single crystals of zinc cut parallel to (0001) planes and the surfaces were prepared in a special way to ensure high neutron intensity. The wavelength of the incident neutron was 1.53 Å, as determined from the elastic incoherent scattering of vanadium, for all experiments performed by this method.

In the other method an incident beam of cold neutrons filtered by liquid air-cooled beryllium was utilized. The energy distribution of the scattered neutrons for the different angular settings of the specimen crystals was measured (at a fixed angle of 90°) using a chopper and time-of-flight method described in detail elsewhere [5]. The flight path from the chopper centre to the detector was 420 cm and a 100-channel time analyser was used.

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

1. Copper

Phonon dispersion relations for copper single crystals were investigated first by JACOBSEN [6] by means of X-rays diffuse scattering, and recently by CRIBIER and JACROT [7, 8] by inelastic scattering of cold neu-

trons. The latter results disagree with those obtained by Jacobsen for the longitudinal branch in the [100] direction and they do not show the transversal branch, found previously by Jacobsen.

The present measurements [9] were carried out on the triple-axis crystal spectrometer. A cylindrical copper single crystals, 5 cm in diam. and 15 cm long, with the axis of the cylinder about 6° off the [100] direction, was used.

The measurements, all in room temperature, were done by appropriate simultaneous variations of the incident and scattering angles using the method of successive approximations [3]. Additional measurements following from the discussion outlined in Section I were made in order to determine the directions of polarization of the vibrations.

Fig. 1 shows a typical experimental curve: counting rate versus wavelength of the scattered neutrons. Fig. 2 shows the reciprocal lattice diagram

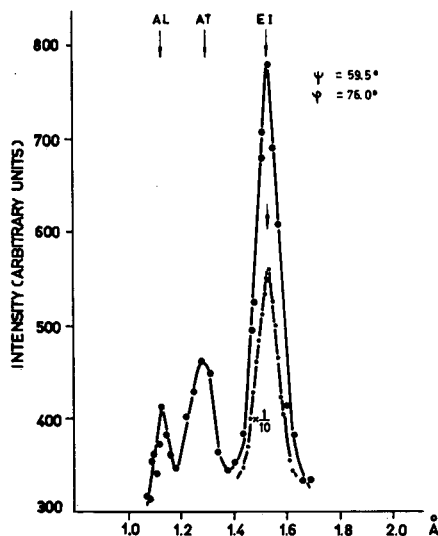


Fig. 1

Typical neutron groups observed.

The vanadium elastic incoherent peak is shown below the copper elastic incoherent peak.

with some of the experimentally determined phonons. Most of the phonon peaks observed result from phonon annihilation processes. Fig. 3 shows the dispersion curves and, as can be seen, the longitudinal and transverse branches were found. The calculations of the directions of the tangentials to the dispersion curves are based on data from a summary of the latest measurement of sound velocities [10].

The experimental points for the longitudinal phonons do not fit either the CRIBIER and JACROT [8] or the Jacobsen dispersion curves. More precise measurements for this branch are still needed.

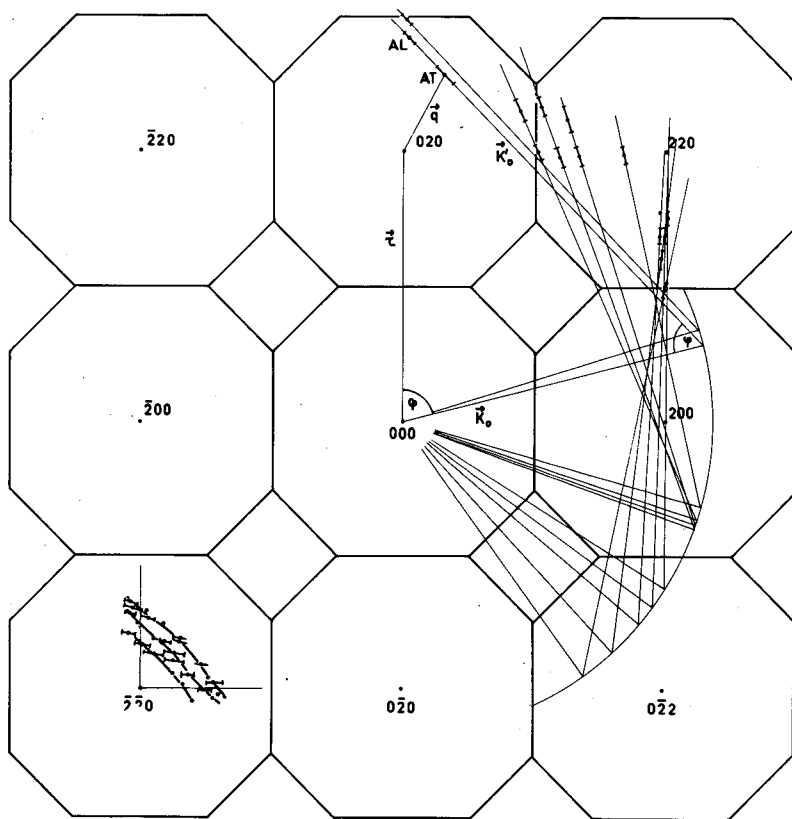


Fig. 2

Reciprocal lattice diagram for the (100) plane for the copper lattice with some of the determined phonons. The symmetry of the inelastic scattering surfaces is shown in the neighbourhood of point $0\bar{2}2$.

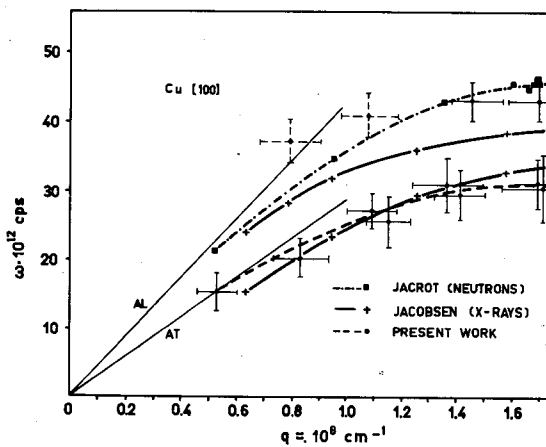


Fig. 3

Dispersion relation for phonons in the [100] direction in copper.

The dispersion curve for the transversal branch (no report on this branch is given in the papers of Cribier and Jacrot), fits in with the recent data of sound velocity, but does not agree with the X-ray results of Jacobsen. The poor fit of the X-ray results with the sound velocity (the lower part of the dispersion curve) is mentioned by the author himself. The discrepancy between our results and Jacobsen's in the upper part of the dispersion curve may be due to the difficulty in the precise calculations of the Compton corrections in the diffuse scattering of X-rays.

2. Zinc and magnesium

Until now extensive experimental studies of phonon dispersion relations by neutron spectrometry have been performed on cubic crystals only. For this reason an attempt has been made to study these relations in hexagonal lattices and zinc and magnesium have been chosen because of their excellent nuclear properties, small capture cross-sections, negligible incoherent scattering, comparatively small atomic masses and availability of large single crystals [11]. In the case of zinc an additional argument was the availability of JOYNSON's [12] results of lattice frequencies measured by means of diffuse X-ray scattering.

The zinc crystal used was of 5 cm diam. and 15 cm long with its axis about 75° off the $[0001]$ axis. The crystal was mounted on a goniometer so that the $(\bar{1}010)$ mirror plane and the $[0001]$ axis were in the horizontal plane of the apparatus.

At first the zinc crystal was investigated [13] using the cold neutron facility and the time-of-flight method. In Fig. 4 the inelastic scattering sur-

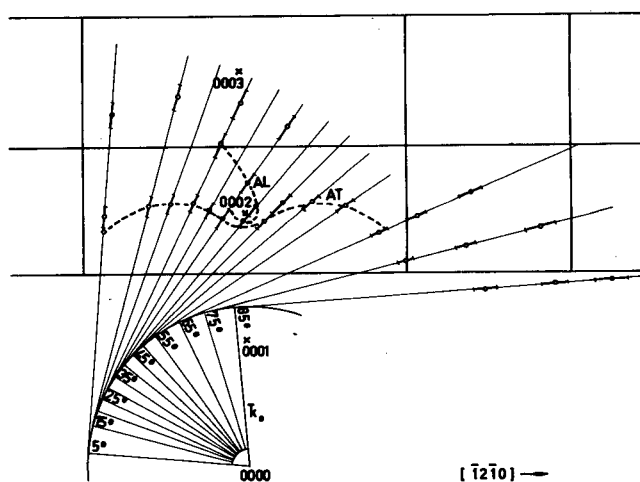


Fig. 4

Reciprocal lattice diagram for $(\bar{1}010)$ plane of zinc with experimentally determined scattering surfaces by the cold neutron method.

faces in the $(\bar{1}010)$ plane obtained by this method are shown in the reciprocal lattice. The majority of the phonons which belong to the acoustical transverse branch are large in intensity owing to the cooperation of factors mentioned in Section I.

Afterwards the measurements were carried out, with the same orientation of the crystal, on the triple-axis crystal spectrometer. The conventional method and the method of successive approximations were applied at pertinent points in the reciprocal space. Some of the typical phonons observed by this method are shown in Fig. 5.

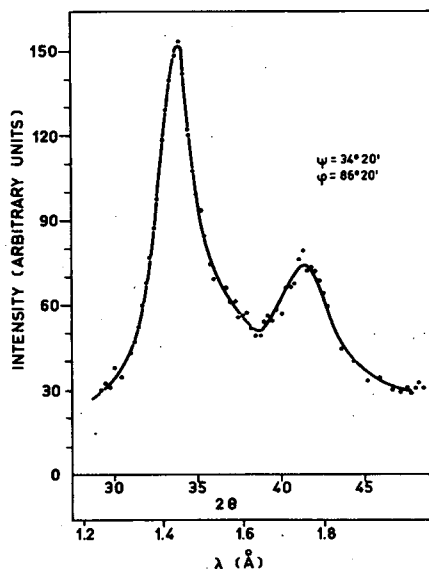


Fig. 5

Some typical neutron groups for zinc plotted as a function of the angle of the analysing spectrometer.

Fig. 6 shows the relations between the angular frequency and the wave vector of the phonons for the $[0001]$ direction compared with the JOYNSON X-rays data [12]. The open circles are the points obtained by the cold neutron method and the filled ones by crystal spectrometer. The errors include contributions from the spread of the incident neutron wavelength, time-of-flight, or wavelength, of the scattered neutrons, crystal orientation, incident angle and scattering angle. The dashed curve for the longitudinal acoustical phonons was calculated from the expression $\nu = C_l(2D/\pi) \sin(\pi q/zD)$ where $D = (6\pi^2/V)^{1/3}$ is the Debye radius and V is the volume of a unit cell and it was an initial slope corresponding to the velocity of sound C_l as computed from the elastic constants [10] for the acoustical modes. As may be seen from Fig. 6 for the AL branch there exists a good agreement between the present results and the calculated curve; however, both are lying slightly

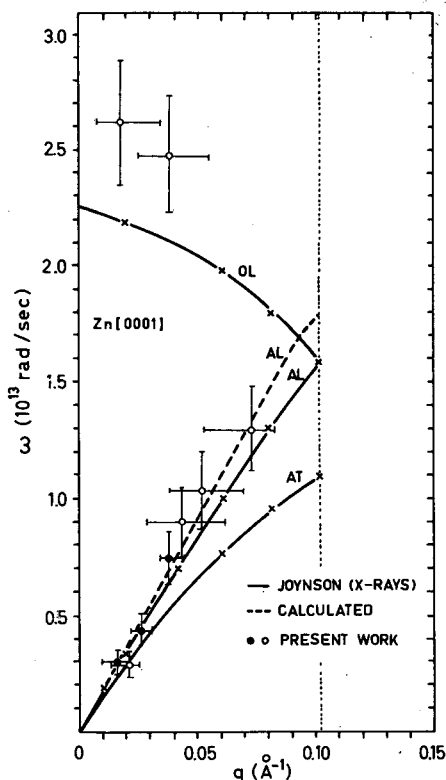


Fig. 6

Part of the dispersion curves for zinc in the [0001] direction compared to X-rays and calculated data.

The results from crystal spectrometer method are shown as filled circles.

The open circles were obtained by filter-chopper method.

above the Joynson curve. Similarly the points found for the OL branch are lying well above the X-ray data.

In Fig. 7 the phonon dispersion relation in zinc in the $[\bar{1}2\bar{1}0]$ direction is shown. The low frequency acoustical branch was identical as transverse AT_2 . The polarization of this branch is normal to the basal plane. For the polarization determination of other phonons additional measurements and calculations are needed and they are under way. Contrary to the results for the [0001] direction, where the dispersion curves are almost straight lines, for the AT_2 branch in the $[\bar{1}2\bar{1}0]$ direction a large dispersion is observed.

These results cannot be compared directly with Joynson's measurements because his has been for the $[01\bar{1}0]$ direction*. However the directions of vibrations for the AT_2 branch both for the $[01\bar{1}0]$ and $[\bar{1}2\bar{1}0]$ directions

* Such a direct comparison has been made at the Symposium but the paper presented there contained a trivial error connected with the orientation of the zinc crystal. Therefore some curves presented in Fig. 4, 7, 8 and 9 have also been redrawn.

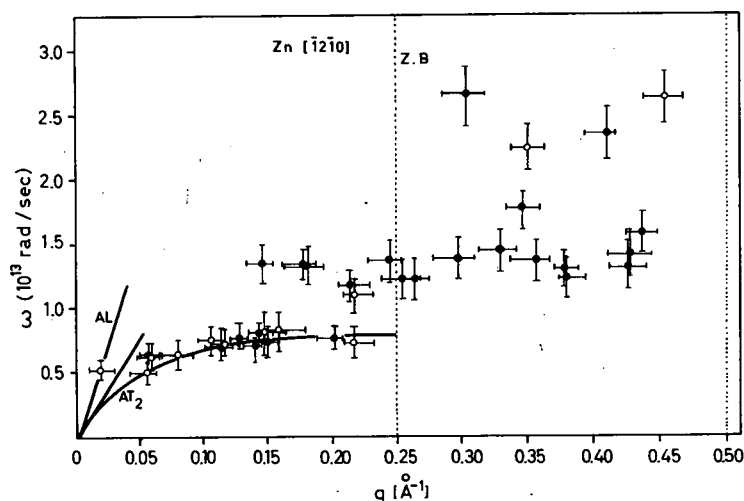


Fig. 7

Dispersion relation for acoustical phonons in the $[11\bar{2}0]$ direction in reciprocal space of zinc. The slope of heavy lines indicates the velocities of sound in the crystal as calculated from elastic constants. The open circles were found by filter-chopper method and those closed by crystal spectrometer method.

are parallel to the $[0001]$ axes and therefore one can assume that for small values of q the dispersion curves for these branches should not differ very much. Such a comparison presented in Fig. 8 shows however a very large discrepancy between the neutron and the X-ray measurements. The final

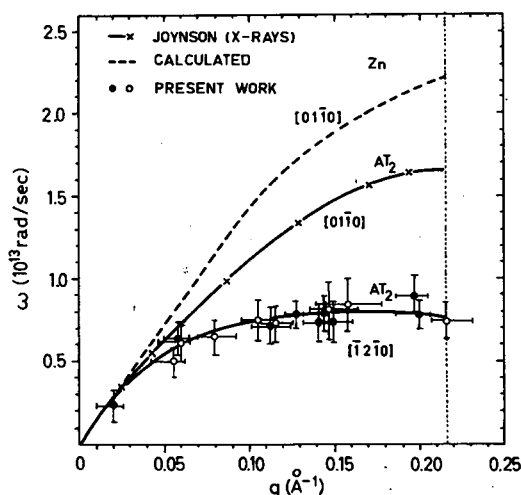


Fig. 8

Acoustical dispersion curves derived from the present measurements in the $[11\bar{2}0]$ direction as compared to X-rays and calculated data for the $[01\bar{1}0]$ direction.

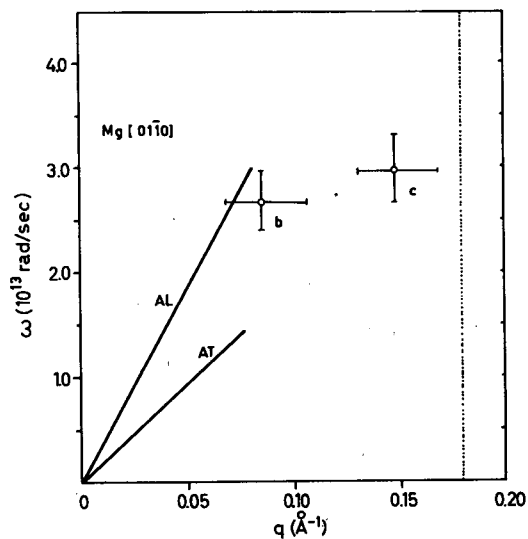


Fig.9

Experimental phonon data for the propagation in the [0001] direction in Mg.

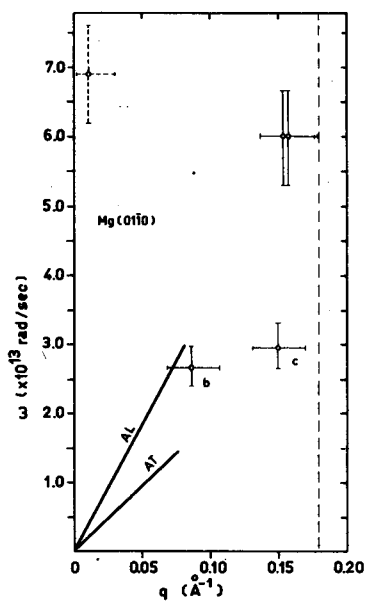


Fig.10

Experimental results for the propagation in the [0110] direction in Mg.

answer to the question whether this discrepancy is connected with the directions or with the methods of measurements used can be obtained by neutron measurements in the $[01\bar{1}0]$ direction, which are now under way. Considering, however, the arguments mentioned above the authors' view is that this extremely large discrepancy cannot be explained by the differences in directions only. In this connection it is interesting to note in Fig. 8 the very good agreement of both sets on neutron measurements, i. e. the cold neutron and crystal spectrometer data.

A magnesium single crystal of similar dimensions as zinc was investigated using the cold neutron method only, some very preliminary results being obtained. Although many phonons lying in the $(\bar{1}010)$ plane have been observed, only a few of them were in the directions $[0001]$ or $[01\bar{1}0]$.

The preliminary results obtained are shown in Figs. 9 and 10 where the heavy lines indicate the slopes of the acoustical branches calculated from the elastic constant data. The phonons "a", "b" and "c" shown in Figs. 9 and 10 belong to the same scattering surface. Assuming a similarity between the phonon dispersion relations in zinc and magnesium in the $[0001]$ direction and taking into account that the phonon "a" lies nearly on the constant velocity line for the AL modes, it is most probable that the phonon "a" belongs to this branch. If this assignment is correct the phonons "b" and "c" shown in Fig. 11 belong to the AL branch in the $[01\bar{1}0]$ direction, and the phonon "d" shown in Fig. 10 as lying well below the phonon "a", belongs to the AT branch in the direction $[0001]$.

Further measurements are under way.

ACKNOWLEDGEMENTS

We wish to take this opportunity of expressing our gratitude to Prof. B. Buras for initiating the studies of lattice dynamics by neutron spectrometry in our laboratory and for his advice in discussions during the progress of the work. Thanks for helpful discussions are also due to Dr. K. Mikke.

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DISCUSSION

A. D. B. WOODS: Do you have any idea how your results for copper compare with the calculations made by Toya?

K. MIKKE: As far as I know from my colleagues a comparison has been made but a good fit was not obtained.

H. HAHN: Was the temperature at which both the X-ray and the neutron measurements were made room temperature in the case of copper as well as of zinc and magnesium?

K. MIKKE: Yes, it was.

H. HAHN: I am glad to see that the small q parts of the X-ray and neutron measurements agree very well, while there is a discrepancy at large q values, which is in accordance with my theory. Admittedly, however, the very large discrepancy shown in some of the figures would be hard to explain by anharmonicity alone. (According to my theory there should be a difference for large two values but only a very small one for anharmonicity contributions).

K. MIKKE: It would be interesting to check your theory in greater detail.

B. BURAS: I think the main reason for such a big difference between the X-ray results and the neutron results is the difficulty in the X-ray case of separating the optical from the acoustical modes. There is always some ambiguity in this separation and in the case of neutrons we are using a straightforward procedure.

DISPERSION RELATIONS FOR PHONONS IN MAGNESIUM

P. K. IYENGAR, G. VENKATARAMAN, K. R. RAO,
P. R. VIJAYARAGHAVAN AND A. P. ROY
ATOMIC ENERGY ESTABLISHMENT, TROMBAY
INDIA

Abstract — Résumé — Аннотация — Resumen

DISPERSION RELATIONS FOR PHONONS IN MAGNESIUM. The dispersion relation for acoustic phonons whose wave vectors lie in the basal plane have been measured by neutron spectrometry. A triple axis spectrometer has been used both in the conventional method and 'constant Q ' method. The results are compared with calculations based on two-neighbour central forces.

RELATIONS DE DISPERSION POUR LES PHONONS DANS LE MAGNÉSIUM. Les auteurs ont mesuré à l'aide d'un spectromètre neutronique la relation de dispersion pour les phonons acoustiques dont les vecteurs d'onde se trouvent dans le plan fondamental. Ils ont utilisé un spectromètre triaxial par la méthode classique et par la méthode de "Q constant". Ils comparent les résultats avec ceux des calculs basés sur les forces centrales s'exerçant entre deux atomes voisins.

ДИСПЕРСИОННЫЕ СООТНОШЕНИЯ ДЛЯ ФОНОНОВ В МАГНИИ. Дисперсионные соотношения для акустических фононов, волновые векторы которых лежат в основной плоскости, измерены методами нейтронной спектроскопии. Трехосевой спектрометр использован как при обычном методе, так и при методе с "постоянным Q ". Результаты сравниваются с расчетами, основанными на использовании центральных сил между двумя соседними атомами.

RELACIONES DE DISPERSIÓN DE LOS FONONES EN EL MAGNESIO. Se ha medido por espectrometría neutrónica la relación de dispersión de los fonones acústicos cuyos vectores de onda están situados en el plano de base. Tanto para el método clásico como para el de "Q constante" se ha utilizado un espectrómetro triaxial. Los resultados se comparan con los cálculos teóricos basados en las fuerzas centrales de los dos átomos más próximos.

I. INTRODUCTION

With the advent of neutron spectrometry, lattice dynamics has been studied in various types of crystals-ionic, covalent and metallic. Of these three types, the nature of the vibrational spectrum in the first two is well understood. This, however, is not true of metallic crystals. The difficulty in the case of metals lies in taking proper account of the influence of the conduction electrons on the phonon spectrum. A start in solving this difficult problem has been made recently and TOYA [1] has succeeded in calculating the dispersion relations for phonons in sodium which are in good agreement with experiment [2]. Sodium is a monovalent metal and extensions of calculations such as Toya's to polyvalent metals have yet to be made.

It is useful in the meantime to study experimentally the phonon spectrum in polyvalent metals and see what inferences one can draw concerning the nature of the interatomic forces. So far the polyvalent metals studied have been mainly of the cubic type [3 - 8]. We report in this paper some results

of an investigation in magnesium, a polyvalent metal of the hexagonal close-packed (HCP) type [9]. Of the various hexagonal close-packed metals, magnesium is particularly interesting since it has a c/a ratio only slightly less than the ideal resulting in a large measure of isotropy in the elastic properties. Section II contains a brief account of the lattice dynamics of HCP lattices and neutron scattering from such lattices. The experimental details including a brief description of the "Constant Q" spectrometer at Trombay are given in Section III while in Section IV are presented the experimental results so far obtained and a discussion of these results.

II. THEORY

Lattice dynamics of HCP lattices

The HCP structure, of which magnesium is an example, contains two atoms in the unit cell with the basis, referred to the hexagonal axes

$$(000, 2/3 \ 1/3 \ 1/2)$$

The ideal HCP lattice has a c/a ratio 1.633 and each atom of this ideal lattice has the following arrangement of nearest neighbours - twelve first neighbours at a distance "a" (six in the basal plane and six on planes at distance $c/2$ away from it) six second neighbours at distance $\sqrt{2}a$ (all confined to the $c/2$ planes) and two third neighbours at distance "c" (located on planes at distance "c" from the basal plane). In magnesium which has a c/a ratio of 1.622, the situation is slightly different. There are six first neighbours at distance $\sqrt{c^2/4 + a^2/3}$ (located on the $c/2$ planes) six second neighbours at distance "a" (lying on the basal plane) six third neighbours at distance $\sqrt{c^2/4 + 4a^2/3}$ (situated once again on the $c/2$ planes) and two fourth neighbours at distance "c" (lying on the "c" planes).

The reciprocal lattice for the hexagonal structure is also hexagonal and the first Brillouin zone is shown in Fig.1 where the symmetry points and directions have been labelled as is customary in electron energy band discussion [10]. Also shown in this figure are the relative orientation of the cartesian axes (X, Y, Z), hexagonal axes (a_1, a_2, a_3) and reciprocal lattice axes (b_1, b_2, b_3).

In the absence of a complete theory for the crystal dynamics of polyvalent metals, it is necessary to understand experimental data within the framework of Born-von Kármán formalism [11]. In this approach it is known that the dispersion relations are obtained as solutions of the characteristic equation

$$| D(q) - M\omega^2 I | = 0 \quad (1)$$

where $D(q)$ is the dynamical matrix, M is the mass of the vibrating atom and I the unit matrix. In the case of magnesium $D(q)$ is a complex (6×6) matrix and the secular determinant (1) is therefore a ($\times 6$) determinant. The solutions of this determinant yield the dispersion relations for the six branches three acoustical and three optical. For q lying in the basal plane

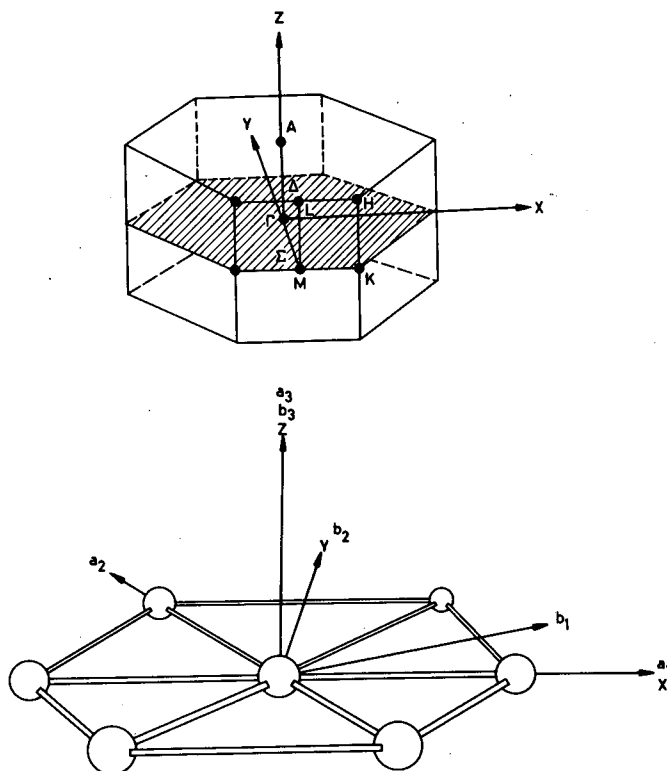


Fig. 1

- (a) Brillouin zone for HCP lattice showing the symmetry points and directions. These have been labelled as in Ref. [10].
- (b) Relative orientation of the various sets of base vectors, the hexagonal (a_1, a_2, a_3), the reciprocal lattice (b_1, b_2, b_3) and the cartesian (X, Y, Z). The orientations of these axes with respect to the atoms in the basal plane are also shown.

which is a mirror plane, the secular determinant factors into a (2×2) and a (4×4) determinant, the (2×2) determinant yielding the frequencies of the two transverse branches having their polarization vectors normal to the basal plane and the (4×4) determinant those for the four branches having their polarization vectors in the plane. In the symmetry direction Σ (i. e. $[01\bar{1}0]$ direction) the (4×4) determinant factors further into two (2×2) determinants and the associated branches become truly longitudinal and transverse respectively. Similar factorization is also achieved for q lying along Δ (i. e. $[0001]$ direction) and one has one set of longitudinal branches and two identical sets of transverse branches.

The exact form of the determinants depends on the specific assumptions made regarding the nature of the interatomic forces and the number of neighbours considered interacting. In the earliest investigations on the subject by BORN and BEGBIE [12], the forces were assumed to be of the general

type (i. e. non-central) and first neighbour interactions alone were considered (two neighbours in the non-ideal HCP lattice). Subsequently POPE [13] formulated the theory for the special case of central forces considering once again only first neighbour interactions. More recently SLUTSKY and GARLAND [14] have revived the central force model extending it to include second neighbour interactions (three neighbours in the non-ideal HCP lattice). The central force approach is particularly attractive in the case of magnesium in view of the near isotropy of the lattice and we have therefore calculated the dispersion relations on the basis of this model. The elements of the dynamical matrix quoted by SLUTSKY and GARLAND contain minor errors [15]. Taking note of these errors, the characteristic equations for q lying along Σ and Δ are as follows:

Σ : $[01\bar{1}0]$ direction

The secular equation is

$$\begin{vmatrix} A_L - M\omega^2 & B_L \\ B_L^* & A_L - M\omega^2 \end{vmatrix} \begin{vmatrix} A_{T_1} - M\omega^2 & B_{T_1} \\ B_{T_1}^* & A_{T_1} - M\omega^2 \end{vmatrix} \begin{vmatrix} A_{T_2} - M\omega^2 & B_{T_2} \\ B_{T_2}^* & A_{T_2} - M\omega^2 \end{vmatrix} = 0 \quad (2)$$

where

$$\begin{aligned} A_L &= 3\alpha (1 - \cos 2\pi q) + 3\beta' + 3\gamma' \\ A_{T_1} &= \alpha (1 - \cos 2\pi q) + 3\beta' + 3\gamma' \\ A_{T_2} &= 9(c^2/a^2) (\beta'/2 + \gamma'/8) \\ B_L &= -[\beta' (2 + \cos 2\pi q) + \gamma' (2 \cos 4\pi q + 1)] \\ &\quad + [\beta' \sin 2\pi q + 2\gamma' \sin 4\pi q] i \\ B_{T_1} &= -3(\beta' \cos 2\pi q + \gamma') + (3\beta' \sin 2\pi q) i \\ B_{T_2} &= -3/4 (c^2/a^2) [2\beta' (1 + 2 \cos 2\pi q) + \gamma'/2 (2 + \cos 4\pi q)] \\ &\quad + 3/4 (c^2/a^2) [4\beta' \sin 2\pi q + \gamma'/2 \sin 4\pi q] i \\ \beta' &= \beta a^2/a^2 + (3c^2/4) \quad \gamma' = \gamma [a^2/a^2 + (3c^2/16)] . \end{aligned} \quad (3)$$

In Eq. (2) the suffixes L , T_1 and T_2 denote respectively longitudinal mode, transverse mode polarized in the basal plane and transverse mode polarized perpendicular to the basal plane.

Δ : [0001] direction

The secular equation is

$$\begin{vmatrix} A_L - M\omega^2 & B_L \\ B_L^* & A_L - M\omega^2 \end{vmatrix} \begin{vmatrix} A_T - M\omega^2 & B_T \\ B_T^* & A_T - M\omega^2 \end{vmatrix} = 0 \quad (4)$$

where

$$A_L = 9 (c^2/a^2) (\beta'/2 + \gamma'/8)$$

$$A_T = 3 (\beta' + \gamma')$$

$$B_L = 9/4 (c^2/a^2) (\beta' + \gamma'/4)(1 + \cos 2\pi q) + i 9/4 (c^2/a^2) (\beta' + \gamma'/4) \sin 2\pi q$$

$$B_T = 3/2 (\beta' + \gamma') (1 + \cos 2\pi q) + i 3/2 (\beta' + \gamma') \sin 2\pi q.$$

In Eq. (4) the suffixes L and T refer to the longitudinal and transverse branches respectively.

The quantities α, β, γ are the force constants between the atom at the origin and the second neighbours, first neighbours and third neighbours respectively. Using the values $\alpha = 9.78 \times 10^3$ dynes/cm, $\beta = 9.54 \times 10^3$ dynes/cm, $\gamma = 0.47 \times 10^3$ dynes/cm, quoted in Ref. [14] the dispersion relations for phonons propagating along Σ and Δ were calculated by solving the determinants given above. For [11 $\bar{2}$ 0] direction since complete factorization is not achieved the equation to be solved is more complicated and the calculations were performed in the TIFRAC computer at the Tata Institute of Fundamental Research*.

The results of the calculation are presented in Fig. 2. As noted earlier the two transverse branches along Δ are degenerate. For phonons propagating in the basal plane, this is not so. However, the near equality of α and β produces an accidental degeneracy which is lifted only near the zone boundary.

Neutron scattering from HCP lattices

Despite the presence of several isotopes, the scattering of neutrons by magnesium is predominantly coherent and therefore quite suitable for the study of phonon dispersion relations. The occurrence of coherent inelastic scattering is governed by the familiar conservation conditions:

$$\underline{k} - \underline{k}' = 2\pi \underline{\tau} - \underline{q} = \underline{Q} \quad (6a)$$

$$|E - E'| = h\nu \quad (6b)$$

Here $\underline{k}$ and $\underline{k}'$ are the incident and scattered neutron wave vectors E and E'

*. We are grateful to Shri Natesh Kumar of the Institute for assistance with the calculations.

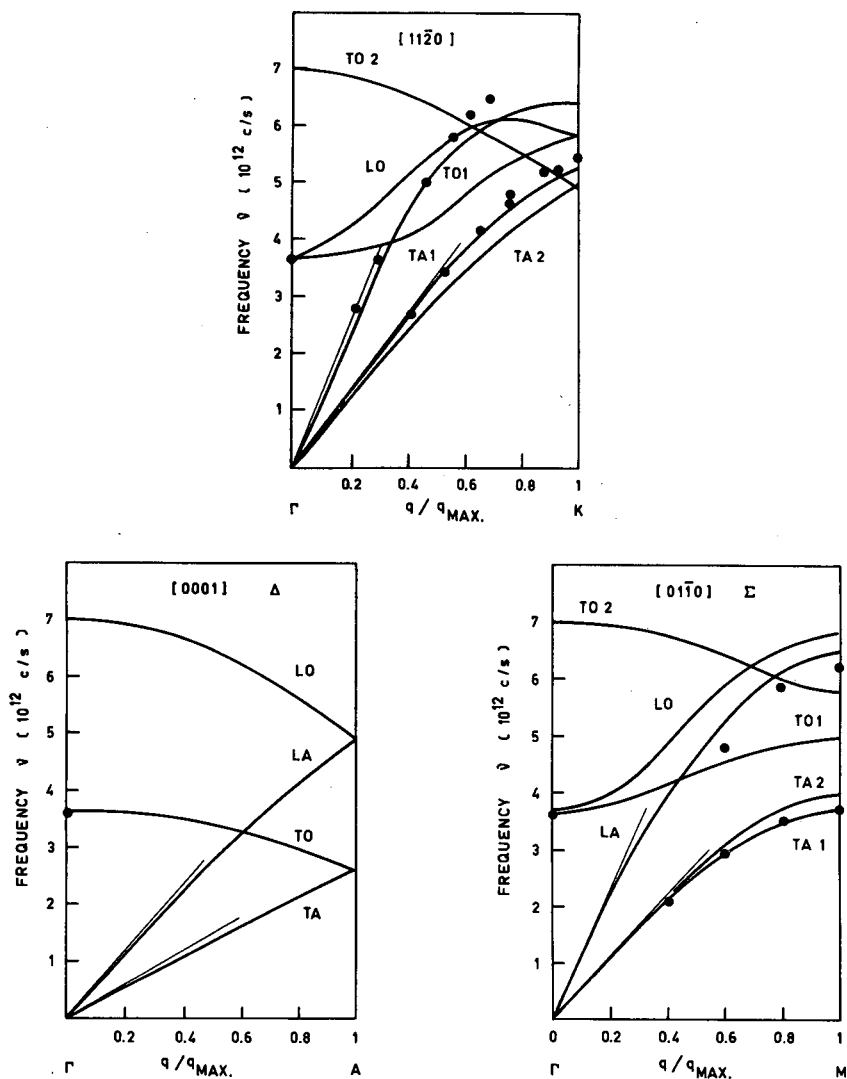


Fig. 2

Dispersion relations for phonons in magnesium along Γ K $[11\bar{2}0]$ Σ $[01\bar{1}0]$ and Δ $[0001]$. The solid lines are curves calculated on the basis of three neighbours central force model described in the text. The measurements are shown by circles, the open ones being from successive approximation method and the solid ones from the constant Q method. The straight lines through the origin give the initial slope of the curves as computed from elastic constants data. Transverse branches having their polarization vectors in the basal plane are labelled (1) while those with it normal to the basal plane are labelled (2). Along the two transverse modes are degenerate; along Γ K the branches having their polarization vectors in the basal plane are not truly transverse or longitudinal. The labelling is by analogy.

are the initial and final neutron energies respectively; τ is a reciprocal lattice vector and ν and q are the frequency and wave vector respectively of the phonon participating in the scattering process. Relations (6) serve to

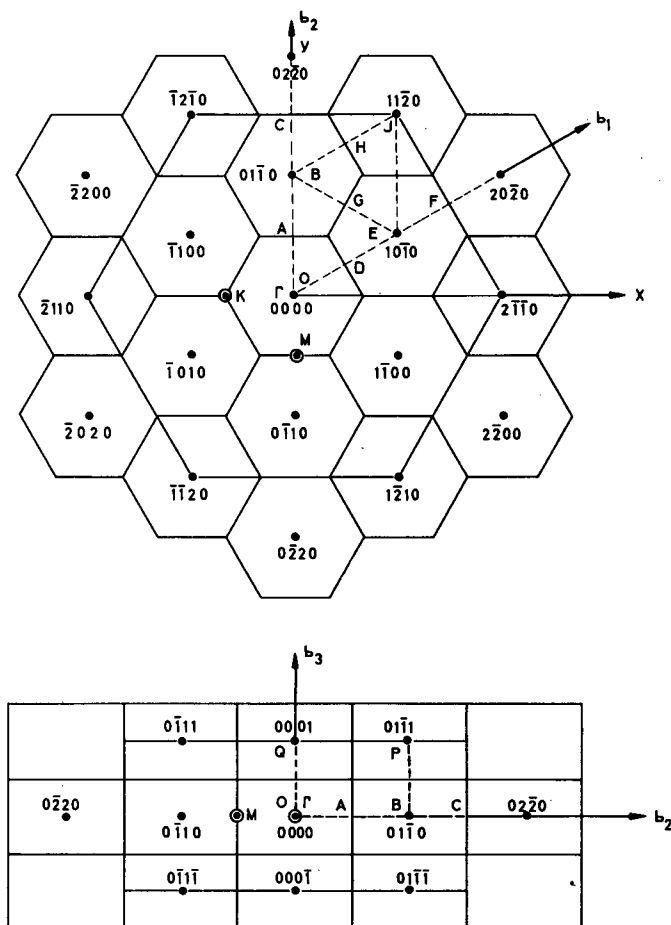


Fig.3

(b_1b_2) and (b_2b_3) planes of the reciprocal lattice of magnesium.

The region bounded by the solid lines is the unit over which the structure factor $g_j^2(\underline{q}, \underline{\tau})$ repeats.

identify the ν and $\underline{q}$ of the phonon associated with the observed scattered neutron group.

The intensity of the scattered neutron group is determined apart from some factors, mainly by two quantities, $g_j^2(\underline{q}, \underline{\tau})$ and J_j . The quantity $g_j^2(\underline{q}, \underline{\tau})$ is peculiar to lattices having a basis and is often referred to as the "structure factor" for inelastic scattering [16]. For magnesium [17] it is given by

$$g_j^2(\underline{q}, \underline{\tau}) = \frac{(b \xi_j \cdot \underline{Q})^2}{2M\nu_j} \left| \frac{\xi_{1j}(\underline{q})}{\xi_{2j}(\underline{q})} + \exp i \underline{Q} \cdot \underline{\tau}(2) \right|^2 \quad (7)$$

where b is the bound atom coherent scattering length. ξ_j is a unit vector in the direction of polarization, $\xi_{1j}(\mathbf{q})$ and $\xi_{2j}(\mathbf{q})$ are respectively the amplitudes of vibrations of the two atoms 1 and 2 in the primitive unit cell in $(\mathbf{q}, j)$ th mode and $r(2)$ is the coordinate of atom 2 with respect to atom 1. The ratio $\xi_{1j}(\nu)/\xi_{2j}(\mathbf{q}_j)$ is related in a simple manner to the elements of the dynamical matrix and is readily calculable. $[J_j]$ is a term which effectively sums over all normal modes contributing to the observed neutron group. In the "Constant Q " mode of observation of phonons $[J_j] = 1$ [18] and g_j is the main factor governing the intensity. To help in choosing proper lattice points for making observations, we have therefore mapped the behaviour of $g_j^2(\mathbf{q}, \tau)$ in reciprocal space for $\mathbf{q}$ lying in the symmetry directions Σ and Δ , and the results are displayed in Fig. 3. The curves of Fig. 3a are pertinent to the observation of phonons along Σ using b_1, g_2 plane as the plane of scattering while those in Fig. 3b are for the study of phonons along Δ using the b_2, b_3 plane as the plane of scattering. In both the figures the region bounded by the dark lines is the unit over which the structure factor repeats.

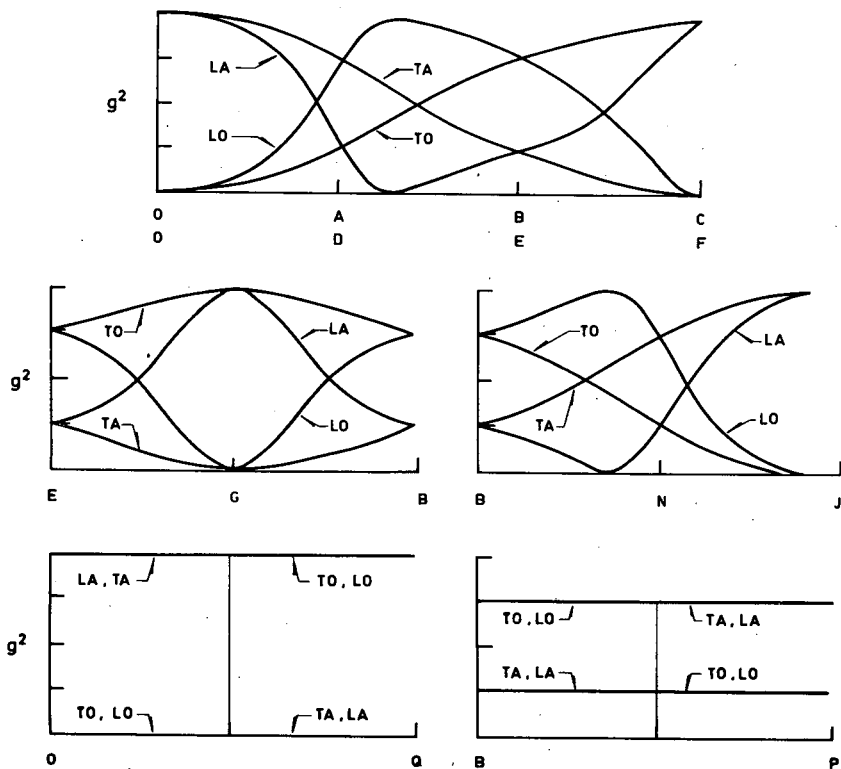


Fig. 4

Inelastic scattering structure factors for magnesium calculated on the central force model

$$\text{plotted in units of } \frac{(b\xi_j Q)^2}{2M\nu_j}.$$

III. EXPERIMENTAL DETAILS

The scattering data were obtained using the crystal spectrometers at the Canada India Reactor (CIR) which is a reactor of the NRX type. The first measurements were made employing the method of successive approximation on the spectrometer described earlier [7]. Subsequently a triple axis spectrometer capable of "Constant Q" mode of operation has been installed and data is at present being collected using this spectrometer. Since this instrument has not been described before, we present below its main features.

The triple axis spectrometer consists of a monochromator followed by a double axis spectrometer to energy-analyse the diffracted beam. The monochromator is a single crystal of aluminium housed inside a large drum with a radial exit port for the emerging beam. The monochromating crystal can be rotated and clamped in any position as the axle supporting the crystal table extends below the drum. Since the drum can be rotated about the axis of the crystal table, it can be positioned suitably to allow the diffracted beam to emerge through the port. The monochromator is not coupled to the double axis spectrometer and continuous variation of incident energy is not possible. Measurements are therefore carried out at some fixed value of the incident energy.

The double axis spectrometer serves both as the positional and the analysing spectrometer. The positional spectrometer is built on a strong column and sleeve assembly conventionally used for a radial drill. On the sleeve is attached a pair of strong plates which support the analysing spectrometer. The angular rotation of the sleeve is indicated by a graduated plate attached to the sleeve against a vernier fixed to the column. The sleeve is rotated electrically by a small fractional horse power motor using a belt and pulley arrangement. The angular increments are 0.125° controlled by a cam and microswitch arrangement. The axle of the positional spectrometer carries the sample table. This can be independently rotated by a motor and gears in steps of 0.05° .

The direction of the scattered beam is defined by a soller collimator in line with the centres of the positional and analysing spectrometers. The analysing spectrometer is a conventional diffraction spectrometer of the type described by HURST *et al.* [19]. It is also driven electrically by a belt and pulley arrangement, the angular increment being controlled by a cam and microswitch arrangement to 0.125° steps. The detector is a 2 in diam., 18 in long proportional counter filled with enriched BF_3 gas to a pressure of 60 cm. The monitor is a thin BF_3 counter placed on the exit port of the monochromator drum. An overall view of the spectrometer can be had in Fig.5.

The spectrometer can be used in the "Constant Q" mode by a programme unit. Of the three variables, ψ the crystal orientation, ϕ the scattering angle and $2\theta_A$ the analysing spectrometer angle, $2\theta_A$ is always moved in steps of 0.125° . The movements of ψ and ϕ are controlled from two programme boards. Starting from the initial set of positions, the increments in the angles ψ and ϕ are computed for successive values of $2\theta_A$ keeping Q constant and set in their respective programme boards. The programme board consists of a large number of banana sockets connected to the contacts of a rotary switch and the process of setting the increment consists in plugging

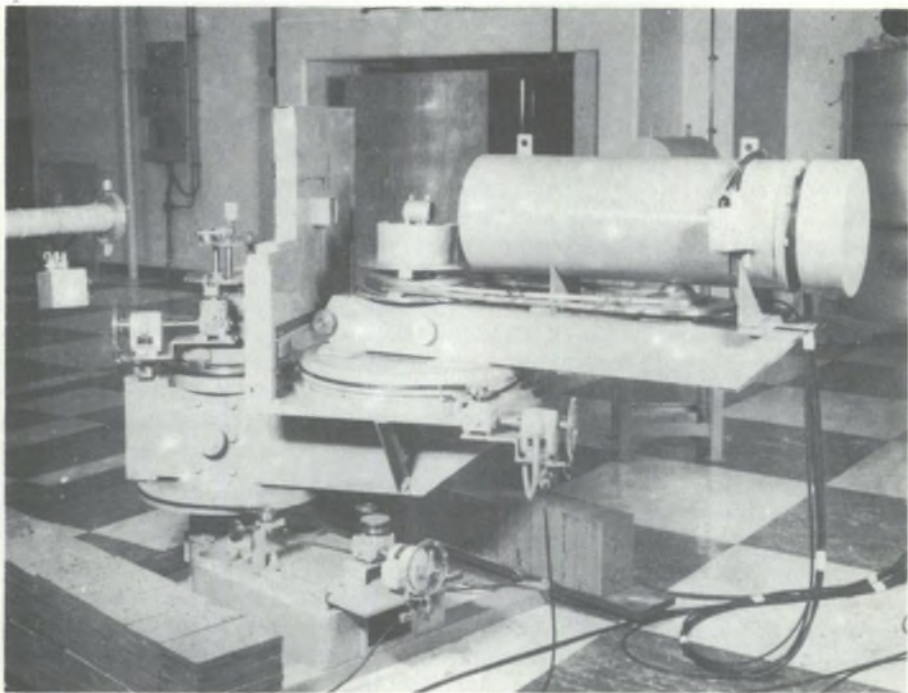


Fig. 5

Photograph of the triple axis spectrometer.

the appropriate sockets to ground. The control unit of the programmer is such that once the motors controlling the ψ and ϕ motion are energized they will run, each cam contact stepping a rotary switch in the controlling unit until the next point plugged is reached. When all the motors, which vary $2\theta_A$, ψ and ϕ come to a stop, the counting operation starts. The usual features of data taking like counting for preset number of monitor counts and taking background by flipping the analyser a few degrees off Bragg position have been incorporated. The total number of positions in each of the boards is 300 giving thus a position control over 15° in ψ and 37° in ϕ . This is sufficient even for scanning two phonons in succession provided the angles do not have to be retraced. A single switch will return the programme stepping switches to their initial positions, making the unit ready for a new set of instructions.

The specimen used in the experiments was in the form of a square slab $5\text{ cm} \times 5\text{ cm} \times 1\text{ cm}$ with the hexad axis nearly parallel to one of the long sides. The crystal was aligned using neutrons to have this axis vertical. Measurements were thus confined to phonons in the b_1 , b_2 plane and only those phonons having their polarization vectors in the basal plane contributed to the scattering.

Measurements made so far have been along Π K [1120] and Σ [0110] directions. It is hoped eventually to map the prism bounded by planes Γ ALM,

Γ AHK and MKHL since this is the irreducible region of the Brillouin zone. The results obtained so far are displayed in Fig. 2 and include both the successive approximation and "Constant Q" measurements. The wavelengths used in the two measurements were 1.19 Å and 1.42 Å respectively.

IV. DISCUSSION

Examination of Fig. 2 shows that the measurements are in substantial agreement with the three neighbour central force model. This result is not altogether surprising. The relatively small departure from the Cauchy relation is itself a pointer in this direction. Further SLUTSKY and GARLAND [14] found that the central force model is reasonably adequate to explain observed lattice specific heats. It is interesting to note that while the transverse branches agree quite well with the model, the longitudinal branches show slight departures. This could conceivably be due to electron gas effects. It would be worthwhile to extend the model to include electron gas effects and see whether any improved agreement is obtained. One could also adopt the view that central forces are not adequate and that general forces must be used. A model built on general forces would involve a considerably larger number of force constants (e.g. twelve for the three neighbours considered here) which are not derivable from elastic constants data alone. They must be derived using neutron and elastic constants data in conjunction. More data is required for this and it is hoped to try this approach eventually.

The main conclusion of the present work is that a short range central force model is able to reproduce the features of the observed phonon spectrum in magnesium quite well. This is in marked contrast to the case of beryllium an isoelectronic substance having the same structure [9]. The difference is perhaps to be expected since the c/a ratio for beryllium is considerably lower than the ideal.

ACKNOWLEDGEMENTS

We are grateful to Dr. R. Ramanna for his keen interest in the work. Our thanks are also due to Shri J.N. Soni for his help in setting the triple axis spectrometer. We are obliged to Shri V. Surya Rao, Superintendent, CIR and the Reactor Operations Division for their co-operation at various stages in the work.

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FREQUENCY DISTRIBUTION OF NORMAL MODES IN GRAPHITE*

B. C. HAYWOOD ** AND I. M. THORSON
ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

FREQUENCY DISTRIBUTION OF NORMAL MODES IN GRAPHITE. The scattering of neutrons in the range 0.03 eV to 0.15 eV from graphite has been studied using the Chalk River thermal neutron analyser. Partial differential cross-sections were obtained over a range of energy and momentum transfers of 0.01 eV to 0.1 eV and 0.02 eV to 0.8 eV respectively and compared to earlier measurements. A scattering law is derived and is analysed to find the frequency distribution, which is then compared with theoretical values.

DISTRIBUTION DE FRÉQUENCES POUR LES MODES NORMAUX. Les auteurs ont étudié la diffusion des neutrons dans le graphite pour des énergies variant entre 0,03 eV et 0,15 eV au moyen de l'analyseur à neutrons thermiques de Chalk River. Les sections efficaces différentielles partielles ont été déterminées pour des gammes de transfert d'énergie et de transfert d'impulsion allant de 0,01 eV à 0,1 eV et de 0,02 eV à 0,8 eV respectivement; elles ont été comparées à des mesures faites précédemment. Les auteurs déterminent la loi de diffusion et ils l'analysent pour obtenir la distribution de fréquences qui est alors comparée aux valeurs théoriques.

ЧАСТОТНОЕ РАСПРЕДЕЛЕНИЕ НОРМАЛЬНЫХ КОЛЕБАНИЙ В ГРАФИТЕ. Изучалось рассеяние нейтронов в пределах от 0,03 до 0,15 эв на графите с помощью анализатора тепловых нейтронов в исследовательском центре Чок Ривер. Парциальные дифференциальные сечения были получены за пределами этих значений энергии и соответственно были получены передачи импульсов от 0,01 до 0,1 эв и от 0,02 до 0,8 эв и сравнены с предыдущими измерениями. Выводится закон рассеяния и проводится анализ для определения частот распределения и последующего сравнения данных с теоретическими данными.

DISTRIBUCIÓN DE FRECUENCIAS DE MODOS NORMALES EN EL GRAFITO. Los autores han estudiado la dispersión de neutrones por grafito en el intervalo 0,03 eV-0,15 eV, utilizando el analizador de neutrones térmicos de Chalk River. Han obtenido las secciones eficaces diferenciales parciales en un intervalo de transmisión de energía y de cantidad de movimiento de 0,01 eV a 0,1 eV y de 0,02 eV a 0,8 eV, respectivamente, y comparan los resultados con los de mediciones anteriores. Deducen una ley de dispersión que analizan para hallar la distribución de frecuencias, que comparan a su vez con los valores teóricos.

1. INTRODUCTION

The vibrations of the atoms in a crystal lattice have been studied experimentally for many years by methods including specific heat measurements [1] and neutron scattering [2]. In low energy neutron scattering experiments the neutron interacts with a nucleus over a finite time so that the atomic vibrations modify the angular distribution of the scattered neutrons. The method of analysis of these angular distributions has been given by VAN HOVE [3] and PLACZEK and VAN HOVE [4], who have shown that the one phonon, incoherent, scattering cross-section for slow neutrons is proportional to

* Joint project between AECL, Chalk River and AERE, Harwell.

** From AERE, Harwell, at present at Chalk River.

the frequency distribution of the vibrations of the atoms in the scattering medium for a cubic crystal. The extension of this theory to the graphite lattice has been justified by PARKS [5]. In this paper, use is made of these results to obtain an experimental frequency distribution for polycrystalline graphite.

The structure of graphite is that of a system of flat plates of carbon atoms with only weak binding between the atoms in different layers, and its frequency distribution will be shown to exhibit some features not found in more normal solids [6, 7]. Of the neutrons scattered by the carbon atoms, over 98% will be scattered coherently, and in order to separate the scattering from a single atom from that modified by correlations between pairs of atoms, a technique due to EGELSTAFF [8] has been used.

2. THEORY

It is possible to define a scattering law for a material by the relationship [8, 9]

$$\frac{d^2\sigma}{d\Omega dE} = \frac{kT}{4\pi} \sigma_f \left(\frac{A+1}{A} \right)^2 e^{-\beta/2} \left(\frac{E}{E_0} \right)^{1/2} S(\alpha, \beta) \quad (1)$$

where

k is Boltzmann's constant;

T is the absolute temperature of the scatterer;

σ_f is the free atom cross-section of the scattering nuclei;

A is the ratio of the mass of the scattering nucleus to the mass of the neutron;

E_0 and E are the incident and scattered neutron energies respectively;

$\beta = (E_0 - E/kT)$;

$\alpha = E_0 + E - 2(E_0 E)^{1/2} \cos \theta / AkT$;

θ is the angle of deflection of a scattered neutron,

$S(\alpha, \beta)$ is the scattering law for the material under investigation.

For polycrystalline materials it can be shown that:

$$\begin{aligned} \lim_{\alpha \rightarrow 0} \frac{S_s}{\alpha} &= \frac{1}{\pi} \int_0^\infty dt e^{i\beta t} \int_0^\infty \frac{\cos \beta t \rho(\beta) d\beta}{\beta \sinh \beta/2} + 0(\alpha) \\ &= \frac{\rho(\beta)}{2\beta \sinh \beta/2} \end{aligned} \quad (2)$$

where

S_s is the scattering law for a single atom of the scattering material, i.e. the experimental scattering law with any interference effects removed;

$S_s(\alpha, \beta) = S(\beta, \beta) - S_d(\alpha, \beta)$;

$\rho(\beta)$ is the frequency distribution of the normal modes of vibrations in the crystal lattice.

Since 98.9% natural carbon is a zero spin isotope, almost all neutron scattering is coherent. EGELSTAFF has shown [11] that for graphite it is possible

to separate the scattering from a single nucleus, proportional to $S_s(\alpha, \beta)$, from scattering modified by correlations in time and position between two nuclei, proportional to $S_d(\alpha, \beta)$. This is possible since $S_d(\alpha, \beta)$ will make a significant contribution to the cross-section only for small α . It has been shown that the first term in Eq.(2) is equivalent to the first term in the Placzek mass expansion [10] and it should be possible to extrapolate the $S(\alpha, \beta)$ curves for fixed β to $\alpha = 0$, from values of α where S_d is insignificant but where the first term in Eq.(2) is still dominant. Graphite results are particularly suitable for analysis in this way because of the high Debye temperature and large planar spacing of the atoms. This has been dealt with more fully in a previous paper [8].

A method of extrapolation in which $\log(S/\alpha)$ is plotted against α has been used for the graphite results presented here to reduce the effects of the terms of the order α, α^2 , etc. indicated by $O(\alpha)$ in Eq.(2). A plot of $\log S/\alpha$ versus α will give an almost straight line [11] which may be readily extrapolated to $\alpha = 0$. The $\lim_{\alpha \rightarrow 0} S/\alpha$ found from runs taken with incident neutrons of different energies agree to $\pm 10\%$.

3. EXPERIMENTAL DETAILS

The experiments described here were carried out using the four rotor neutron velocity selector at the NRU reactor at Chalk River. Bursts of neutrons from this velocity selector were scattered by a thin specimen of graphite and the scattered neutrons detected by an array of counters around the specimen. The velocities of the scattered neutrons were determined by time of flight analysis of the detector pulses.

Apparatus

The neutron monochromator [12,13] consists of four slotted rotors running synchronously at high speed. A schematic diagram is given in Fig.1. The relative phasing of these rotors is continuously variable, and by choice of rotors with suitable slot curvature it is possible to select a monoenergetic pulsed beam of neutrons over a wide range of energy. At an operating speed of 24 000 rpm the neutron bursts had a standard deviation of $3.8 \mu\text{s}$ in time of arrival at the specimen position and $1.1 \mu\text{s/m}$ in reciprocal velocity.

The thin plane specimens were made of extruded graphite 0.02 cm thick which scattered $\sim 12\%$ of the incident neutrons. Experiments performed with the extrusion direction at different orientations to the incoming neutrons were found to give similar results. The specimens were held in a holder at 45° to the incident neutron beam and, during the time that results were being recorded, the specimen and a suitable blank which simulated the specimen holder were alternated in the beam at 15 min intervals. Information from the alternate 15 min intervals was accumulated separately and subtracted to yield the net scattering from the specimen.

Neutrons scattered from the specimen or blank were detected in two banks of scintillation counters at a distance of 1.29 m from the specimen position (Fig.1). The 12 counters in the bank in the first quadrant were at angles between 10° and 90° with respect to the incident beam and had scintil-

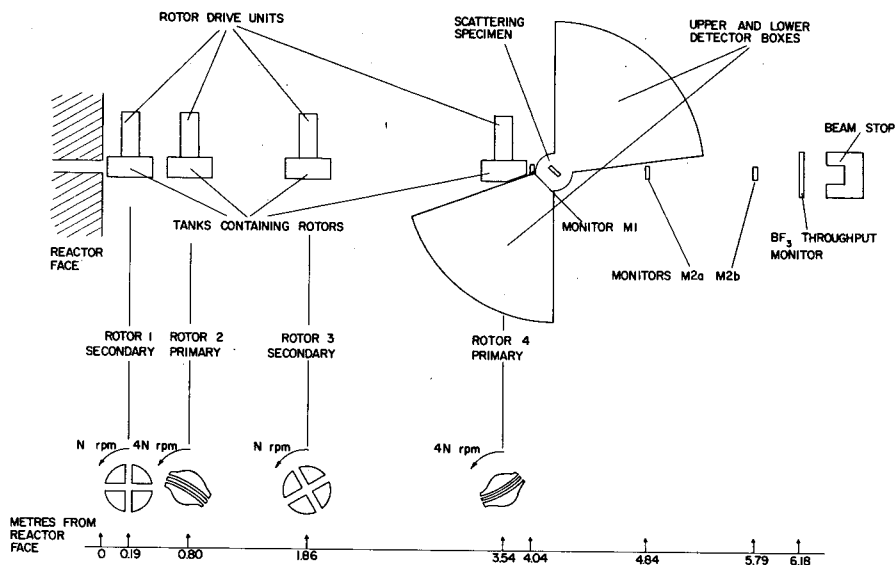


Fig. 1

Schematic diagram of experimental apparatus
showing the principal dimensions.

lators 15 cm by 7.6 cm. The 10 counters in the other bank were in the third quadrant at angles between 80 and 160° and had scintillators 12 cm square. Pulses from these detectors were fed into the input circuits of a time analyser [14] started by a pulse derived from rotor No. 4, and were sorted into a series of 270 time channels each $6\mu\text{s}$ long.

Three fission chamber monitors were placed in the beam. Monitor M1 was installed in the short space between rotor No. 4 and the specimen and monitors M2a and M2b were in the beam path behind the specimen 90 cm apart. The pulses from these fission chamber monitors were also time analysed in the same way as those from the detectors.

From the ratios of monitor counts with the specimen or blank in the beam position the net transmission was determined to $\pm 1\%$. Analysis of the time sorted monitor pulses yielded the resolution function of the apparatus and the time-of-flight of the incident neutrons. In all measurements the efficiency of these monitors was assumed to follow the fission cross-section of uranium-235. Data were read out of the time analyser as punched binary cards which were subsequently processed on the IBM 704 at the Argonne National Laboratory.

Calibration and data processing

The efficiencies of the detectors relative to the monitor M1 were found by subsidiary measurements using a vanadium scattering specimen. In these experiments it was assumed that the elastic scattering of neutrons with energy less than 0.04 eV was proportional to the Debye-Waller factor, and that

above 0.03 eV the total scattering cross-section was that derived by PLACZEK [10]. In the overlapping energy region 0.03 eV to 0.04 eV both methods gave similar values for the efficiency of the detectors.

The variation of detector efficiency with incident neutron energy had been determined previously and a suitable curve fitted to the results. This curve was normalized to the average efficiency for each detector found from vanadium results at the same incident neutron energy. Detector efficiencies were thus obtained under similar conditions to those prevailing during the graphite runs and allowed for any differences in geometry factors between detectors.

Neutron scattering runs were carried out continuously for 4-6 d in order to obtain a sufficient number of counts in each time channel. The data from each 24 h run were combined to give the total number of neutrons scattered into time channel 'i' of detector 'j' by use of the formula

$$N_{ij} = \Sigma (\$_{ij} - \gamma_r B_{ij}) / \epsilon_{ij} \quad (3)$$

where

$\$_{ij}$ and B_{ij} are the respective number of counts recorded in time channel 'i' of detector 'j' with the specimen and the blank in the beam;

ϵ_{ij} is the efficiency of the detector 'j' for neutrons with energy corresponding to channel 'i' ;

γ_r is the ratio for run 'r' of monitor M1 counts with the specimen in the beam to the M1 counts with the blank in the beam.

These values of N_{ij} are converted to Egelstaff's $S(\alpha, \beta)$ by the IBM 704 which evaluated the expressions

$$S_{ij}(\alpha, \beta) = 1.1957 \times 10^{-5} T / \sigma_G m n t_i^4 e^{\beta/2} / \delta t t_0 N_{ij} \quad (4)$$

$$\beta_{ij} = 6.0576 \times 10^7 / T (1/2_{t_{(i)}} - 1/2_{t_{(0)}}) \quad (5)$$

$$\alpha_{ij} = 6.1121 \times 10^7 / MT (1/2_{t_i} + 1/2_{t_0} - 2 \cos \theta_j / t_0 t_i) \quad (6)$$

t_0 and t_i are the incident reciprocal velocity and the reciprocal velocity of time channel 'i' respectively;

n is the total number of neutrons incident on the specimen corrected for the specimen transmission;

T is the absolute temperature of the sample;

m is the number of scattering atoms per cm^2 of beam calculated from the transmission of the specimen;

σ_b is the bound atom cross-section in barns
 $= (\text{free atom cross-section}) \times (A + 1/A)^2$;

M is the mass in a.m.u. of a carbon atom;

δt is the channel width at the detectors in $\mu\text{s/m}$;

θ_j is the mean scattering angle for neutrons detected in counter 'j'.

Since the detectors are all equidistant from the scattering specimen, the average energy transfer for a given time channel will be the same for all detectors. Thus a plot of $\log (S/\alpha)$ against α for any time channel will be a constant energy plot and may thus be extrapolated to $\alpha = 0$. This method

of analysis has proved to be superior to that described in [8] in which a smoothed S versus time channel curve is drawn and points at constant β are picked off for use in the (S/α) extrapolation.

4. RESULTS

A curve of the information obtained from a detector at 86.9° accumulated continuously over 5 d is shown in Fig. 2a. As can be seen, most of the neutrons are scattered into a Bragg peak. The peak in the distribution at time channel 148 is due to the rotation of rotor No. 2 and has been discussed elsewhere [13]. The cross-sections for inelastic scattering can be seen from Fig. 2b to fall off rapidly as $[-\beta]$ increases and the net number of neutrons scattered with an energy transfer greater than $-2kT$ can be seen to be small. However, with some loss of resolution, values of S may be obtained with greater accuracy by adding together consecutive time channels. The values of $S(\alpha, \beta)$ obtained from the results of Fig. 2b are shown in Fig. 2c.

No structure of the kind described by BROCKHOUSE [16] has been observed and it has now been established that the peaks reported in [16]* were Debye Scherrer lines [17].

Typical curves of (S/α) plotted against α are shown in Fig. 3 for individual time channels. For α above 0.3 the experimental points lie approximately on a straight line and this line is extrapolated to $\alpha = 0$. In extrapolating S/α versus α to $\alpha = 0$ the mean slopes of the curves are constrained to vary smoothly with β . This is done by first plotting the slope of the estimated best line against β for each time channel; a smooth curve is then drawn through these points and the slope used in the final extrapolation of S/α is read from this curve. By this method some smoothing of (S/α) as a function of β is achieved and the accuracy of $\lim_{\alpha \rightarrow 0} (S/\alpha)$ is improved. A plot of $\lim_{\alpha \rightarrow 0} (S/\alpha)$ against β is shown in Fig. 4 and, as can be seen, the points define a smooth curve. In Fig. 4 the information obtained from two runs, each of five days duration at incident neutron energies of 0.16 and 0.036 eV, have been combined and agree with one another in the overlapping β range. The frequency distribution which is given by

$$\rho(\beta) = 2\beta \sinh \beta/2 (S/\alpha)_{\alpha \rightarrow 0}$$

is shown in Figs. 5 and 6 and has been obtained from the curve drawn through the points in Fig. 4.

5. DISCUSSION OF RESULTS

On the basis of a continuous two dimensional, harmonic oscillator model, the extreme anisotropy of the graphite lattice should make the frequency distribution of the normal modes of vibration, $\rho(\beta)$, proportional to β except at very low values of β . Since

$$\rho(\beta) = 2\beta \sinh \beta/2 \lim_{\alpha \rightarrow 0} (S/\alpha)$$

* Only the graphite results in [16] will be affected by this phenomenon.

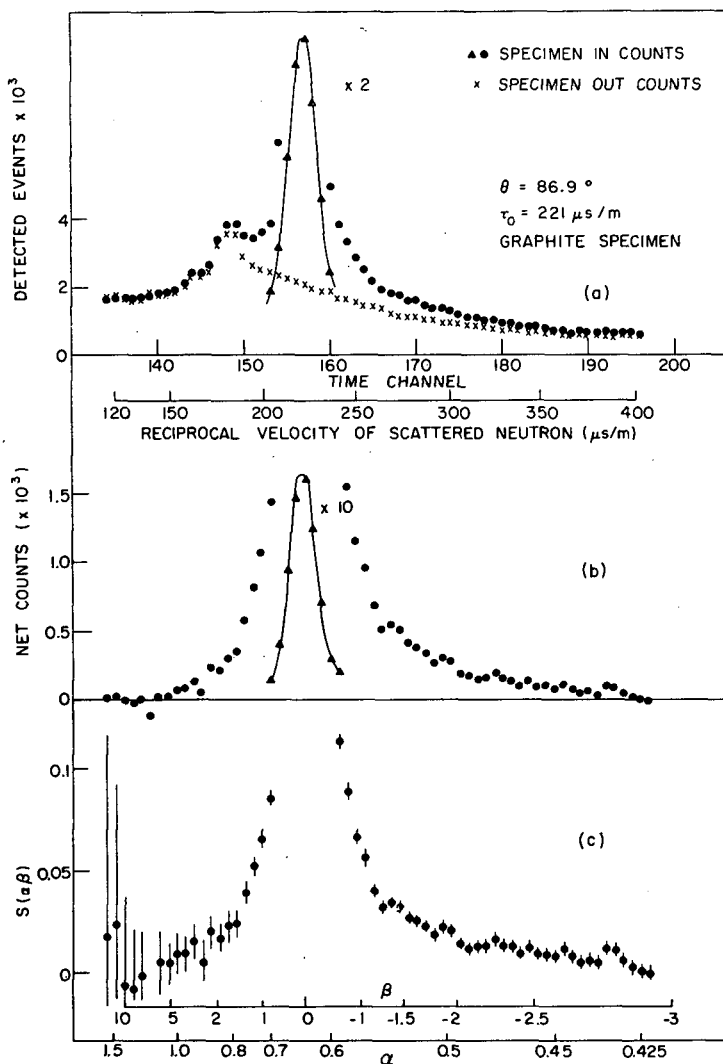
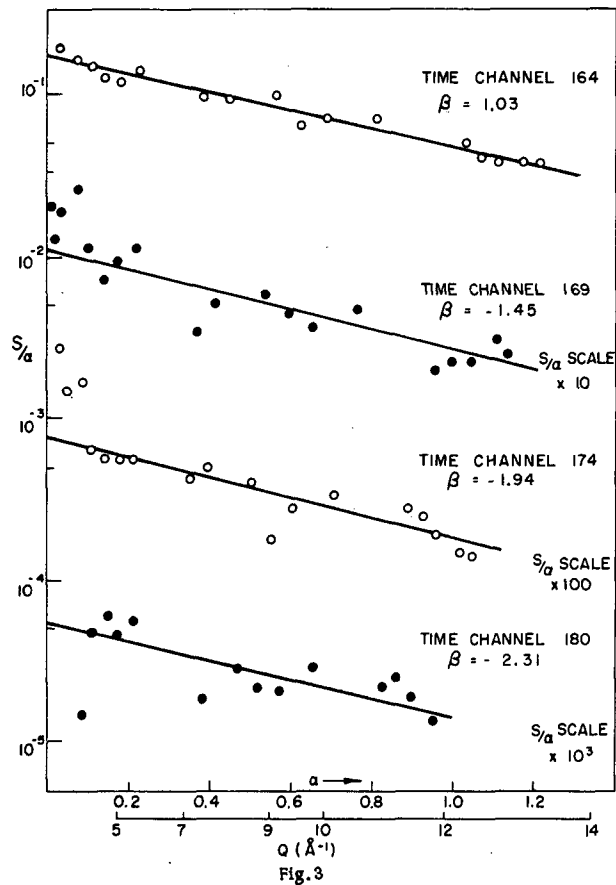


Fig. 2

Steps in the data analysis.

- (a) Shows the data accumulated over a period of 5 d with the specimen and with the blank in the beam,
- (b) Shows the values of N_{ij} obtained by use of Eq.(3),
- (c) Shows the values of $S(a, \beta)$ obtained from Eq.(4).

this implies that $\lim_{\alpha \rightarrow 0} (S/\alpha)$ must be proportional to $(\sinh \beta/2)^{-1}$. This is found to be approximately true for β between 1.5 and 3.0 as can be seen in Fig. 4. Comparisons of the experimental $\rho(\beta)$ with those derived from models proposed by BALDOCK [6] and by YOSHIMORI and KITANO [7] are



Typical curves of $\log (S/a)$ versus a for individual time channels.

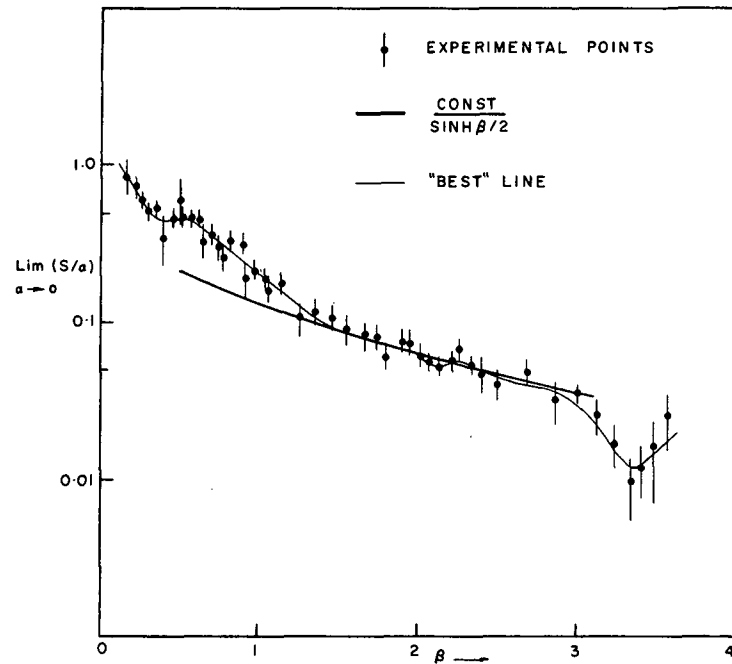


Fig. 4

The values of $\text{Lim}_{a \rightarrow 0} \left(\frac{S}{a} \right)$ versus β . A curve of $A(\sinh \beta / 2)^{-1}$ where A is a constant shows where $\rho(\beta)$ is proportional to β .

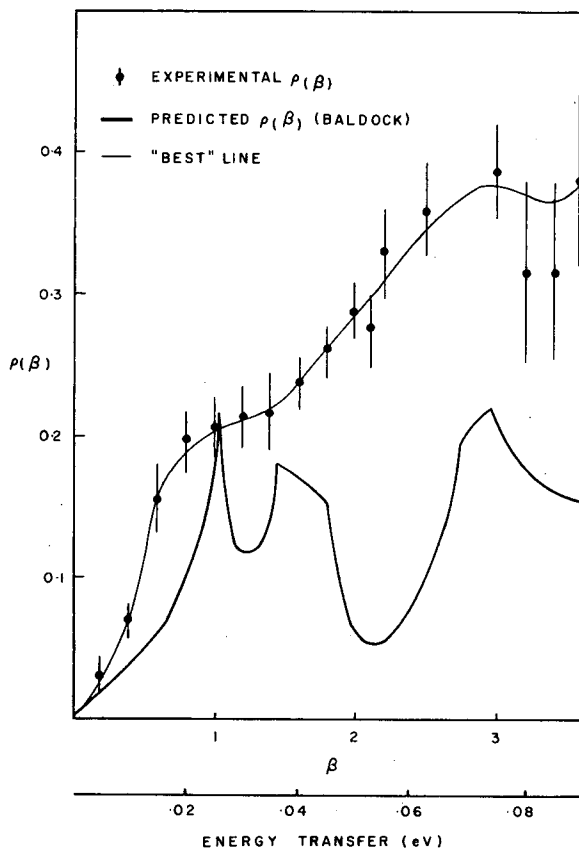


Fig. 5

Comparison of the experimental values of $\rho(\beta)$
with the predictions of BALDOCK [6].

shown in Fig. 5 and Fig. 6 respectively. In general the predictions of Baldock (Fig. 5) are in poor agreement with the experimental results; it is likely that the model, which assumes minimum coupling between adjacent planes in the graphite lattice, is inadequate. The predictions of Yoshimori and Kitano (Fig. 6), at least as regards to position in β of structure in $\rho(\beta)$, are in somewhat better agreement with the experimental results. The initial rise and sharp change of slope at $\beta = 0.6$ correspond well with the spectrum predicted for vibrations perpendicular to the planes. The cutoff energy of a transverse mode of vibrations in the planes at $\beta = 3.2$ can also be seen in Fig. 6. The cutoff of the higher energy modes of vibrations perpendicular to the planes at $\beta = 2.1$ does not show up either in Fig. 4 or Fig. 6, however.

The experimental and analysis difficulties most likely to cause significant errors in the experimental $\rho(\beta)$ are interference effects, i. e., extrapolation of S/α results from values of α where S_d is not negligible, and

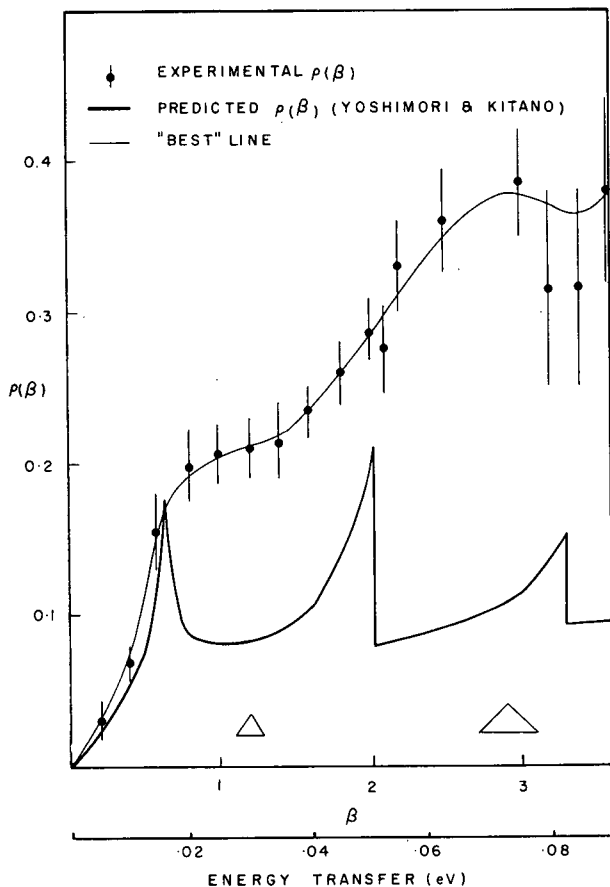


Fig. 6

Comparison of the experimental values of $\rho(\beta)$
with the predictions of YOSHIMORI and KITANO [7].

inadequate correction for multiphonon effects and multiple scattering effects. Due to the high specimen transmission, ~ 0.88 , multiple scattering should not be significant except at the highest values of β for all α and the lowest values of α for all β . The low α points are ignored in the extrapolation of $\log S/\alpha$ used for reasons of interference effects in any case so only $\rho(\beta)$ at high β should be affected by multiple scattering. This could not, however, explain the factor of 2 to 3 discrepancy at $\beta = 3$ between the experimental and theoretical curves.

Multiphonon effects should be adequately removed by the logarithmic extrapolation procedure but extensive numerical calculations are required to establish whether the frequency distribution so derived is unique. This will be done using the LEAP programme [18].

Lacking quantitative calculations, the effects of the interference scattering, proportional to $S_d(\alpha, \beta)$, are difficult to judge. At $\beta = 0$, $S_d(\alpha, 0)$ is

given by the structure factor for any polycrystalline material; at $\beta \neq 0$ no quantitative estimates exist for $S_q(\alpha, \beta)$ but the absence of structure in the S/α versus α plots indicates very strong damping of the interference effects with an increase in β . Modest experimental resolution in α , especially for data taken at low scattering angles, should also average out interference effects.

Finally, since the absolute cross-section scale is probably accurate to $\pm 25\%$, the experimental $\rho(\beta)$ indicates that considerably more weight must be given to the lower energy motions than the theoretical models indicate. This implies that the theoretical models do not adequately account for coupling between the planes in the graphite lattice.

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DISCUSSION

K. S. SINGWI: To judge by your curves, it is very hard to realize $\lim_{\alpha \rightarrow 0} (S_s/\alpha)$. For you only go to $Q = 5$, but when you go below $Q = 5$, the extra-

polarization becomes something different. To what extent would this account for the discrepancy in $\rho(\beta)$?

K. HAYWOOD: In extrapolating these results, one normally ignores the points below $Q = 5$. We can extrapolate only from high values of Q .

K. S. SINGWI: I have my doubts concerning this Egelstaff extrapolation procedure which you use for determining the frequency distribution function. I would like to see at least one case in which the frequency distribution function as determined by Egelstaff's procedure is compared with that determined by the standard normal procedure.

K. E. LARSSON: In plotting $\log(S/\alpha)$ against α , it seems to me that non-linear terms, i. e. multiphonon terms, must appear. These would cause the line $\log(S/\alpha)$ against α to be non-linear. Would not this effect necessitate a correction in your extrapolated values of $\lim_{\alpha \rightarrow 0} (S/\alpha)$? This would be particularly important at temperatures such that $T > \theta_D$.

K. HAYWOOD: The non-linearity is always present, but for the case shown it is quite small. This means that a good initial estimate of the frequency function is obtained from a linear extrapolation and small corrections for non-linearity are made by the iterative procedure described by Egelstaff in his paper entitled "Practical Analysis of Neutron Scattering Data into Self and Interference Terms"*. However, in cases where $T > \theta_D$, we have to be careful and treat each set of results on its individual merits. Generally speaking, we find that the correction for coherent effects is much larger than that for non-linearity.

P. EGELSTAFF: Replying to both Mr. Singwi and Mr. Larsson, let me point out that the extrapolation technique, subject to the precautions discussed in the paper to which Mr. Haywood has referred, is the only rigorous method of extracting the frequency distribution from data such as that given in the present case. (Even for the vanadium data, this extrapolation method should be used in preference to the calculation technique generally employed.) If results obtained in this way were compared with those computed from the dispersion curves, I would in fact regard this as a test of the force-constant models used to extrapolate and interpolate the dispersion curves rather than as a test of our extrapolation technique.

Let me emphasize, in reply to Dr. Singwi's comment, that ours is a technique for correcting, in a rather direct and general way, for the multiphonon terms. What we are trying to show is that the one-phonon self-term extends to a region where the interference terms have died out. We seek to extrapolate the self-term through the region where the interference term is important to the value of $\alpha = 0$. If you do a numerical calculation for graphite, you will find this actually happens and that there is a flat region where the self-term is dominant. In other words, we are saying that if you do a proper numerical calculation, you can show that this method of extrapolation is very reliable, to a matter of a per cent or so. There is no difference between our method and what he calls the normal method, except that our approach is more rigorous and exact.

To some extent, exactly the same answer can be given to Dr. Larsson's question. What we are doing is to perform a Fourier-transform of an exponential function in order to get a phonon expansion. This operation yields

* See these Proceedings.

something that is very much like an exponential function, provided that the initial function is fairly compact. To find out whether this applies in the case of graphite, we must again do a numerical computation. If we take the frequency distributions of the type of Baldock or of Yoshimori and Kitano, and calculate what scattering laws they would predict and then plot $\log(S/\alpha)$ against α , we find that they give almost exact straight lines, within a few per cent, for the region covered by these experiments.

K. E. LARSSON: I could agree if the sample you were investigating was one in which the Debye temperature was high and the temperature at which you were investigating was low, so that the multiphonon terms were also low. But what happens at a high temperature?

P. EGELSTAFF: Essentially, this is what we have in the case of graphite, where the Debye temperature is about 2000° and is being observed at a temperature of about 300° .

N. A. TCHERNOPOLEKOV: It seems to me that it is difficult to speak of a Debye temperature in the case of a highly anisotropic structure like that of graphite.

B. N. BROCKHOUSE: I would like to point out that the position of the "critical point" in the experimental curves of Fig. 5 and 6 of the paper, at about 0.016 eV, is in good agreement with the figure of 3.8×10^{12} c/sec which Dolling and I obtained for the frequency of the longitudinal mode in the hexagonal direction at the zone boundary, in some measurements we recently made in pyrolytic graphite*. Thus this feature of the distribution is correct.

* To be published (Phys. Rev., issue of 1 Nov. 1962).

ИССЛЕДОВАНИЕ ФОНОННОГО СПЕКТРА И ДИСПЕРСИОННЫХ КРИВЫХ ДЛЯ ВАНАДИЯ

М.Г. Землянов, Ю.М. Каган, Н.А. Черноплеков, А.Г. Чичерин
Ордена Ленина Институт атомной энергии им. И.В. Курчатова
Академии наук СССР, Москва
СССР

Abstract — Résumé — Аннотация — Resumen

A STUDY OF THE PHONON SPECTRUM AND DISPERSION CURVES FOR VANADIUM. Measurements of the spectrum of inelastically-scattered cold neutrons in a vanadium sample were made with a time-of-flight neutron spectrometer. The phonon spectrum of the vanadium and dispersion curves were established from the experimental data by means of an electronic computer.

ÉTUDE DU SPECTRE DE PHONONS ET DES COURBES DE DISPERSION DANS LE VANADIUM. Au moyen d'un spectromètre à temps de vol, les auteurs ont déterminé le spectre de diffusion inélastique des neutrons froids dans un échantillon de vanadium. En partant des données expérimentales, ils ont reconstitué, à l'aide d'une calculatrice électronique, le spectre de phonons du vanadium et les courbes de dispersion.

ИССЛЕДОВАНИЕ ФОНОННОГО СПЕКТРА И ДИСПЕРСИОННЫХ КРИВЫХ ДЛЯ ВАНАДИЯ. На нейтронном спектрометре методом времени пролета проведены измерения спектра неупруго рассеянных холодных нейтронов на образце ванадия. С помощью электронно-счетной машины на основании экспериментальных данных определены фоновый спектр ванадия и дисперсионные кривые.

ESTUDIO DEL ESPECTRO DE FONONES Y CURVAS DE DISPERSIÓN DEL VANADIO. Aplicando la espectrometría neutrónica basada en la medida del tiempo de vuelo, los autores determinaron el espectro de los neutrones fríos dispersos inelásticamente en una probeta de vanadio. A partir de los datos experimentales reconstituyeron, con ayuda de una calculadora electrónica, el espectro fonónico del vanadio y las respectivas curvas de dispersión.

1. ВВЕДЕНИЕ

В физике твердого тела большое значение имеет знание фоновый спектра вещества $g(\omega)$ и законов дисперсии для фононов. До недавнего времени основным экспериментальным методом установления вида фоновый спектра был калометрический метод-исследование температурной зависимости теплоемкости вещества при постоянном объеме. Однако, как было показано теоретически [1,2], восстановление спектра возбуждений бозе-системы по ее теплоемкости, связанное с решением интегрального уравнения с неустойчивым ядром, при современном состоянии калориметрического эксперимента не может быть однозначным.

Возможность прямого восстановления $g(\omega)$ из экспериментальных данных появилась лишь в недавнее время в связи с начатыми исследованиями неупругого рассеяния холодных и медленных нейтронов веществом и изучением эффекта Моссбауера. В этих экспериментах измеряемые величины являются линейными функциями $g(\omega)$,

и задача восстановления фоновнного спектра значительно упрощается [3,4,5,6].

Одним из первых веществ, на котором было проведено исследование неупругого рассеяния нейтронов с целью восстановления $g(\omega)$, явился ванадий, одноизотопный металл с кубической объемно-центрированной решеткой [7,8,9,10]. В силу спиновой некогерентности сечение когерентного рассеяния нейтронов на нем пренебрежимо мало, и поэтому измеряется сечение неупругого некогерентного рассеяния, имеющее простую связь с функцией $g(\omega)$ [3]. В работах [8] и [9] приведены в общих чертах согласующиеся данные по спектру ванадия, восстановленному из нейтронных измерений. Однако соотношение ординат максимумов фоновнного спектра и их ширины несколько противоречивы. Поэтому было проведено новое измерение спектра, возникающего при неупругом рассеянии холодных нейтронов на образце ванадия с использованием нейтронного спектрометра по времени пролета с более высоким, чем в предыдущих работах разрешением, и проанализирована корректность поправок, вводимых при восстановлении фоновнного спектра. Кроме того, полученные экспериментальные данные по $g(\omega)$ были использованы для восстановления кривых дисперсий фононов в ванадии.

2. ПРОВЕДЕНИЕ ИЗМЕРЕНИЙ

Измерения спектра неупруго рассеянных нейтронов были проведены на установке, смонтированной на реакторе ИРТ-1000 [11]. Образец ванадия в виде пластины с размерами $15 \times 18 \times 1 \text{ см}^3$ устанавливался в камере рассеивателя под углом 45° к падающему пучку. Температура образца составляла $\sim 293^\circ\text{K}$, содержание ванадия в образце превышало 99,7%. Измерение спектра рассеянных нейтронов проводилось в интервале энергий $10^{-2} - 5 \cdot 10^{-2}$ эв под углом 90° к падающему пучку. При этом использовался прерыватель с шириной щели $S = 8 \cdot 10^{-2} \text{ см}$, скорость вращения ротора прерывателя была равна 4500 об/мин, а ширина каналов временного анализатора - 32 мксек. При выбранной скорости вращения прерывателя максимум функции пропускания соответствовал приблизительно середине исследуемого интервала энергии, а на границах его она равнялась 0,5. Проведение измерений спектра при энергиях ниже 10^{-2} эв не представляло интереса, поскольку эта часть кривой рассеяния легко может быть рассчитана по упругим постоянным ванадия [12] и дополнительной физической информации не содержит.

Указанные измерения спектра неупруго рассеянных нейтронов проводились при работе реактора на номинальной мощности, и интенсивность рассеянных нейтронов составляла 0,6 н/канал в минуту при фоне 0,3 н/канал в минуту. Поэтому для обеспечения удовлетворительной статистической точности потребовалось время измерений более 100 часов.

Поскольку прерыватель спектрометра по времени пролета с параболическими щелями и работает как грубый монохроматор, то для получения истинного вида спектра неупруго рассеянных нейтронов в первичные экспериментальные данные необходимо ввести поправку

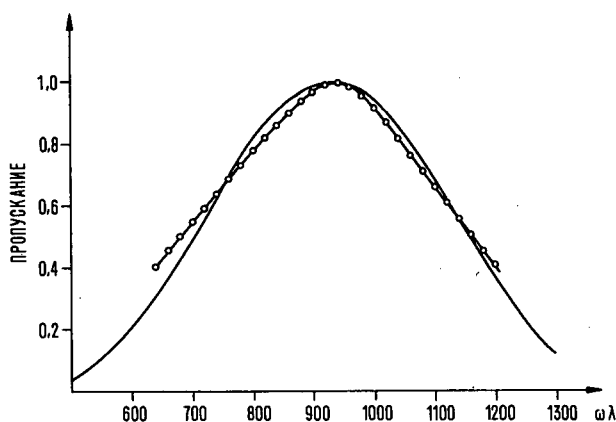


Рис.1

Сравнение экспериментально определенной функции пропускания прерывателя с расчетной.

Линия с точками - эксперимент.

на деформацию спектра функцией пропускания прерывателя. Для использованного прерывателя функция пропускания определялась экспериментально. На рис.1 представлены результаты этого определения и проведено сравнение с теоретически рассчитанной кривой функции пропускания.

Кроме того, при обработке исходных данных по спектру неупруго рассеянных нейтронов необходимо учитывать отклонение эффективности детектора установки от закона $1/v$ и различное ослабление нейтронов разных энергий воздухом, находящимся между прерывателем и детектором, принимая во внимание влияние накопления за счет рассеяния. На рис.2 приведена зависимость суммарной поправки η от волнового числа рассеянного нейтрона, учитывающей все три фактора, а на рис.3 экспериментальная кривая спектра неупруго рассеянных нейтронов с учетом указанных поправок.

3. ВОССТАНОВЛЕНИЕ ФОНОННОГО СПЕКТРА

Как уже отмечалось в случае ванадия, вероятность рассеяния нейтрона с поглощением или излучением одного фонона частоты ω пропорциональна плотности спектра фононов при данной частоте [3]:

$$W^{(\pm 1)} = F(E, \bar{n}, E', \bar{n}') g(E - E'), \quad (1)$$

где $F(E, \bar{n}, E', \bar{n}')$ - множитель, содержащий как специфические для рассеяния, так и просто нормировочные функции;

E и $\bar{n}$ - энергия и единичный вектор направления рассеянного нейтрона;

E' и $\bar{n}'$ - то же для падающего нейтрона.

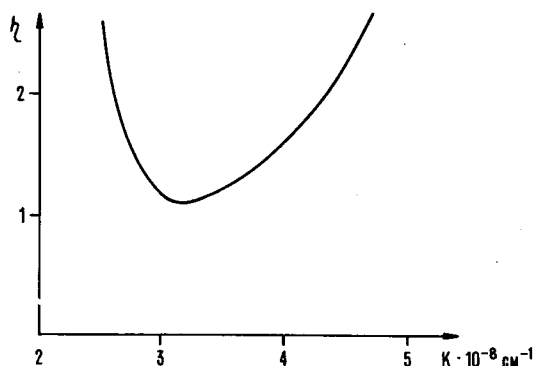


Рис.2

Зависимость суммарной поправки η от волнового числа рассеянного нейтрона.

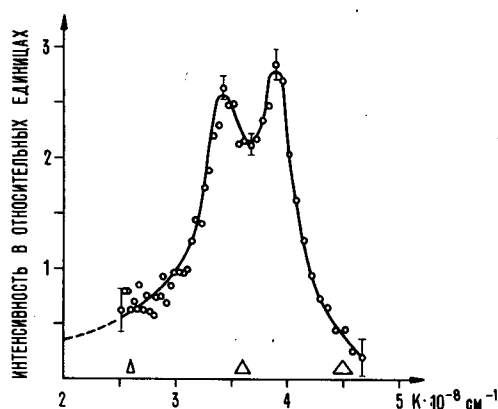


Рис.3

Интенсивность рассеянных нейтронов как функции волнового числа нейтронов.

Приблизительно можно считать, что экспериментально полученный спектр неупруго рассеянных нейтронов (рис.3) позволяет, согласно выражению (1), непосредственно судить о фононном спектре исследуемого вещества. Однако, анализ, проведенный в указанном приближении, не дает возможности восстановить $g(\omega)$ с максимальной для данного эксперимента точностью. Действительно, выражение (1) применимо лишь к спектру нейтронов, рассеянных на бесконечно тонком образце при вычете вклада многофононного рассеяния, измеренному прибором с бесконечно высокой разрешающей способностью.

В эксперименте эти требования не выполняются. Поэтому при восстановлении $g(\omega)$ из нейтронного эксперимента необходимо учесть влияние деформации спектров падающих и рассеянных нейтронов по толщине образца, вклад многофононных и многократных однофононных процессов, а также учесть влияние немонохроматичности первичной спектральной линии холодных нейтронов и конечной разрешающей способности спектрометра по времени пролета, которые определяют полное разрешение установки.

Целесообразно процедуру восстановления $g(\omega)$ провести в два этапа:

1) приведение экспериментально измеренного спектра неупруго рассеянных нейтронов к спектру на бесконечно тонком образце и вычет вклада многофононных и многократных процессов;

2) восстановление из спектра на бесконечно тонком образце функции $g(\omega)$ с учетом полного разрешения установки.

Влияние факторов, рассматриваемых на первом этапе восстановления, определяется интегралами от $g(\omega)$ с весовыми функциями, которые в свою очередь также зависят от $g(\omega)$, но при известном фононном спектре могут быть вычислены с любой точностью. При этом как первое приближение к $g(\omega)$ используется дебаевский фононный спектр. На втором этапе производится учет влияния функции разрешения (аппаратной функции), изменяющей вид весовых функций, связывающих интенсивность рассеянных нейтронов $I(E)$ с интегралами от их произведения на функцию $g(\omega)$. Поэтому задача восстановления $g(\omega)$ из экспериментальных данных по неупругому рассеянию холодных нейтронов сводится, в принципе, к определению неизвестной функции по заданным с конечной точностью интегралам от произведения ее на известные функции, причем число интегралов равно числу экспериментальных точек. Математические подробности указанной обработки экспериментальных данных приведены в приложении.

Полное решение задачи восстановления $g(\omega)$ для ванадия было выполнено с помощью электронно-счетной машины ЦМ-2. На рис.4 и 5 представлены последовательные этапы восстановления функции $g(\omega)$, а на рис.6 - окончательный результат. Причем $g(\omega)$ на экспериментально исследованном интервале восстановлена в виде разложения:

$$g(\omega) = \sum_{\alpha=0}^{13} g_{\alpha} f_{\alpha}(\omega) \quad (2)$$

по некоторой системе базисных функций $f_{\alpha}(\omega)$, определяемой соотношением:

$$f_{\alpha}(\omega) = \sum_{\beta=0}^{\alpha} f_{\alpha\beta} \cos \pi\beta \frac{\omega - \omega_0}{\Omega}, \quad (3)$$

где α и β - целочисленные индексы;

- g_{α} и $f_{\alpha\beta}$ - коэффициенты разложения;
 ω_0 - нижняя граница исследованной области спектра;
 Ω - весь частотный интервал, в котором проводилось восстановление.

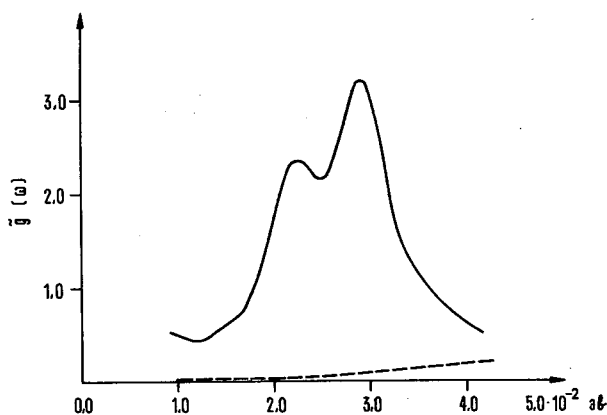


Рис. 4

Фононный спектр ванадия, восстановленный в предположении δ -функционального вида полной функции разрешения. Штриховой кривой приведен вклад двукратных и двуфононных процессов.

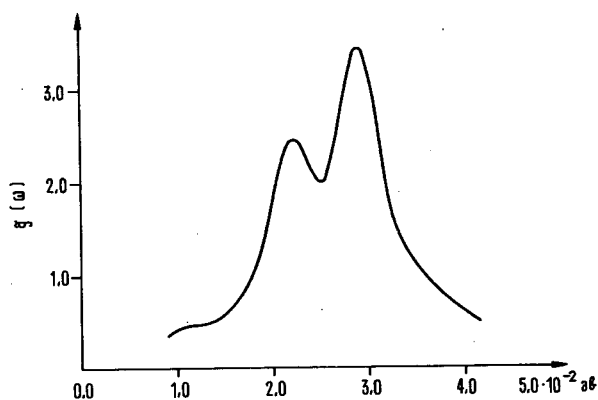


Рис. 5

Фононный спектр ванадия, восстановленный с учетом немонохроматичности спектральной линии холодных нейтронов.

ТАБЛИЦА 1

КОЭФФИЦИЕНТЫ РАЗЛОЖЕНИЯ ФУНКЦИИ $g(\omega)$

(Функция $g(\omega)$ представлена как $\beta\omega^2$ на интервале от $\omega = 0$ до $\omega_0 = 1,52 \cdot 10^{13}$ сек $^{-1}$

и как $g(\omega) = c \sum_{\alpha=0}^{\beta} g_{\alpha} f_{\alpha}(\omega)$, при $\omega > \omega_0$, где $f_{\alpha}(\omega) = \sum_{\beta=0}^{\alpha} f_{\alpha\beta} \cos \pi\beta \frac{\omega - \omega_0}{\Omega}$; c -коэффициент нормировки,

равный 0,021764, а $\beta = 0,0579$)

α	0	1	2	3	4	5	6	7	8	9	10	11	12	13
g_{α}	62,04	1,3436	-26,2531	-2,0964	5,9094	1,8881	4,2427	1,9797	-5,2092	-2,2031	3,7667	1,7547	-1,4733	-0,5545
$f_{\alpha\beta}$														
$\alpha \backslash \beta$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	0,04325													
1	-0,02224	0,07861												
2	+0,02409	-0,02169	-0,08552											
3	0,0003778	0,05286	-0,02344	0,08552										
4	0,02842	-0,000689	0,05530	-0,02796	0,09167									
5	-0,00007743	0,06122	-0,00211	0,06275	-0,03052	0,1025								
6	0,03378	-0,00062	0,06991	-0,00270	0,07562	-0,0357	0,1131							
7	-0,00051	0,07865	-0,00105	0,08438	-0,00555	0,0886	-0,0460	0,13043						
8	0,04648	-0,00094	0,09622	-0,00342	0,09963	-0,0129	0,1101	-0,05882	0,15063					
9	-0,00062	0,11429	-0,00391	0,11513	-0,01093	0,1235	-0,0230	0,13645	-0,07926	0,17920				
10	0,07125	-0,00129	0,13999	-0,00837	0,14543	-0,0180	0,1545	-0,03680	0,17467	-0,10362	0,21947			
11	-0,00181	0,17512	-0,00759	0,17724	-0,01765	0,1833	-0,0337	0,1976	-0,06036	0,23119	-0,14604	0,27041		
12	0,10851	-0,01050	0,22176	-0,01745	0,22451	-0,0340	0,2358	-0,05749	0,26068	-0,09989	0,30676	-0,20803	0,34574	
13	-0,01078	0,27803	-0,02510	0,28363	-0,03842	0,2917	-0,0629	0,31265	-0,10231	0,34938	-0,16711	0,42699	-0,30835	0,45396

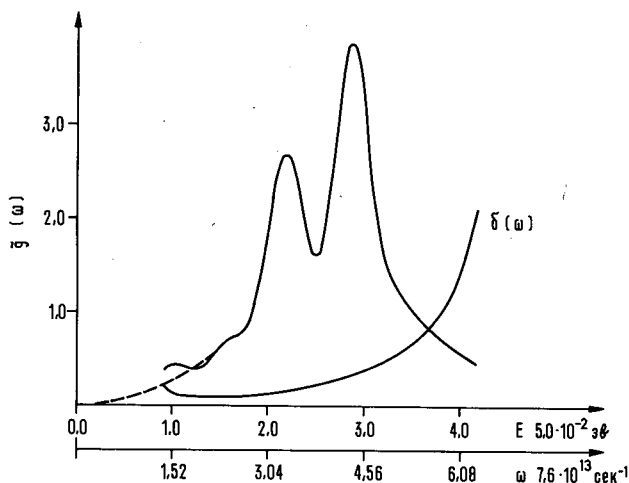


Рис.6

Фононный спектр ванадия, восстановленный с учетом полной функции разрешения. Кривая $\delta(\omega)$ характеризует точность восстановления спектра. Штриховой кривой показана низкочастотная часть дебаевского спектра с $\theta = 338^\circ\text{K}$.

Полученные в результате восстановления значения коэффициентов разложения приведены в табл.1. Представление фононного спектра ванадия в виде указанного разложения является очень удобным, поскольку позволяет легко проводить расчеты величин (теплоемкость, фактор Дебая-Валлера и др.), зависящих от фононного спектра, а также для восстановления из данных по фононному спектру решетки ванадия дисперсионных кривых. На рис.6, наряду с функцией $g(\omega)$, приведена кривая ошибки $\delta(\omega)$, с которой эта функция восстановлена:

$$\delta(\omega) = \left\{ \sum_{\alpha=0}^{13} f_{\alpha}^2(\omega) \right\}^{\frac{1}{2}} \quad (4)$$

и штриховой линией проведена низкочастотная часть функции $g(\omega)$, рассчитанная в предположении дебаевской характеристической температуры ванадия $\theta = 338^\circ\text{K}$. Ограничение разложения 14 гармониками связано с наложенным на решение задачи восстановления требованием "гладкости" функции ошибок $\delta(\omega)$. Теперь остановимся на восстановлении закона дисперсии для фононов [16]. Функция распределения частот $g(\omega)$ несет исчерпывающую информацию о фононной ветви возбуждения для термодинамического описания кристалла. Однако, для всех кинетических задач эта информация является неполной, так как необходимо знать закон дисперсии $\omega(\vec{f}, \alpha)$ и векторы поляризации $\vec{V}_j(\vec{f}, \alpha)$ для всего фазового пространства векторов $\vec{f}$

и всех ветвей α (j - номер атома в элементарной ячейке). Возникает вопрос о том, каким образом по результатам опытов по некогерентному неупругому рассеянию нейтронов можно восстановить закон дисперсии и вектора поляризации фононов.

Поскольку в таких опытах находится одномерная информация о спектре, а мы хотим перейти к трехмерной, возникает необходимость привлечения уравнений, описывающих динамику кристалла. Если ограничиться диэлектриками и переходными металлами с преобладающей ролью ковалентной связи, то можно воспользоваться известной системой уравнений Борна-Кармана. Свойства кристалла в этих уравнениях входят через коэффициенты динамической матрицы. Для рассматриваемого типа кристаллов существенную роль в задаче колебаний играют только несколько ближайших соседей. Если симметрия решетки достаточно высокая, то учет нескольких координационных сфер предполагает знание сравнительно небольшого числа независимых параметров.

Как было впервые показано Ван Говом [15], функция распределения частот регулярного кристалла должна иметь по крайней мере две особые точки, в которых $\partial g(\omega)/\partial \omega$ обращается в бесконечность. В большинстве случаев этим точкам соответствуют максимумы кривой $g(\omega)$. С другой стороны, на обоих концах частотного интервала функция $g(\omega)$ обращается в ноль, как ω^2 при $\omega \rightarrow 0$ и как $(\omega_{\max}^2 - \omega^2)^{\frac{1}{2}}$ при $\omega \rightarrow \omega_{\max}$.

Ясно, что форма такой кривой заключает в себе большую информацию о силовых постоянных. Поэтому, если дополнить экспериментально определенную кривую $g(\omega)$ значениями модулей упругости монокристалла C_{ik} , то вся эта совокупность данных может явиться хорошей основой для решения обратной задачи, т.е. определения достаточно большого числа коэффициентов динамической матрицы, а вместе с тем нахождение закона дисперсии и векторов поляризации. При таком методе восстановления закона дисперсии может быть не разрешена тонкая структура на поверхности постоянной частоты, обусловленная далекими взаимодействиями. Однако, в отличие от электронного спектра, где наличие тонкой структуры может выявиться в магнитном поле, наличие ее в фононном спектре должно сказываться очень слабо во всех кинетических явлениях.

Остановимся кратко на самом методе решения обратной задачи. Система уравнений для определения $\omega(\vec{f}, \alpha)$ и $\vec{V}(\vec{f}, \alpha)$ имеет обычный вид (для простоты приводится выражение для случая одного атома в элементарной ячейке):

$$m \omega^2 \vec{v}^i = \sum_{\vec{n}} A^{ik}(\vec{f}_{\vec{n}}) e^{i\vec{f}\vec{r}_{\vec{n}}} \vec{v}^k. \quad (5)$$

Знание "р" экспериментальных значений C_{ik} для кристалла данной симметрии приводит к "р" линейным соотношениям между коэффициентами матрицы $A^{ik}(\vec{f}_{\vec{n}})$. Если в последней принимаются во внима-

ние q независимых коэффициентов, то, решая задачу о собственных значениях и находя $g(\omega)$, приходим к функции, заданной параметрически в $(q - p)$ мерном пространстве. Обозначим эту функцию как $g_{c_1, \dots, c_{q-p}}(\omega)$. При некогерентном однофононном рассеянии нейтронов на кристалле с параметрами $c_1, \dots, c_{q-p}$ наблюдалась бы величина (см. приложение):

$$I_{c_1, \dots, c_{q-p}}(E) = \int \tilde{g}_{c_1, \dots, c_{q-p}}(\omega) \Omega_E(\omega) d\omega.$$

Поэтому в качестве величины, характеризующей отклонение теоретического спектра от экспериментального естественно выбрать взвешенное квадратичное отклонение:

$$\sum_i \frac{\left[I_{c_1, \dots, c_{q-p}}(\omega_i) - I(\omega_i)_{\text{эксп.}} \right]^2}{\delta_i^2} = \chi^2_{c_1, \dots, c_{q-p}}$$

(суммирование по экспериментальным точкам, которым соответствует ω_i и средняя квадратичная ошибка δ_i^2). С помощью машины ЦМ-2 находится минимум χ^2 в $(q - p)$ параметрическом пространстве.

Прямое вычисление $I_{c_1, \dots, c_{q-p}}$ для всего пространства параметров практически невозможно. Однако, для нахождения областей минимального χ^2 можно воспользоваться эффективным методом, предложенным И.М. Гельфандом, так называемым "методом оврагов". После нахождения $c_1, \dots, c_{q-p}$ непосредственное определение $\omega^2(\bar{f}, \alpha)$ и $\bar{v}(\bar{f}, \alpha)$ на основе (5) не представляет труда.

Подобная программа решения обратной задачи была реализована для ванадия на основании описанных выше экспериментальных данных при учете четырех типов ближайших соседей, как можно непосредственно показать, матрица $A^{ik}(\Sigma_n)$ будет содержать 9 независимых силовых постоянных. Если воспользоваться тремя модулями упругости, определенными в работе [12], то мы приходим к задаче с 6 параметрами. Эта задача на основе использования "метода оврагов" решалась на ЦМ-2. В результате расчетов было найдено, что в пределах трех первых координационных сфер резкого падения силовых постоянных не происходит. Такое падение имеет место только начиная с четвертых соседей. Для совокупности параметров, отвечающих минимальному значению χ^2 были определены $\omega(\bar{f}, \alpha)$ и $\bar{v}(\bar{f}, \alpha)$.

4. ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ

Сравнение полученных в этой работе данных по $g(\omega)$ с результатами работ Эйзенхауера и др. [9] и Стюарта и Брокхауза [8] показывает, что фононный спектр, приведенный на рис. 6, ближе к данным Эйзенхауера и др., и хотя энергетическое положение особых точек спектра практически не изменилось, однако, произошло зна-

чительное обострение максимумов спектра и изменение соотношения между их ординатами. Максимум, соответствующий более высоким частотам в спектре, стал выше. Такое изменение характера фононного спектра свидетельствует о заметном влиянии нецентральных взаимодействий в решетке ванадия, чем можно было ожидать на основании работ [8] и [9], т.к. фононный спектр еще резче отличается от того, который предсказывается расчетами по объемно-центрированным решеткам с центральным взаимодействием [13] и [14]. Этот результат следует для ванадия считать естественным, поскольку ванадий является переходным металлом, в котором определяющую роль играют ковалентные связи, характеризующиеся большой нецентральностью.

На основании результатов восстановления кривых дисперсии для фононов можно сделать вывод, что в ванадии значительное затухание силовых постоянных начинается с четвертой координационной сферы, причем силовые постоянные центрального и нецентрального взаимодействия приблизительно одинаковы. Кроме того, у ванадия наблюдается значительный слой открытых энергетических поверхностей для фононов. В дальнейшем эти результаты будут использованы для вычисления гальвано-магнитных явлений.

В заключение авторы выражают благодарность М.И. Певзнеру за обсуждение результатов и коллективу ЦМ-2, способствовавшему успешному проведению расчетных работ.

ПРИЛОЖЕНИЕ

А. Приведение к однофононному рассеянию на бесконечно тонком образце.

Для правильного учета процессов поглощения падающих и рассеянных нейтронов в пластине использовалось следующее интегральное уравнение для плотности потока нейтронов в бесконечно широкой пластине конечной толщины при падении на нее равномерно-го потока нейтронов интенсивности $I_0(E)$ в направлении $\vec{n}_0$:

$$\begin{aligned} \rho(E, \vec{n}, z) = & \int L_e(E, \vec{n}, \vec{n}', z, z') I_0(E) \delta(\vec{n} - \vec{n}_0) \delta(z) dz + \\ & + \iint L_e(E, \vec{n}, \vec{n}', z, z') \sigma_f(E, \vec{n}, E', \vec{n}') \rho(E', \vec{n}', z') dE' dz' \end{aligned} \quad (6)$$

где: z - расстояние от передней плоскости пластины;

$\vec{n}$ - направление движения нейтронов;

E - его энергия;

$\sigma_f(E, \vec{n}, E', \vec{n}')$ - полное сечение неупругого рассеяния;

$L_e(E, \vec{n}, \vec{n}', z, z')$ - резольвента интегрального уравнения для плотности нейтронов в пластине при учете только их поглощения и упругого рассеяния при заданной энергии.

Под dz в (6) и в дальнейшем понимается интегрирование по геометрическим переменным: направлению движения нейтрона и толщине пластины. Таким образом, первое слагаемое правой части

уравнения (6) представляет собой распределение потока нейтронов без учета неупругого рассеяния. Это распределение, во-первых, может быть вычислено без знания спектра, из одного лишь первичного потока, который аппроксимировался максвелловским распределением, и известных экспериментально сечений поглощения и упругого рассеяния; во-вторых, - является хорошим приближением к истинному распределению, так что влияние второго слагаемого можно рассмотреть в теории возмущений, оставив только первый и второй порядки по однофону рассеянию и только первый порядок по двухфону рассеянию.

Так как рассеянные нейтроны измерялись при энергиях выше максимальной энергии первичного пучка, то для них можно опустить первое слагаемое в (6). Таким образом получим три следующих слагаемых в рассеянном пучке:

$$\begin{aligned} \rho(E, \bar{n}, z) = & \int dE' \int dz' L_e(E, \bar{n}, \bar{n}', z, z') \sigma_f^{(1)}(E, \bar{n}, E', \bar{n}') \rho_e(E', \bar{n}', z') + \\ & + \int dE' \int dz' L_e(E, \bar{n}, \bar{n}', z, z') \sigma_f^{(2)}(E, \bar{n}, E', \bar{n}') \rho_e(E', \bar{n}', z') + \\ & + \iint dE' dE'' \iint dz' dz'' L_e(E, \bar{n}, \bar{n}', z, z') \sigma_f(E, \bar{n}, E', \bar{n}') \times \\ & \times L_e(E', \bar{n}', \bar{n}'', z', z'') \sigma_f^{(1)}(E', \bar{n}', E'', \bar{n}'') \rho_e(E'', \bar{n}'', z''). \quad (7) \end{aligned}$$

Первое слагаемое - однократное однофонное рассеяние, второе - однократное двухфонное, третье - двукратное однофонное рассеяние, причем после каждого неупругого рассеяния включалось поглощение и упругое рассеяние, так что по отношению к этим процессам ни на одном этапе не вводилось никаких приближений.

Сечение однофонного и двухфонного рассеяния линейно и квадратично по спектру нейтронов соответственно, причем коэффициенты известны и зависят от вида спектра только через фактор Дебая-Валлера, для которого достаточно взять дебаевское приближение. Вводя таким образом спектральную функцию в (7) и отделяя интегрирование по энергии от интегрирования по геометрическим параметрам, мы приходим к следующему уравнению, выражающему интенсивность рассеянных от пластины нейтронов через спектральную функцию:

$$\begin{aligned} I(E) \equiv \rho(E, \bar{n}, z=0) = & \int g(E-E') \gamma(E, E') dE + \\ & + \iint g(E-E') g(E'-E'') b(E, E', E'') dE' dE'', \quad (8) \end{aligned}$$

где во втором слагаемом справа объединены два последних слагаемых уравнения (7). Функции γ и b были вычислены на электронной машине, для фактора Дебая-Валлера было взято значение в дебаевском приближении.

Первым этапом работы было получение приближенного спектра, достаточного для учета двухфонных процессов. Для этого в пред-

положении δ - функционального разрешения установки функция $\gamma(E, E')$ также была заменена следующим образом:

$$\gamma(E, E') = \gamma(E) \delta(\Delta), \quad (9)$$

где
$$\gamma(E) = \int \gamma(E, E') dE',$$

а Δ равна средней энергии нейтрона в первичном пучке. В таком приближении значения спектра получаются простым делением:

$$g^\circ(E - \Delta) = I(E) / \gamma(E) \quad (10)$$

Отнормированная кривая спектра была подставлена во второе слагаемое уравнения (8) и получен вклад двухфононных процессов. Результаты приведены на рис.4.

Б. Учет полного разрешения установки

Для определения полного разрешения установки нужно учесть, во-первых, что поток рассеянных нейтронов из-за ширины пучка является интегралом (8) от спектральной функции, во-вторых, экспериментально измеренная плотность потока нейтронов при энергии E_n на самом деле является интегралом по энергии от рассеянного потока нейтронов с весовой функцией $\rho_n(E_n - E)$, описывающей разрешающую способность самого прибора. Объединяя обе функции

$$\tilde{g}_n \equiv g(E_n) = \iint \rho_n(E_n - E) dE \gamma(E, E') g(E - E') dE' \quad (10 \text{ а})$$

получим новую:

$$\tilde{g}_n = \int \Omega_n(E_n, E) g(E) dE; \quad (10 \text{ в})$$

$$\Omega_n(E_n, E) = \int \rho_n(E_n - E') \gamma(E', E' - E) dE'$$

характеризующую полное разрешение эксперимента. Теперь можно точно сформулировать задачу восстановления спектра из экспериментальных данных.

Итак, измерены N (в случае ванадия $N = 48$) величины $\tilde{g}_n$ с независимыми статистическими ошибками δ_n . Независимость и статистичность ошибок позволяет оценить математическую вероятность того, что истинные значения равны $\tilde{g}_n$ в виде гауссовой экспоненты:

$$W\{\tilde{g}_n\} = A \exp \left\{ - \sum_{n=1}^N \left(\frac{\tilde{g}_n - \tilde{g}_n}{\delta_n} \right)^2 \right\}. \quad (11)$$

Каждая из этих величин является интегралом от искомой спектральной функции с известной весовой функцией (10в). Следовательно, мы можем оценить при помощи экспоненты (11) вероятность того, что некоторая функция $g(\omega)$ является истинной спектральной функцией: для этого достаточно получить значения интегралов (10в) и подставить их в экспоненту (11). Функция $g(\omega)$, заданная на некотором интервале, содержит бесконечное количество информации, в то время как эксперимент дает только N величин $\tilde{g}_n$, поэтому особенно важным становится вопрос о классе функций, в котором ищется наиболее вероятный вид функции $g(\omega)$ и определяется ошибка, с которой эта функция восстанавливается. Линейная зависимость $\tilde{g}_n$ от $g(\omega)$ позволяет искать $g(\omega)$ в виде линейного разложения по некоторым базисным функциям $f_\alpha(\omega)$:

$$g(\omega) = \sum_{\alpha=0}^S g_\alpha f_\alpha(\omega). \quad (12)$$

Таким образом, задача восстановления $g(\omega)$ сводится к задаче восстановления коэффициентов разложения g_α , а определение точности восстановления — к определению точности восстановления этих коэффициентов. Очевидно, что число базисных функций не должно превышать число экспериментальных точек и задача восстановления становится корректной: по N экспериментальным точкам нужно восстановить $S \leq N$ коэффициентов g_α .

Рассмотрим построение базисных функций $f_\alpha(\omega)$. Воспользовавшись разложением (12), получаем:

$$\tilde{g}_n = \sum_{\alpha=0}^S g_\alpha \Omega_{n\alpha},$$

где

$$\Omega_{n\alpha} = \int \Omega_n(\omega) f_\alpha(\omega) d\omega.$$

Теперь $W[g(\omega)]$ является функцией коэффициентов g_α :

$$W[g(\omega)] = W(g_\alpha) = A \exp \left\{ - \sum_{n=1}^N \left(\frac{\sum_{\alpha=0}^S g_\alpha \Omega_{n\alpha} - \tilde{g}_n}{\delta_n} \right)^2 \right\}. \quad (13)$$

Преобразуем показатель экспоненты, переименовав порядок суммирования:

$$\sum_{n=1}^N \left(\frac{\sum_{\alpha=0}^S g_\alpha \Omega_{n\alpha} - \tilde{g}_n}{\delta_n} \right)^2 = \sum_{n=1}^N \left(\frac{\tilde{g}_n}{\delta_n} \right)^2 - 2 \sum_{\alpha=0}^S g_\alpha \sum_{n=1}^N \frac{\Omega_{n\alpha} \tilde{g}_n}{\delta_n^2} +$$

$$\sum_{\alpha=0}^S \sum_{\beta=0}^S g_{\alpha} \left(\sum_{n=1}^N \frac{\Omega_{n\alpha} \Omega_{n\beta}}{\delta_n^2} \right) g_{\beta}. \quad (14)$$

Матрица

$$\Gamma_{\alpha\beta} = \sum_{n=1}^N \frac{\Omega_{n\alpha} \Omega_{n\beta}}{\delta_n^2}$$

является симметричной, положительно определенной матрицей, следовательно, она имеет ортогональный базис, число независимых векторов которого меньше или равно N . Если в качестве функции f_{α} выбраны базисные векторы этой матрицы, то она становится диагональной:

$$\Gamma_{\alpha\beta} = \Gamma_{\alpha\alpha} \delta_{\alpha\beta}.$$

Нормируем базисные векторы так, чтобы

$$\Gamma_{\alpha\beta} = \frac{\delta_{\alpha\beta}}{2},$$

теперь выражение (14) приобретает более простой вид:

$$\sum_{n=1}^N \left(\frac{\tilde{g}_n}{\delta_n} \right)^2 - 2 \sum_{\alpha=0}^S g_{\alpha} R_{\alpha} + \sum_{\alpha=0}^S g_{\alpha}^2 / 2, \text{ где } R_{\alpha} = \sum_{n=1}^N \frac{\Omega_{n\alpha} \tilde{g}_n}{\delta_n^2},$$

который распадается на сумму квадратичную по g_{α} и слагаемые, не зависящие от g_{α} :

$$\sum_{\alpha=0}^S \left(\frac{g_{\alpha} - \sqrt{2} R_{\alpha}}{\sqrt{2}} \right)^2 + \sum_{n=1}^N \left(\tilde{g}_n / \delta_n \right)^2 - \sum_{\alpha=0}^S R_{\alpha}^2$$

а вероятность $W[g(\omega)]$, в свою очередь, распадается на произведение независимых экспонент:

$$W(g_{\alpha}) = A_{\exp} \left\{ - \left[\sum_{n=1}^N \left(\tilde{g}_n / \delta_n \right)^2 - \sum_{\alpha=0}^S R_{\alpha}^2 \right] \right\} \prod_{\alpha} \exp \left\{ - \left(\frac{g_{\alpha} - \sqrt{2} R_{\alpha}}{\sqrt{2}} \right)^2 \right\}.$$

Последнее означает, что в выбранном базисе коэффициенты имеют независимые гауссовские распределения вокруг среднего значения $\sqrt{2} R_{\alpha}$, причем средний квадрат отклонения для всех α равен 1.

Таким образом, наиболее вероятный вид $g(\omega)$ будет:

$$g(\omega) = \sum_{\alpha=0}^S \sqrt{2} R_{\alpha} f_{\alpha}(\omega) \quad (15)$$

и ошибка определения $g(\omega)$, как можно показать, составляет:

$$\delta \left\{ g(\omega) \right\}^2 = \sum_{\alpha=0}^S f_{\alpha}^2(\omega) \quad (16)$$

Однако, нахождение собственных векторов матрицы $N \times N$ при большом N операция слишком трудоемкая, поэтому рационально воспользоваться более простым методом.

Выберем некоторую полную систему функций, усложняющихся с номером α , например, $\cos \pi \alpha \frac{\omega}{\Omega}$ и используем матрицу $\Gamma_{\alpha\beta}$ в определении нового скалярного произведения $(x \Gamma y)$. В этом случае процессом последовательной ортогонализации можно из первичной системы функций $e_{\alpha} = \cos \pi \alpha \frac{\omega}{\Omega}$ получить последовательность функций $f_{\alpha}(\omega)$:

$$f_0(\omega) \equiv A_0 = A_{00} e_0(\omega); \quad f_1(\omega) = A_{10} e_0(\omega) + A_{11} e_1(\omega) \text{ и т.д.,}$$

которые диагонализуют матрицу $\Gamma_{\alpha\beta}$, так что все приведенные выше выражения сохраняют свое значение. Отличие полученных таким образом f_{α} от собственных векторов заключается в том, что они не ортогональны в обычном смысле, но это, как можно убедиться, не входит во все приведенные выражения.

Конкретное восстановление $g(\omega)$ в виде разложения (12) приведено согласно рассмотренной здесь упрощенной методике, и его результаты представлены на рис.6. Кроме этого на рис.8 представлен вид полной функции разрешения (кривая 4), с использованием

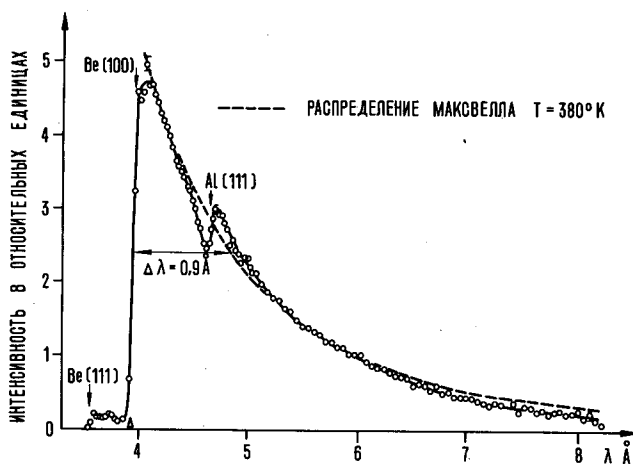


Рис.7

Спектральная линия холодных нейтронов.

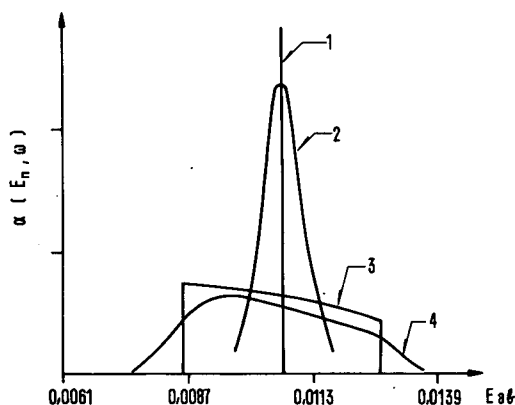


Рис. 8

Кривые функции разрешения:

- 1 - δ -функциональная;
- 2 - функция разрешения нейтронного спектрометра по времени пролета в гауссовском представлении;
- 3 - функция разрешения, учитывающая только немонахроматичность линии холодных нейтронов;
- 4 - полная функция разрешения установки с учетом немонахроматичности линии холодных нейтронов.

которой проводилось восстановление $g(\omega)$, а на рис.5. в качестве иллюстрации, приведен фоновый спектр, восстановленный с учетом только немонахроматичности первичной спектральной линии (кривая 3, рис.7). Сравнение кривых, приведенных на рис.4,5,6, показывает какое значение при восстановлении $g(\omega)$ имеет учет полной функции разрешения.

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DISCUSSION

B.N. BROCKHOUSE: I think your description of the central and non-central forces is not quite correct. These first and second neighbours for example could be central; the third one is non-central of course, but the fourth one could also be central, because you need two parameters to describe central forces. I would refer you to the paper given by Dr. Woods in the first part of Session III (Crystal Dynamic from Neutron Spectrometry). I wonder if you have a slide showing a comparison of your calculated and measured distributions?

N. A. TCHERNOPOLEKOV: I did not quite understand Dr. Brockhouse's remark. These coefficients of the dynamic matrix were written down in an arbitrary way, so that the electronic computer could identify them. These values for the coefficients - which, I would emphasize, are given here in units which are quite arbitrary, though normalized with respect one to another - were obtained subsequently. I do not quite understand why we should need two coefficients for describing a central interaction between first and second neighbours and other more distant neighbours. It is not quite clear to me.

I am afraid I cannot show the comparative plots themselves. I can only say what was the value of χ^2 which we finally adopted. I should make it clear that we still do not regard these results as final. The fact is that determination of the G-atomic function in the parametric space in which we were working is practically impossible, owing to the vast amount of computation involved. Normally we have used another method which is very convenient for this purpose. But even here we still have to spend a great deal of time exploring, if I may so express myself, all this parametrical space in order to find the minima, i.e. to determine the true value of the centre of dynamic matrix. We have recently developed a somewhat improved variant of the method for processing these data by means of which we hope to obtain much quicker results and to be in a position to complete analysis of all this space. Then we shall be able, on the basis of the experimental data which we have to say: here is the main minimum and the most reliable coefficients are therefore such and such.

With regard to this experimental data, I may say that the value of χ^2 works out, on average, at less than one experimental error per plot. You see, we sum along the whole series of plots and on average we get approximately half an error per plot. That is the kind of agreement we now get between experiment and theory; that is how the two coefficients compare.

W. KLEY: As you know, the Cauchy relation does not apply to metals like vanadium, because C^{12}/C^4 equals almost three. According to Fuchs, you have to take the electron effects into account, and I am wondering if you can give a physical picture of how you do this in your calculation.

N. A. TCHERNOPLEKOV: For our purpose there is no need to take the influence of electronic effects into account or to consider what proportion of the coefficients is due to the contribution of electrons and what proportion to pure inter-atomic interaction. We simply write down the Born-von Kármán motion equations and solve them so as to obtain the value of the constant for inter-atomic interaction. Dr. Kley's question refers rather to the interpretation of the data obtained. For the time being the authors would rather not attempt any interpretation, however, since they do not regard the results they have obtained as final.

G. DOLLING: Were any corrections made for multiphonon effects in your experimental results?

N. A. TCHERNOPLEKOV: Yes, of course, we made such corrections. The process of restoring the phonon spectrum from the experimental data was actually carried out in two stages. First, the experimental scattering curve was adjusted in terms of scattering on an infinitely thin sample, that is to say, a count was taken of the recurrent processes of all kinds and of the distortion in the spectrum of the incident scattered neutrons. The second stage in restoring the spectrum was to deduct the contribution of multiphonon processes.

I. WALLER: With regard to your force-constant values, I notice that you still get a rather high value for the fourth co-ordination sphere. Now, that raises the question of how well this procedure of taking more and more co-ordination spheres into account will really converge; one can probably not expect a very good convergence without somehow taking into account the force-constants for very distant atoms - for very long-range interactions - because you certainly have interactions of that kind in a metal. To use this procedure with force-constants for a metal one should therefore first have some means of estimating these long-range interactions.

N. A. TCHERNOPLEKOV: If I understood Prof. Waller correctly, my reply would be as follows: if I were to write down the fifth co-ordination sphere, you would find that I got zero values both for the central and for the non-central forces. In other words, the reason why we stopped where we did was that we had to. As far as the influence of the remainder of the crystal is concerned, that is all the long-range effects, this was taken into account by means of a single potential-value with one constant, naturally in a central approximation. But I must once again point out that we do not regard these results as final, and I therefore saw no point in explaining all the intermediate steps.

As regards your second point, it seems to me that those force constants for which we obtain soundly-based values will undoubtedly have definite physical significance. I should mention that the necessary calculations are at present being made to determine a number of physical properties (thermodynamic and kinetic) for vanadium, and even these tentative results are leading to some very interesting conclusions. However, this work is not yet complete and I cannot therefore discuss it.

A. SJÖLANDER: Have you done these experiments at different temperatures? If not, do you intend to do so?

N. A. TCHERNOPLEKOV: These experiments were all done at room temperature, and the values obtained for the force-constants of interactions also correspond to room temperature. We know that Dr. Egelstaff has made measurements in a wide temperature interval. If analysis of Dr. Egelstaff's data and our own should show the need for certain refinements, I would like to say straight away that, unfortunately, very often we do not attach sufficient importance to the form in which results are published. Results published in the form of a curve are not directly usable, though this is the form in which we usually obtain them. Such results, if I may say so, are not computable, i. e. they cannot be used directly for computation, but can only be used for making some quantitative interpretations. I hope I will be able to talk about this informally with Dr. Egelstaff. If we can make such quantitative comparisons and if we find questions that require experimental checking, we shall certainly make such measurements, since we would like to have complete information on phonon excitation, even if only for one element and really be able to use it in all physical calculation that have to be made.

THE PHONON FREQUENCY DISTRIBUTION OF VANADIUM

R. HAAS, W. KLEY, K.H. KREBS AND R. RUBIN

DEPARTMENT OF REACTOR PHYSICS, EURATOM, C.C.R., ISPRA (VARESE)
ITALY

Abstract — Résumé — Аннотация — Resumen

THE PHONON FREQUENCY DISTRIBUTION OF VANADIUM. The inelastic scattering of vanadium has been measured by the beryllium filter time-of-flight method. The resolution of the instrument is about 20 $\mu\text{s/m}$ at the beryllium cut-off with a flight path length of 5.5 m. Besides the usual corrections the measurements have been corrected also for the resolution and for the incident spectrum.

The vibrational frequency spectrum derived from the scattering data is qualitatively in agreement with earlier measurements. However, the spectrum extends to higher frequencies than it has been assumed previously. A comparison was made with theoretical spectra based on models given by Fine, De Launay and Bhatia. The best agreement is found for the last model.

DISTRIBUTION DE FRÉQUENCES DES PHONONS DANS LE VANADIUM. On a mesuré la diffusion inélastique dans le vanadium par la méthode du temps de vol, en utilisant un filtre de béryllium. La résolution de l'instrument est d'environ 20 $\mu\text{s/m}$ à la coupure d'énergie du béryllium, avec une base de temps de vol de 5,5 m. Outre les corrections habituelles, on a également rectifié les mesures en tenant compte de la résolution et du spectre incident.

Le spectre des fréquences des vibrations dérivé des données de diffusion concorde qualitativement avec les mesures antérieures. Cependant, le spectre s'étend à des fréquences plus élevées qu'on ne l'avait prévu précédemment. On l'a comparé à des spectres théoriques fondés sur des modèles fournis par Fine, De Launay et Bhatia. C'est avec le dernier modèle que l'on trouve la meilleure concordance.

ЧАСТОТНОЕ РАСПРЕДЕЛЕНИЕ ФОНОНОВ ВАНАДИЯ. Неупругое рассеяние ванадия измерялось методом времени пролета с использованием бериллиевого фильтра. Разрешающая способность прибора составляла около 20 мксек/м на границе поглощения в бериллии с длиной пролета 5,5 м. Помимо обычных поправок, в измерения были внесены также поправки на разрешающую способность и спектр падающих частиц.

Спектр колебательных частот, полученный из данных по рассеянию, находится в качественном согласии с более ранними измерениями. Однако этот спектр простирается до более высоких частот, чем предполагалось ранее. Результаты сравнивались с теоретическими спектрами, основанными на моделях, предложенных Файном, Де Лоная и Батия. Наилучшее согласие получено с последней моделью.

DISTRIBUCIÓN DE LA FRECUENCIA FONÓNICA EN EL VANADIO. Se midió la dispersión inelástica del vanadio por el método del tiempo de vuelo con filtro de berilio. El poder de resolución del instrumento es de alrededor de 20 $\mu\text{s/m}$ en el obturador de berilio, con una trayectoria de vuelo de 5,5 m. En las mediciones se introdujeron las correcciones usuales y, además, las necesarias para tener en cuenta el poder de resolución y el espectro incidente.

El espectro de frecuencias de vibración obtenido a partir de los datos de dispersión concuerda cualitativamente con los resultados de mediciones anteriores. Sin embargo, el espectro abarca frecuencias más elevadas de lo que se había supuesto anteriormente. Se efectuó una comparación con los espectros teóricos basados en modelos propuestos por Fine, De Launay y Bhatia. El último modelo es el que presentó la concordancia más satisfactoria.

I. INTRODUCTION

The measurement of the phonon frequency distribution function of vanadium has been the subject of several groups working with cold neutron fa-

cilities, such as EISENHAUER, PELAH, HUGHES and PALEVSKY [1], STEWART and BROCKHOUSE [2], and recently TURBERFIELD and EGELSTAFF [3]. Vanadium was chosen for the experiments since the scattering data obtained can be interpreted without difficulty as the scattering is almost entirely incoherent. These experiments showed a double peak in the frequency distribution in good agreement to what is expected from general lattice dynamics. Since not only the dispersion curves depend on the force model applied, but also the frequency distribution shows a considerable dependence on the model chosen, it is of great interest to know accurately the shape, size and position of the peaks in the measured frequency distribution to get conclusive results for the theory of metallic body-centred cubic crystals. The theory itself is in a rather complex stage and the large discrepancy in the Debye temperature derived from caloric and elastic constant measurements (caloric data: 338°K, elastic constants: 399°K) requires precise measurements of the phonon frequency distribution.

The scattering data of the experiments mentioned show a discrepancy at higher frequencies as well as a difference in shape and the position of the two peaks in the frequency distribution. With somewhat improved techniques and thinner samples we could reduce the correction factors in the experiment in scattering data with results that are more suitable for the comparison with theory. Since the elastic constants of vanadium have been measured by ALERS [4], we could also calculate the phonon frequency distribution on the basis of a simple non-central force model according to the general theories developed for metallic body-centred cubic crystals by FINE [5], DE LAUNAY [6] and BHATIA [7]. The calculated frequency distribution shows a considerable variation of the position of the two peaks. A good agreement with the experimental data is surprisingly given also by Fine's model, where the conduction electrons of the metal are treated free and a separation of the ionic lattice and the conduction electrons is made.

II. APPARATUS

For experiments using cold neutrons for inelastic scattering on crystals or liquids it is extremely important to keep the fast and thermal neutron contamination as small as possible. To meet this requirement, we used the 8-in tangential beam hole of the CP-5 research reactor at Ispra. The cold neutron facility is shown schematically in Fig. 1. Neutrons from the graphite scatterer are collimated by lead, concrete and borated paraffin shielding to form an incident beam with a full angular spread of 3° at the sample position. Without the beryllium filter in place a cadmium ratio of 180 was measured with $1/v$ BF₃ counter. A curved slit chopper is placed before the position of the samples and pulses at a rotational speed of 10 000 rpm, the cold neutrons on an area of $6 \times 10 \text{ cm}^2$. The velocity of the scattered neutrons is then measured by time-of-flight in a drift tube of 3 or 5.4 m in length.

Different angles of observation can be chosen by changing the direction of the flight path. A second flight path of 3 m in length is now being installed.

The detector system consists of a bank of 2×6 BF₃ counters or a bank of photomultipliers, fitted with 3-in Li^6J scintillators of 2-mm thickness.

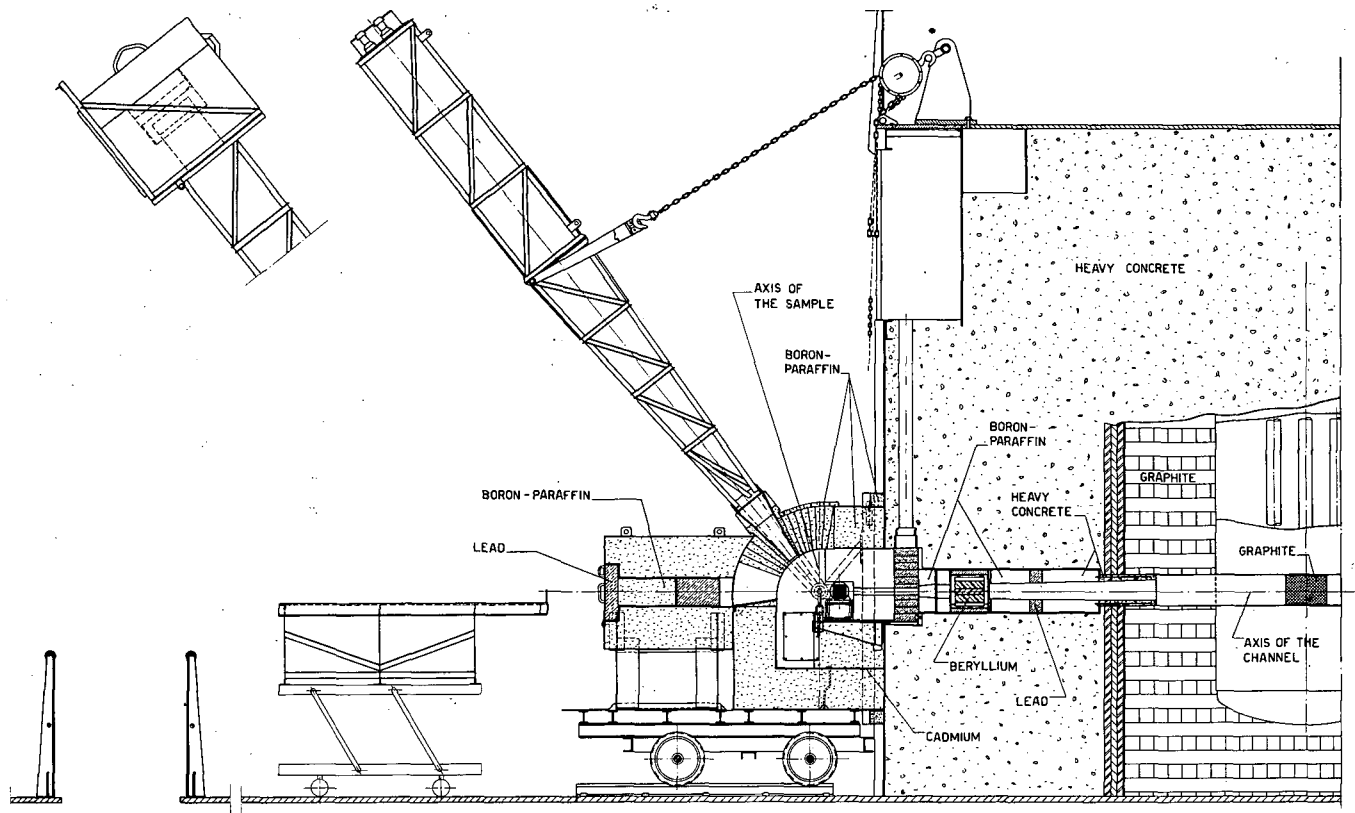


Fig 1

The cold neutron facility at Ispra.

A 200 channel time-of-flight analyser is used to take the data. To increase the detection efficiency two layers of 6 BF_3 counters were used. The flight time uncertainty due to the use of two layers of BF_3 counters (5-cm thick) is reduced by an automatic time-of-flight corrector that delays the pulses from the first layer corresponding to their velocity determined by the flight time from sample to counterbank. The total resolution of the facility including effects from geometry, burst time, detection time, sample size and channel width, is about $10\mu\text{s}/\text{m}$, leading to a resolution of 1% for beryllium cut-off neutrons. The main part contributing to the resolution is caused by the 3° collimation. However, that can be improved, if it is necessary, only at the cost of intensity.

An experiment was made to study the velocity distribution of the beryllium-filtered neutrons by placing a BF_3 counter in the direct beam, 1.7 m away from the chopper. Fig. 2 shows the result of this measurement. A

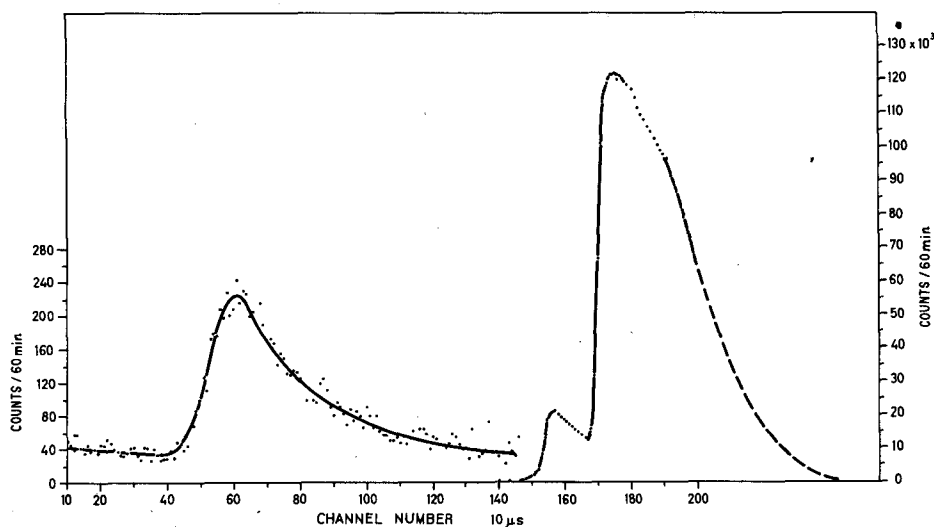


Fig. 2

The time-of-flight spectrum of the filtered beryllium neutrons measured with a counter placed in the direct beam 1.7 m away from the chopper.

pronounced thermal peak can be seen. But the ratio of the peak height at the beryllium cut-off to the thermal peak is as high as 530. The ratio of cold neutrons to thermal neutrons in this experiment was as high as 3 000. These figures give a very satisfying condition for all inelastic scattering experiments.

III. EXPERIMENTAL RESULTS AND CORRECTIONS

In Fig. 3, the time-of-flight spectrum of the inelastically scattered neutrons is given. For this measurement a vanadium sample of 3.25-mm thick-

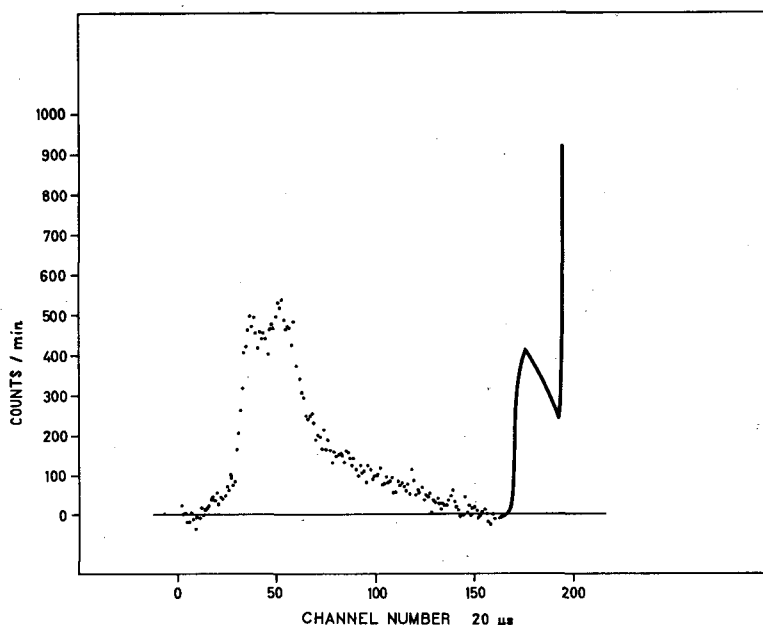


Fig. 3

The time-of-flight spectrum of inelastically-scattered neutrons after subtraction of background and frame overlap (about 20% of the double peak intensity).

ness was used. The vanadium plate was placed under 45° and the scattered neutrons were observed at an angle of 85° respectively to the neutrons impinging on the sample. The transmission through the sample was 50%, and about 12% of the neutrons were scattered. The double peak structure is clearly resolved and some extra intensity is observed at the high energy side of the spectrum. The points to the right of channel 180 display the double peak due to neutrons elastically scattered, hence of energy equal to that of the incident beam.

Because of the low counting rate it was necessary to run the facility for 4 d to obtain sufficient statistical accuracy to establish the detailed structure of the inelastic scattered neutron spectrum. An important source of background neutrons is the air in the region of the incident beam that can be seen by the detector. To eliminate this source of background the sample was placed in a vacuum chamber.

The neutron spectrum from vanadium obtained, as is shown in Fig. 3, cannot be used directly to derive the frequency distribution. A number of corrections must be applied to the data that count for the loss of neutrons in the sample; the flight path and the sensitivity of the detector bank. Since the chopper is placed in front of the sample, the chopper function does not enter the correction term. With this arrangement a major source of errors is already eliminated from our data. The final correction term is given in

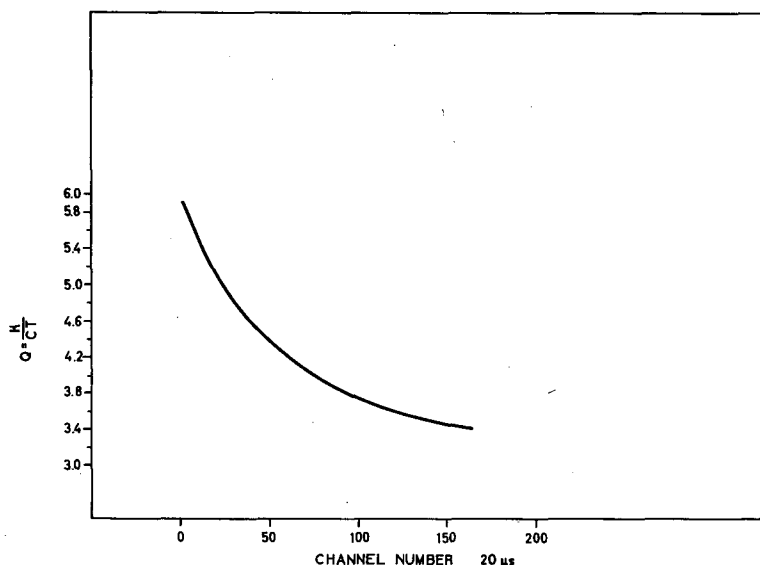


Fig. 4

Final correction factor that counts for sample thickness,
counter efficiency and air scattering in the flight path.

Fig. 4. The correction due to the sample thickness has been taken into account by the factor:

$$S(E) = \frac{\sqrt{2} N [\sigma_t(\bar{E}_0) + \sigma_a(E)] d}{1 - \exp [\sqrt{2} N (\sigma_t + \sigma_a) d]}$$

where $\bar{E}_0 = 3.8 \text{ meV}$ is the average neutron energy of the filtered beam, E the energy of the scattered neutrons, and $d = 3.25 \text{ mm}$ is the sample thickness.

The counter efficiency was calculated from the stated pressure, enrichment and size of the counter taking the geometrical effects from the two layers into account. The efficiency of the counter bank is now being checked by a transmission experiment with a straight slit chopper, so that this part of the correction can also be experimentally determined. The spectrum of inelastically-scattered neutrons obtained after application of the final correction term from Fig. 4, is given in Fig. 5.

The dashed line in Fig. 5 shows the contribution of two-phonon interactions. The effect is of about 2% of the one-phonon interaction. The spectral shape of these effects is calculated by approximating the lattice vibration spectrum with a Debye curve. The inelastic neutron spectrum in Debye approximation is given in Fig. 6. Before making the calculations for the frequency distribution, the two-phonon contribution has to be subtracted. Since the sample is very thin (3.25 mm), the multiple scattering correction was not carried out, however, it should not be higher than 1%. At the pres-

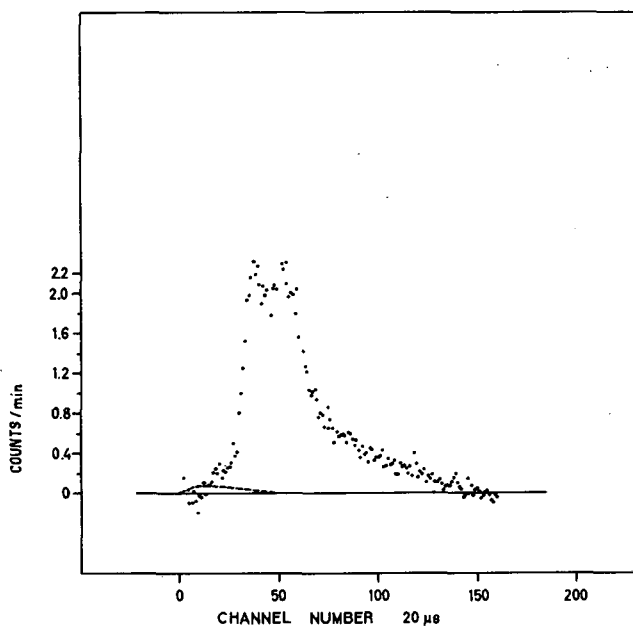


Fig. 5

The neutron spectrum after applying the correction ten.
The dashed line represents the two phonon contribution.

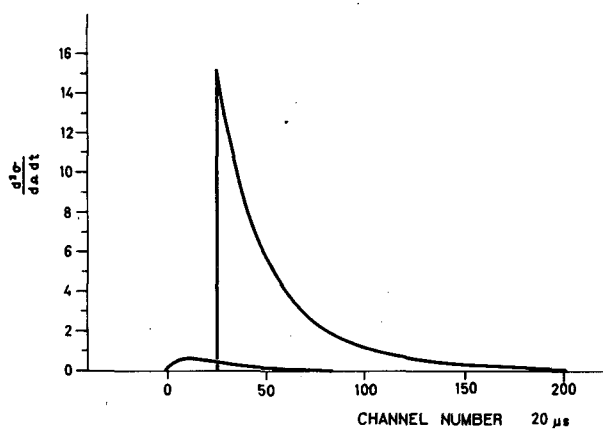


Fig. 6

Inelastic neutron spectra for one and two phonon processes
as expected from Debye's approximation ($\theta = 388^\circ\text{K}$).

ent time, a Monte-Carlo calculation is carried out to count for resolution effects on the spectrum of inelastically-scattered neutrons. In this calculation also the effects of multiple-scattered neutrons will be taken into account.

IV. FREQUENCY DISTRIBUTION

The differential incoherent scattering cross-section for one-phonon energy gain process is given by:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\sigma_{\text{incoh.}}^{\text{bound}}}{4\pi} \frac{K}{K_0} \exp(-2W) \frac{\hbar Q^2}{2M} \frac{f(\omega - \omega_0)}{2(\omega - \omega_0)} \left[\coth \frac{\hbar(\omega - \omega_0)}{2K_B T} - 1 \right]. \quad (1)$$

Here $\sigma_{\text{incoh.}}^{\text{bound}}$ is the incoherent scattering cross-section for bound nuclei, e^{-2W} is the Debye-Waller factor, k_0 the wave vector of the incident neutrons, k the wave vector of the scattered neutrons, $Q = k_0 - k$, and M the mass of the scattering nucleus.

Since the incident cold neutrons are not mono-energetic, the frequency distribution $f(\omega_{\text{ph}}) = f(\omega - \omega_0)$ can not be derived in a straight forward manner from [1]. Following the analysis of EISENHAEUER, PELAH, HUGHES and PALEVSKY, we write for the approximate frequency distribution:

$$f_1(\omega) = f_1(\omega - \tilde{\omega}_0) \sim \frac{d^2 N}{d\Omega dt} / F(E, \tilde{E}_0) \quad (2)$$

$$\text{with } F(E, E_0) = \frac{E^2}{\sqrt{E_0}} \frac{E + E_0}{E - E_0} e^{-2w} \left(\coth \frac{E - E_0}{2K_B T} - 1 \right)$$

and with the approximation for a monochromatic incident beam of an effective energy E_0 that is defined by:

$$F(E, \tilde{E}_0) = \frac{\int F(E, E_0) \cdot \varphi(E_0) \cdot dE_0}{\int \varphi(E_0) dE_0}$$

With this correction for the energy spread by the incident beam, the phonon frequency distribution can be computed. In Fig. 7 the phonon frequency distribution is given.

As one can see, there is a high energy wing in the distribution that can not wholly be attributed to the multiple processes. In order to check whether the impurities in the sample affect the result, a spectroscopical analysis was carried out. The result of this analysis is given in Table I. These figures show that iron and oxygen are predominantly the impurities in the sample. Since the analysis of the sample shows such a low content of light elements like hydrogen, nitrogen and oxygen, no attempt was made to correct the neutron spectrum. Because of insufficient statistics in the neutron spectrum, it cannot be clearly deduced if the high energy wing is a real part of the frequency distribution.

In that energy range the counter efficiency enters considerably in the correction term. Conclusive results for this energy region can only be obtained by using black detectors that make the counter efficiency-correction negligible. With the L_i^6 J scintillators which are now being installed, we

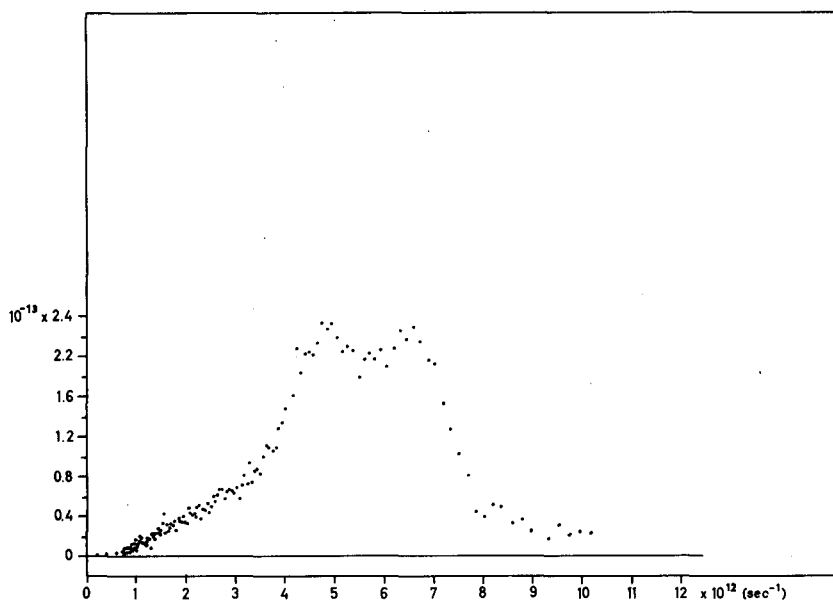


Fig. 7

The phonon frequency distribution in vanadium.

TABLE I

SPARK-SPECTROSCOPICAL ANALYSIS OF IMPURITIES OF
SAMPLE USED FOR NEUTRON MEASUREMENTS

Elements	O	N	H	Fe	Na, Cu, Zn, Hg, Ca, Pd, Mn, Mg, Al, Si, Cd
Contents in ppm	728 $\pm$ 1%	308 $\pm$ 1%	8.1 $\pm$ 1%	several 100	some ppm

hope to get conclusive measurements on this part of the frequency distribution.

Since the elastic constants have been measured by ALERS [4], a comparison with theory could be made.

In Fig. 8 the computed phonon frequency distribution is given for a simple non-central force model and for the models assumed by FINE [5], De LAUNAY [6] and BHATIA [7]. The measured distribution is shown as a solid line in the histograms. A good fit is obtained for Fine's model, where the conduction electrons of the metal are treated free and a separation of the ionic lattice and the conduction electrons is made.

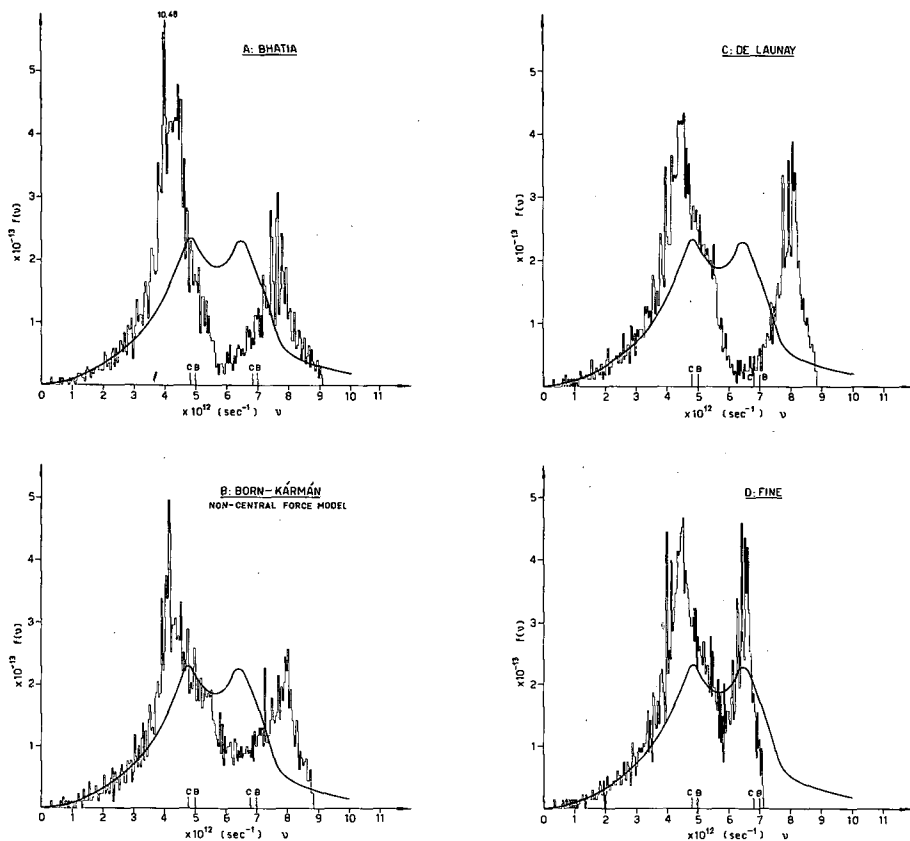


Fig.8

The computed and measured phonon frequency distribution of vanadium.
The measured distribution is shown as a solid line.

ACKNOWLEDGEMENT

It is a great pleasure to thank Dr. Peretti for many helpful discussions in connection with the calculations of the frequency distribution for the models applied to vanadium.

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OBSERVATION OF A LOW ENERGY PEAK IN THE PHONON FREQUENCY DISTRIBUTION OF VANADIUM

L. PELAH*, R. HAAS, W. KLEY, K. H. KREBS, J. PERETTI AND R. RUBIN
DEPARTMENT OF REACTOR PHYSICS,
EURATOM, ISPRA (VARESE),
ITALY

Abstract — Résumé — Аннотация — Resumen

OBSERVATION OF A LOW ENERGY PEAK IN THE PHONON FREQUENCY DISTRIBUTION OF VANADIUM

A low energy peak was observed in the frequency distribution of vanadium at a phonon energy of (8 ± 1) meV. This peak can be explained with regard to its energy value and magnitude as a "Kohn Effect".

OBSERVATION D'UN PIC DE BASSE ÉNERGIE DANS LA DISTRIBUTION DE FRÉQUENCES DES PHONONS DANS LE VANADIUM. On a observé un pic de basse énergie dans la distribution de fréquences des phonons dans le vanadium pour une énergie de (8 ± 1) meV. On peut expliquer la valeur de l'énergie et la grandeur de ce pic en considérant qu'il s'agit d'un «Effet de Kohn».

НАБЛЮДЕНИЕ ПИКА НИЗКОЙ ЭНЕРГИИ В РАСПРЕДЕЛЕНИИ ЧАСТОТ ФОНОНОВ ВАНАДИЯ. Пик низкой энергии наблюдался в распределении частот в ванадии при энергии фононов (8 ± 1) мэв. Происхождение пика и величина его энергии могут быть объяснены "эффектом Кона".

OBSERVACIÓN DE UN PICO DE BAJA ENERGÍA EN LA DISTRIBUCIÓN DE FRECUENCIAS DE LOS FONONES EN EL VANADIO. En la distribución de frecuencias en el vanadio, en correspondencia con una energía de (8 ± 1) meV de los fonones, se observó un pico de baja energía. La presencia de este pico puede explicarse, por lo que respecta a su valor energético y a su magnitud, como un "Efecto Kohn".

The Debye temperature of vanadium derived from caloric [1] and elastic constant measurements [2] show a large difference well outside the experimental errors (caloric data: 338°K, elastic constants: 399°K). A deviation of the frequency distribution from the ω^2 dependence at low frequencies could explain such a difference. The heat conductivity of vanadium also shows a quite different behaviour at low temperatures than normal metals. Measurements of the frequency distribution at low phonon energies may clarify these points.

The measurement of the frequency distribution in the low energy range is a difficult experiment because of the small inelastic cross-section. By using time-of-flight chopper techniques, we tried to optimize the intensity, background and resolution factors involved. A slow chopper, running at 9000 rpm, was placed between a beryllium filter and a vanadium sample, 3.25-mm thick. The chopped incident beam had an energy of (4.5 ± 0.5) meV. Two BF₃-counters (40-cm length, 5-cm thick, 1 atm) were used at the end of a well shielded flight path of 1.54 m in length. For this arrangement, the time-of-flight and incident energy resolution both contribute 8% to the energy resolution at 13 meV.

In Fig. 1, the measured time-of-flight spectrum at a 90° scattering angle is shown. A small peak is observed at a scattered neutron energy of

* On leave from the Israel Atomic Energy Commission.

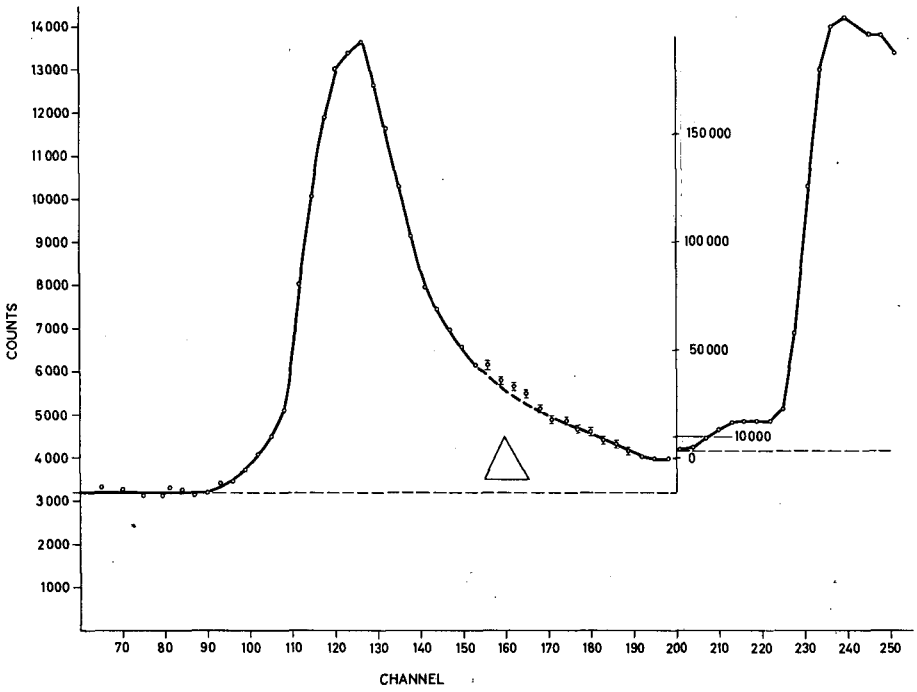


Fig. 1

Inelastic time-of-flight spectrum of vanadium.

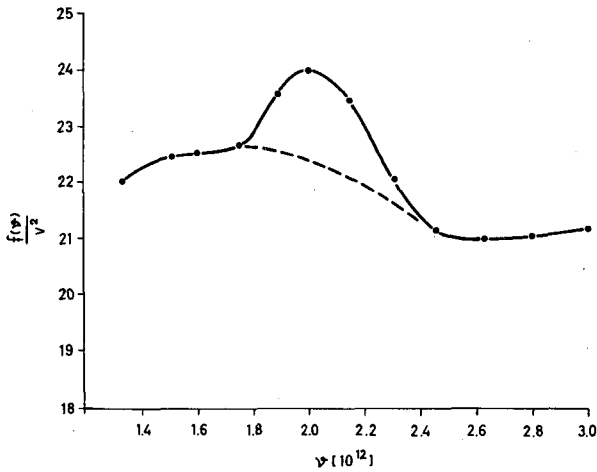


Fig. 2

Low energy part of the frequency spectrum of vanadium.

13 meV. The height of the peak is about 8% of the smooth curve and extends over four channels, $24 \mu\text{s}$ in width, which is about the experimental resolution. The counting statistics in each channel are better than 2.5%.

In Fig. 2, the low energy peak of vanadium is shown. The phonon energy at this peak is found to be (8 ± 1) meV. In the Brookhaven data on vanadium [3] one can barely see a small peak at about the same energy position.

The Debye approximation should be rather good for vanadium in the low energy region since vanadium is a body-centred cubic crystal with one atom per unit cell. As our observed peak falls in this energy region, one could hardly explain it by a simple Born-von Kármán model. Also the intensity of the observed peak is small, of the order of percents. If one assumes the existence of the KOHN effect [4], this peak can be explained as regards its energy value and magnitude [5]. It can be shown that in vanadium an additional peak [5] may occur at another energy value. This peak might influence the specific heat and thermal conductivity at low temperatures. However, this peak might not be observable by neutron scattering experiments.

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DISCUSSION

W. WOODS: For the following two reasons it is quite likely that vanadium is favourable for observation of the Kohn effect. Firstly, in order to fit $[00\zeta]$ L and $[00\zeta]$ T branches - which have very different initial slopes but the same zone-boundary frequency - it is necessary to include strong long-range interactions. This may be indicative of a strong Kohn effect (compare lead). Secondly, vanadium becomes superconducting at a fairly high temperature and hence may have a rather high electron phonon interaction.

However, the increase in intensity at $\nu \approx 2 \times 10^{12}$ c/sec is not surprising on the basis of the Born-von Kármán theory. Similar departures from the Debye spectrum at corresponding relative frequencies occur in sodium and in this case no Kohn effect has been observed. I would like to mention also that it is not surprising that the calculations based on models like that of Bhatia do not show agreement with experiment as this theory violates the symmetry of the body-centred cubic lattice.

W. KLEY: I quite agree that you have a point in the assumption that the increase of intensity at $\nu \approx 2 \times 10^{12}$ c/sec might possibly be explained by the Born-von Kármán theory. However, our calculated dispersion curves - which I do not have with me, show no indication in this direction. Since large single crystals of vanadium are now available, one should use X-ray

technique to measure the dispersion curves of vanadium. Such measurements could confirm our results.

Your remark concerning Bhatia's theory is right.

T. RISTE: I should like to tell you about some recent measurements by Shull of MIT who has been looking for magnetic effects in vanadium. He finds that there is Pauli paramagnetism at room temperature and nuclear polarization under such moderate conditions as 10° Kelvin and 13 000 Gauss. I think both these facts point to a strong influence of the electrons in vanadium.

G. SQUIRES: I would like to ask Dr. Kley whether he has calculated the frequency distribution function using different sets of force-constants in the Born-von Kármán theory. The reason I ask this is because I have found, in doing these calculations with aluminium, that quite small changes in the force-constants gave quite different frequency distribution functions, both as regards the position and the height of the peaks. I think it possible that similar small changes in the force-constants might give a better fit than you have here, although whether this will be significant or not is another question.

W. KLEY: No, we haven't done anything yet along these lines owing to lack of time. We shall continue the experiments on vanadium, especially at low temperatures. We will cool it down to liquid nitrogen to see if we can find the bump there.

ИССЛЕДОВАНИЕ ФОНОННОГО СПЕКТРА НИКЕЛЯ

Н.А. Черноплеков, М.Г. Землянов, А.Г. Чичерин, Б.Г. Лященко
Ордена Ленина Институт атомной энергии
им. И.В. Курчатова, Москва,
СССР

Abstract — Résumé — Аннотация — Resumen

INVESTIGATION OF THE PHONON SPECTRUM OF NICKEL. Using a neutron spectrometer and time-of-flight data, the authors have made a study of the inelastic scattering of cold neutrons in nickel. The sample used was an alloy of nickel isotopes and the amplitude of coherent neutron scattering was zero. From the spectrum of inelastically-scattered neutrons, the phonon spectrum of the face-centred cubic lattice of nickel was obtained and a comparison made with the phonon spectrum of the body-centred cubic lattice of vanadium.

ÉTUDE DU SPECTRE DE PHONONS DANS LE NICKEL. A l'aide d'un spectromètre à temps de vol, les auteurs ont étudié la diffusion inélastique des neutrons thermiques dans le nickel. Ils ont utilisé comme échantillon un alliage d'isotopes du nickel, la diffusion cohérente des neutrons ayant une amplitude nulle. En partant du spectre des neutrons diffusés inélastiquement, ils ont reconstitué le spectre de phonons du réseau cubique à faces centrées du nickel, en le comparant au spectre de phonons du réseau cubique centré du vanadium.

ИССЛЕДОВАНИЕ ФОНОННОГО СПЕКТРА НИКЕЛЯ. На нейтронном спектрометре по времени пролета проведено исследование неупругого рассеяния холодных нейтронов на никеле. В качестве образца использовался сплав изотопов никеля с нулевой амплитудой когерентного рассеяния нейтронов. Из спектра неупруго рассеянных нейтронов восстановлен фоновый спектр гранецентрированной кубической решетки никеля и проведено сравнение с фоновым спектром объемноцентрированной кубической решетки ванадия.

ESTUDIO SOBRE EL ESPECTRO DE FONONES DEL NÍQUEL. Con un espectrómetro de tiempo de vuelo, los autores de la presente memoria investigaron la dispersión inelástica de los neutrones fríos en el níquel. Como muestra utilizaron una aleación de isótopos del níquel, cuya dispersión coherente de neutrones era de amplitud nula. Basándose en el espectro de dispersión inelástica de los neutrones, reconstituyeron el espectro de fonones en el níquel de red cúbica centrada en las caras y lo compararon con el espectro de fonones de la red cúbica centrada en el cuerpo correspondiente al vanadio.

1. ВВЕДЕНИЕ

Как известно, исследование неупругого некогерентного рассеяния медленных и холодных нейтронов веществом позволяет проводить для него безмодельное восстановление функции распределения частот [1,2,3]. Такое же восстановление принципиально можно провести по результатам измерения когерентного неупругого рассеяния (дисперсионных кривых) для некоторой симметричной части зоны Бриллюэна кристалла, однако, подобный эксперимент является чрезвычайно трудоемким и не выполнен до настоящего времени ни для одного вещества. Поэтому единственным элементом, для которого по данным о неупругом рассеянии холодных нейтронов проведено восстановление фоновый спектр, является ванадий [4,5,6], имеющий в силу спиновой некогерентности, пренебрежимо малое сечение когерентного рассеяния.

Другую возможность исследования фононного спектра с помощью неупругого рассеяния нейтронов представляют сплавы изотопов ряда элементов (Li, Ni, Sn) с амплитудами рассеяния нейтронов противоположного знака. При определенной концентрации таких изотопов возможно обеспечить нулевую среднюю амплитуду когерентного рассеяния нейтронов и по спектру неупруго рассеянных нейтронов провести прямое восстановление спектра распределения частот. Ниже будут сообщены данные по измерению неупругого рассеяния нейтронов на сплаве изотопов Ni с нулевой средней амплитудой когерентного рассеяния и результаты восстановления фононного спектра из этих измерений.

2. ПРИГОТОВЛЕНИЕ ОБРАЗЦА И ПРОВЕДЕНИЕ ИЗМЕРЕНИЙ

Образец приготавливался сплавлением естественного никеля высокой чистоты с изотопом Ni^{62} , имеющим отрицательную амплитуду когерентного рассеяния нейтронов. Состав сплава определялся на основании данных по амплитудам когерентного рассеяния естественной смеси изотопов никеля и изотопа Ni^{62} ($\sim 46\%$ естественного никеля с амплитудой $a = 1,03 \cdot 10^{-12}$ см и $\sim 54\%$ Ni^{62} с $a = -0,87 \cdot 10^{-12}$ см). После изготовления образца была проведена его нейтронографическая проверка. Оказалось, что тип магнитной решетки и ее параметр, определенные по магнитной нейтронограмме, совпадает с данными для кристаллической решетки чистого никеля. Измерения интенсивности отражений (111) и (200) показали, что интенсивность рефлексов приблизительно на 1% выше величины фона. Причем, эти рефлексы практически полностью исчезают при наложении на образец магнитного поля в направлении вектора рассеяния нейтронов. Из учета погрешности измерений следует, что средняя амплитуда ядерного когерентного рассеяния для приготовленного образца никеля $a = \pm 0,08 \cdot 10^{-12}$ см.

Спектр неупруго рассеянных холодных нейтронов на образце никеля при комнатной температуре исследовался в интервале энергий рассеянных нейтронов от $1,4 \cdot 10^{-2}$ эв до $5 \cdot 10^{-2}$ эв. Измерения проводились на установке, описанной в [7]. Скорость вращения ротора прерывателя с шириной щели $S = 0,08$ см составляла ~ 5000 об/мин, а ширина каналов временного анализатора 64 мксек. Относительно большая величина ширины каналов временного анализатора была выбрана исходя из соображений увеличения интенсивности регистрации, так как исследуемый образец был весьма мал.

На рис.1 представлены результаты измерений спектра неупруго рассеянных нейтронов на сплаве изотопов никеля после введения поправок на функцию пропускания прерывателя, отклонение эффективности детектора от закона $1/V$ и на ослабление рассеянных нейтронов воздухом. Указанные данные были получены в течение ~ 300 -часового эксперимента.

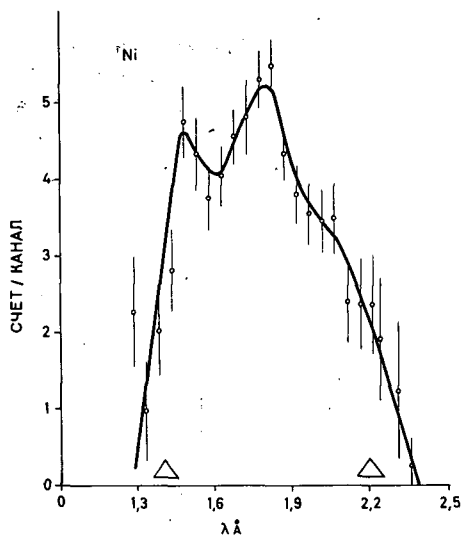


Рис.1

Спектр нейтронов, неупруго рассеянных
на образце никеля.

3. ОБРАБОТКА ЭКСПЕРИМЕНТАЛЬНЫХ РЕЗУЛЬТАТОВ

Так как никель обладает кубической гранецентрированной решеткой, то для него однофонное сечение неупругого некогерентного рассеяния нейтронов является линейной функцией фононного спектра [1]:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{S}{M} \frac{K}{8\pi K_0} \frac{\kappa^2}{\epsilon} \frac{g(\omega)}{e^{\epsilon/kT}-1} e^{-2W} \quad (1)$$

Здесь M - масса атома, S - сечение некогерентного рассеяния для связанного ядра, K_0 и K - импульс нейтрона до и после рассеяния, κ - передача импульса решетке, ϵ - изменение энергии нейтрона при рассеянии $\epsilon = \hbar\omega$. Поскольку статистическая точность измерений спектра неупруго рассеянных нейтронов из-за малых размеров образца невысока, первый этап восстановления функции $g(\omega)$ ров образца невысока, первый этап восстановления функции $g(\omega)$ проводился приближенно. Учет деформации падающего и рассеянных пучков нейтронов по толщине образца производился в предположении б-функционального вида первичной линии холодных нейтронов, фактор Дебая-Валлера учитывался в дебаевском приближении с $\theta = 400^\circ\text{K}$, вклад от многофонных и многократных процессов считался пренебрежимо малым. Кроме того, пренебрегалось также вкладом от неупругого магнитного рассеяния. Использованные предположения не

приводят к заметному ухудшению результатов. Малость вклада много-фононных и многократных процессов очевидна из работ по восстановлению фононного спектра ванадия [4,5,6], сечение же магннного рассеяния на никеле составляет всего $\sim 2\%$ от сечения фононного рассеяния. Функция распределения частот $g(\omega)$, полученная после первого этапа обработки, показана на рис.2. На этом же рисунке

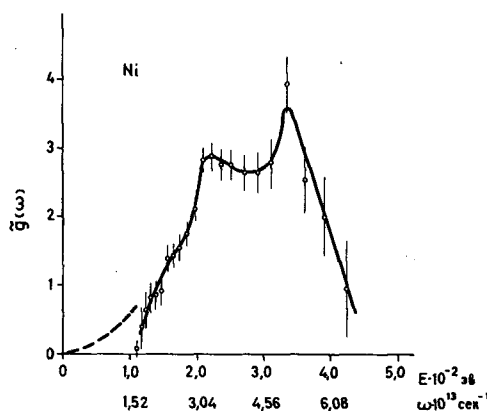


Рис.2

Фононный спектр никеля, восстановленный в предположении δ -функционального разрешения установки. Штриховой кривой проведена низкочастотная часть спектра в предположении дебаевской характеристической температуры $\theta = 400^\circ\text{K}$.

штриховой кривой изображена низкочастотная часть дебаевского спектра никеля.

На втором этапе обработки проводится учет полной функции разрешения экспериментальной установки и, так же, как в случае ванадия [6], фононный спектр восстанавливается в виде разложения:

$$g(\omega) = \sum_{\alpha=0}^7 g_{\alpha} f_{\alpha}(\omega), \quad (2)$$

с ошибкой:

$$\delta(\omega) = \left\{ \sum_{\alpha=0}^7 f_{\alpha}^2(\omega) \right\}^{\frac{1}{2}}. \quad (3)$$

Окончательный результат восстановления фононного спектра никеля $g(\omega)$ приведен на рис.3, а в табл.1 приведены коэффициенты разложения $g(\omega)$ согласно выражению (2).

Таблица 1

КОЭФФИЦИЕНТЫ РАЗЛОЖЕНИЯ

(Коэффициенты разложения функции $g(\omega)$ для $N=7$ $g(\omega) = \sum_{\alpha=0}^7 g_{\alpha} f_{\alpha}(\omega)$, где $f_{\alpha}(\omega) = \sum_{\beta=0}^{\alpha} f_{\alpha\beta} \cos \pi\beta \frac{\omega - \omega_0}{\Omega}$

на интервале ω от $\omega_0 = 1,53 \cdot 10^{13}$ сек $^{-1}$ до $\omega_1 = 6,84 \cdot 10^{13}$ сек $^{-1}$ $\Omega = \omega_1 - \omega_0$.

При частотах $\omega < \omega_0$ функция $g(\omega) \sim \omega^2$.

Коэффициенты разложения приведены для ненормированного на единицу спектра.)

α	g_{α}	$f_{\alpha\beta}$							
		$\beta = 0$	1	2	3	4	5	6	7
0	24,5	0,0515							
1	-13,4	-0,0656	0,125						
2	- 7,92	0,0743	-0,118	0,121					
3	- 1,08	-0,0398	0,122	-0,111	0,127				
4	- 1,15	0,0457	-0,0619	0,126	-0,112	0,142			
5	+ 1,72	-0,0194	0,0943	-0,0561	0,142	-0,118	0,160		
6	- 1,52	0,0505	-0,0255	0,111	-0,0508	0,166	-0,131	0,191	
7	- 2,06	-0,00157	0,125	-0,00937	0,139	-0,0490	0,208	-0,144	0,229

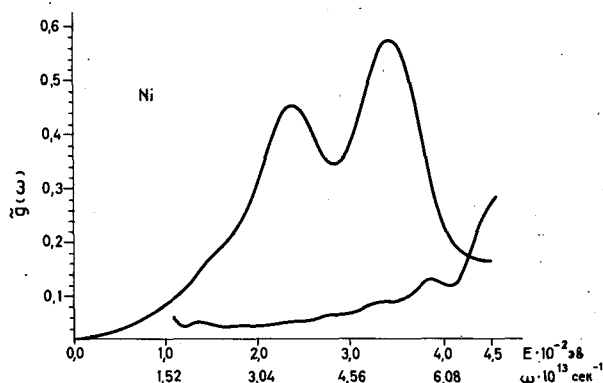


Рис.3

Окончательный результат восстановления фононного спектра никеля.

Кривая под фононным спектром представляет ошибку восстановления.

4. ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ

К настоящему времени опубликовано значительное количество работ, посвященных теоретическому расчету спектра гранецентрированной кубической решетки [8 - 12] и одна экспериментальная работа [13], в которой на основании анализа диффузного рассеяния рентгеновских лучей проведено восстановление фононного спектра алюминия. При этом для расчета использовалась модель с девятью силовыми постоянными, три из которых определялись по данным об упругих постоянных, а шесть остальных из измерений дисперсионных кривых в некоторых симметричных направлениях в кристалле. К сожалению, восстановление фононного спектра по рентгеновским измерениям требует весьма сложной процедуры выделения интенсивности диффузного рассеяния вблизи максимумов упругого рассеяния рентгеновских лучей и поэтому связано со значительной ошибкой. Кроме того, методика восстановления фононного спектра в этом случае не является безмодельной. Поэтому, полученные в настоящей работе данные по фононному спектру никеля являются практически первыми безмодельными данными по функции распределения частот гранецентрированной кубической решетки.

Из сравнения экспериментальной $g(\omega)$ для Ni с упоминавшимися расчетами для г.ц.к. решеток можно сделать следующее заключение. Наблюдается качественное соответствие экспериментального фононного спектра с расчетными. Максимум при более низких частотах ниже и шире максимума при высоких, однако, этим соответствие практически ограничивается. Детали фононного спектра: ординаты максимумов, их ширины и т.д. как и следовало ожидать, заметно отличаются от расчетных. Это в первую очередь объясняется тем,

что расчеты проводились для металлов типа Al, Ag и Au и учитывались, главным образом, центральные взаимодействия, в то время как никель является переходным металлом и в нем существенную роль играют нецентральные взаимодействия.

Определенный интерес представляет сравнение фононных спектров двух переходных металлов: ванадия и никеля, обладающих соответственно о.ц.к. и г.ц.к. решетками. Такое сравнение проведено на рис.4, на котором представлены фононные спектры указанных

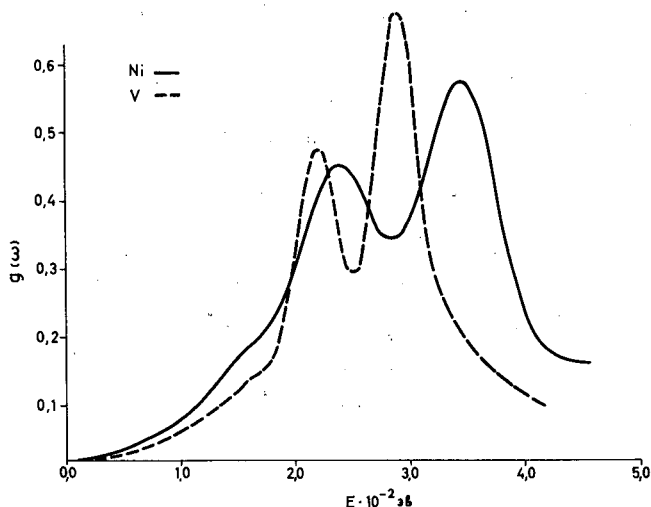


Рис.4

Сравнение фононных спектров ванадия и никеля.
Кривые относительно друг друга не нормированы.

элементов. Как следует из этого сравнения максимумы фононного спектра ванадия заметно острее максимумов спектра никеля, расположены при более низкой энергии и ближе друг к другу (22 и 29 мб для ванадия и 24 и 35 мб для никеля). Качественно указанное обстоятельство (более высокие частоты максимумов и границы фононного спектра никеля) представляется возможным объяснить тем, что в силу различия электронных конфигураций атомов и различия строения кристаллических решеток, соответствующие силовые постоянные взаимодействия между атомами в случае никеля заметно превосходят силовые постоянные для ванадия. Более подробно указанное обстоятельство может быть проанализировано после восстановления из данных по упругим постоянным никеля и спектру частот дисперсионных соотношений для фононов.

В заключение авторы выражают благодарность М.И.Певзнеру за интерес к работе и участие в обсуждении, Е.З. Винтайкину и Л.И. Новаку за помощь в изготовлении образца, М.А. Комарову,

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DISCUSSION

B.N. BROCKHOUSE: Now that you have this useful and expensive specimen, I hope that you will do some magnetic scattering experiments with it. Two come readily to mind. One is to study the paramagnetic scattering in the polycrystalline specimen perhaps as it actually exists, where because of the very flat nuclear scattering you could separate out a small magnetic component. And for the other experiment, if you made a single crystal of this material you could study spin waves very nicely in it. Both of these experiments are exceedingly difficult to do with normal nickel.

N.A. TCHERNOPLEKOV: Of course, to make such an expensive toy and then not to use it for neutron research on magnetic properties would be, if I may use the expression, blaspheming against science.

MEASUREMENTS OF THE VIBRATIONAL FREQUENCY SPECTRUM OF NICKEL-PALLADIUM ALLOYS*

B. MOZER AND K. OTNES
BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK
UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

MEASUREMENTS OF THE VIBRATIONAL FREQUENCY SPECTRUM OF NICKEL-PALLADIUM ALLOYS. Considerable theoretical effort has been expended to predict the vibrational frequency spectrum and distribution of random binary alloys. We have selected nickel-palladium alloys which form continuous random solid solutions to study experimentally the vibrational frequency spectrum using inelastic neutron scattering. Cold neutron inelastic scattering experiments on 0, 5, 10, 20 and 100% polycrystalline nickel-palladium alloys at room temperature were performed at the Brookhaven cold neutron facility. The inelastic neutron scattering cross-section was measured at several scattering angles. Results for the low nickel concentration alloys indicate that one of the peaks in the inelastic neutron scattering data corresponds to a simple defect mode of vibration confirming theoretical predictions.

MESURES DU SPECTRE DE FREQUENCE DES VIBRATIONS DANS LES ALLIAGES DE NICKEL-PALLADIUM. Des efforts considérables ont été consacrés à la prévision théorique du spectre et de la distribution de fréquence des vibrations dans les alliages binaires aléatoires. Les auteurs ont choisi des alliages de nickel-palladium formant des solutions solides aléatoires continues pour procéder à l'étude expérimentale du spectre de fréquence des vibrations à l'aide de la diffusion inélastique des neutrons. Ils ont procédé, à l'installation pour neutrons froids de Brookhaven, à des expériences de diffusion inélastique de neutrons froids dans des alliages polycristallins de nickel-palladium ayant des compositions de 0, 5, 10, 20 et 100%, à la température ambiante. La section efficace de diffusion inélastique a été mesurée pour plusieurs angles de diffusion. Pour les alliages à faible teneur en nickel, les résultats montrent que l'un des pics de la diffusion inélastique des neutrons correspond à un mode de vibration d'un défaut simple ce qui confirme les prévisions théoriques.

ИЗМЕРЕНИЯ СПЕКТРА КОЛЕБАТЕЛЬНЫХ ЧАСТОТ СПЛАВОВ НИКЕЛЯ С ПАЛЛАДИЕМ. Предприняты теоретические попытки определить характер спектра колебаний частот и их распределение для произвольных двойных сплавов. Были выбраны никеле-палладиевые сплавы, образующие сплошной случайный ряд твердых растворов, чтобы изучить экспериментально спектр частот колебаний методом неупругого рассеяния нейтронов. В Брукхейвене на канале для холодных нейтронов были проведены опыты по неупругому рассеянию на 0-, 5-, 10-, 20- и 100-процентных поликристаллических сплавах никеля с палладием. Поперечное сечение неупругого рассеяния нейтронов было измерено при нескольких углах рассеяния. Результаты, полученные в опытах со сплавами с низким содержанием никеля, показывают, что один из максимумов в данных по неупругому рассеянию нейтронов соответствует колебаниям за счет простых дефектов, что подтверждает теоретические предположения.

MEDICIONES DEL ESPECTRO DE FRECUENCIA DE VIBRACIÓN DE LAS ALEACIONES DE NÍQUEL-PALADIO. Se han realizado considerables trabajos teóricos para predecir el espectro de frecuencias de vibración y la distribución de las aleaciones binarias aleatorias. Los autores han escogido aleaciones de níquel-paladio, que forman soluciones sólidas aleatorias continuas, para estudiar experimentalmente el espectro de frecuencias de vibración por dispersión inelástica de neutrones. Han realizado a temperatura ambiente experimentos de dispersión inelástica de neutrones fríos en aleaciones policristalinas de níquel-paladio al 0, 5, 10, 20 y 100%, utilizando la instalación de neutrones fríos de Brookhaven. Han medido las secciones eficaces de dispersión inelástica de neutrones en diferentes ángulos. Los resultados obtenidos con las aleaciones de bajo contenido de níquel muestran que en los datos relativos a la dispersión inelástica, uno de los picos corresponde a un modo deficitario simple de vibración, lo que confirma las previsiones teóricas.

* Work performed under the auspices of the United States Atomic Energy Commission.

A knowledge of the vibrational frequency distribution of random binary alloys would be of great value for solving many thermodynamic and transport problems in alloys, e. g. the influence on long and short range order or thermal conductivity. Considerable theoretical effort has been devoted to obtaining the vibrational spectra of random alloys with special emphasis on the easiest mathematically tractable problem of the disordered diatomic linear chain [1]. Nearest and next-nearest neighbour forces are usually only considered in obtaining a frequency distribution. The pertinent results of such calculations can be summarized as follows: (a) For low concentrations of light mass solute atoms in a heavy mass solvent, one expects to see the appearance of a strong impurity band at a higher frequency than the maximum frequency of a perfect chain with only heavy mass atoms. This band is distributed about the frequency of a defect mode of vibration associated with a single light mass substitutional impurity in the heavy mass chain. At these small concentrations other impurity bands are expected but with much smaller strength than the above mentioned band. (b) As the concentration of the light mass is increased, bands other than that associated with the defect mode of vibration become more important, new bands appear, and finally for high concentrations of the solute the bands overlap and merge into a continuum with characteristics of the frequency distribution of a chain of light atoms. The frequency spectrum for disordered three-dimensional lattices would be expected to exhibit impurity bands at least for low concentration of light mass solute atoms. A frequency distribution of a disordered three-dimensional simple cubic lattice has been calculated [2]. The results of this calculation for a 50% concentration of the solute atoms show considerable smearing of the impurity bands but the accuracy of the method of obtaining the spectrum may be open to question. Theoretical information on the frequency spectrum of disordered three-dimensional lattices other than simple cubic structures is lacking and difficult to obtain. Thus, the question of the existence of well defined impurity bands remains only a reasonable conjecture. Furthermore there has been no experimental data to compare with existing theory and provide further incentive for more extensive calculations. In the following we shall describe an experiment initiated to provide information on the frequency distribution of a simple random binary alloy.*

Inelastic neutron scattering experiments have been very successful in providing information on the vibrational spectra of solids [3]. One could also use these techniques to study the vibrational spectra of binary random alloys. We have selected the nickel-palladium system, whose alloys form a continuous series of face-centred cubic solid solutions to study the vibrational spectra of random alloys using the cold neutron facility at the BNL graphite reactor [4]. Measurements of the inelastic neutron cross-section were obtained at room temperature on polycrystalline samples of pure palladium, pure nickel, and three alloys containing 5, 10 and 20 atomic per cent nickel.** Fig. 1 shows the raw data (background subtracted) from one set

* Work by A. A. Maradudin and one of the authors on a calculation of the frequency spectrum of disordered alloys is in progress. Results to terms linear in the concentration will be presented and compared with experiment.

** Preliminary results in inelastic neutron experiments on the nickel-palladium system have been reported elsewhere [5].

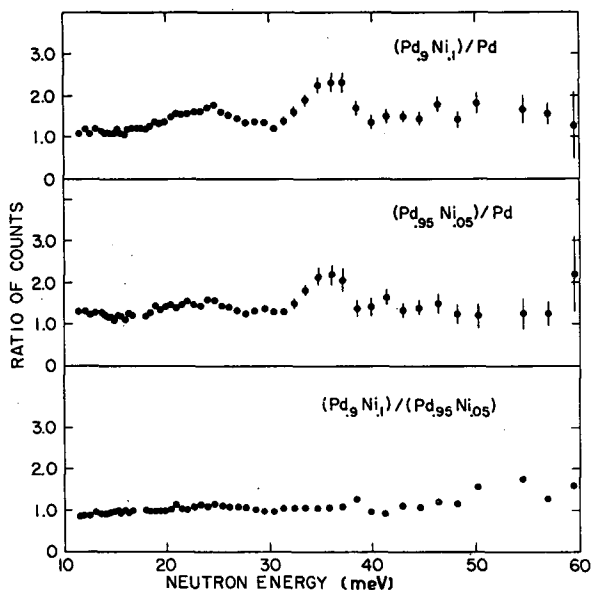


Fig. 1

The inelastic scattering data (background subtracted) at scattering angle of 90° of cold neutrons from nickel-palladium alloys. The energy of the lattice vibration can be obtained from the inelastic scattering data by subtracting 5 meV from the scattered neutron energy. The size of the dots in the figure represent the statistical error. Part of the elastic scattering peak is shown in the data at energies near 5 meV.

of measurements of the inelastic neutron scattering on four specimens. The statistical errors are represented by the size of the dots. The energy of a lattice vibration can be obtained from the data by subtracting 0.005 eV from the scattered neutron energy. One observes that the spectrum of the scattering cross-section of the alloys is more like that of palladium than nickel, the maxima in the scattering data of the alloys occur at the same neutron energies as the maxima in the data for pure palladium.

Frequency distributions for either the pure material or the alloys cannot easily be obtained from the data and as far as these authors are aware, there is no other measured vibrational spectrum of these alloys. If one assumes that the neutron scattering from the pure metals and alloys is incoherent, then frequency distributions can easily be obtained from the data. Such derived frequency distributions qualitatively agree with the few existing measured [6] or theoretical distributions [7] for face-centred cubic metals. Changes in the vibrational spectra of the alloys compared to the pure palladium spectra can be most easily obtained from the data in Fig. 1 by taking the ratio of the observed cross-section in the alloys to the observed cross-section in pure palladium at each energy (or equivalently at each channel corresponding to a given time-of-flight of the scattered neutron). The ratios of the counts per channel for various pairs of samples are shown in Fig. 2 as a function of the scattered neutron energy. One observes a well defined peak at 0.036 eV neutron energy corresponding to lattice vibrational

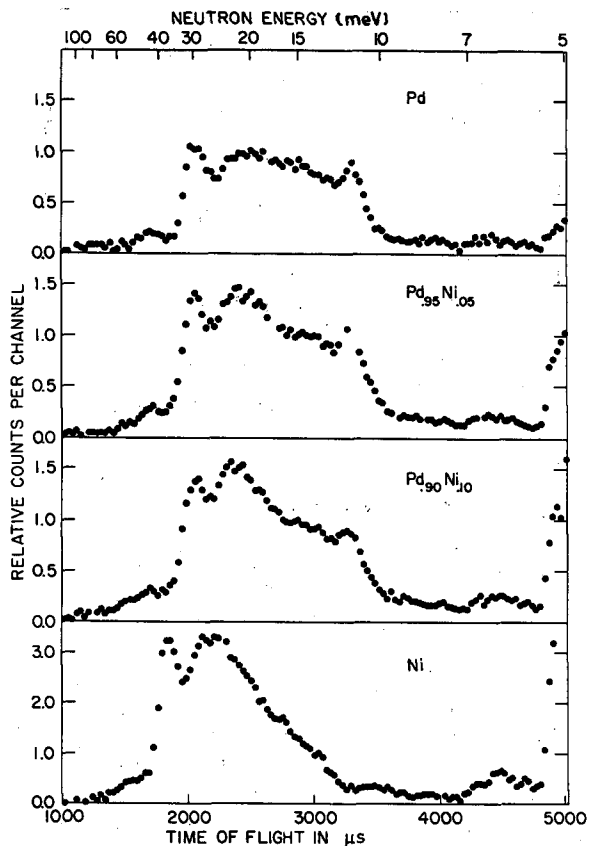


Fig. 2

The ratio of the counts per channel for various pairs of alloys and pure palladium at each neutron energy averaged for several sets of measurements. The energy of the lattice vibration at the exhibited peak is 31 meV. The statistical errors of the ratios for a given set of measurements are also indicated on the figures except for neutron energies less than 32 meV where the size of the dots represent the errors.

quanta of 0.031 eV. This peak was previously identified with a defect mode of vibration [5]. The peak at 0.036 eV neutron energy according to the theoretical results should consist of several defect bands but at present it is not possible to resolve these bands if they exist. A possible way of observing the growth of other bands is to observe the broadening of the defect band. The ratio of the data for the two alloys, the 10% to the 5% is exhibited in Fig. 2, but any broadening of the impurity band is somewhat obscured by instrumental resolution. Higher concentration alloys show a broadening of the impurity band but no well resolved set of impurity bands.

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DISCUSSION

K.E. LARSSON: In the elements you have used in your investigation there is a large percentage of coherent cross-section. One would imagine that the spectra you presented on nickel at several angles should be a mixture of the incoherent scattering picture and an integral over the coherent one-phonon peaks. Would not these coherence effects also affect the other results you have shown?

B. MOZER: Not to a significant extent.

N.A. TCHERNOPLEKOV: I should like to make an observation which to some extent answers Dr. Larsson's question. If we compare the results of the study of inelastic scattering on natural nickel carried out by Dr. Mozer and Dr. Otnes with the results we ourselves obtained on an alloy of nickel isotopes of zero coherent-scattering amplitude, we see that the critical points of the spectra coincide, and that there is also good agreement as regards the position of the peaks and their width. In the case of nickel that should not be regarded as unexpected, since it possesses a 70% incoherent cross-section. Of course, when we say that the critical points coincide, it must be borne in mind that we have the results of Dr. Mozer's and Dr. Otnes' work before us in the shape of a diagram only.

B.N. BROCKHOUSE: Can you verify in any way that it is a localized mode you observe, and not a flat band in Q-space?

B. MOZER: Well, that's what it is when there are a lot of impurities and you are really into an alloy system. We are going to try and look at this with a modification of the Mössbauer experiment and we will look at a 0.1% alloy. The only other evidence I could find now, apart from theoretical calculation, to prove that such things exist was the work by J.P. Schiffer on alkali halides, and subsequent measurements have confirmed that this is exactly what he sees. The concentration of the hydrogen ions in that system is 10^{17} so it is a well-defined localized mode and the mass ratios are so large that it just sits there and bounces back and forth.

On the other hand, there is no evidence at all that what we observed was in fact an optical band.

I. WALLER: I think it is very interesting that it has been possible, in this way, to see localized modes in metals. This method of Schiffer was limited to substances where strong dipole moments are connected with these vibrations.

ИССЛЕДОВАНИЕ НЕУПРУГОГО РАССЕЯНИЯ НЕЙТРОНОВ НА СПЛАВЕ Ti-Zr

Н.А. Черноплеков, М.Г. Землянов, Е.Г. Бровман, А.Г. Чичерин
Ордена Ленина Институт атомной энергии им. И.В. Курчатова
Академии наук СССР, Москва
СССР

Abstract — Résumé — Аннотация — Resumen

A STUDY OF THE INELASTIC SCATTERING OF NEUTRONS IN A Ti-Zr ALLOY. Using a time-of-flight neutron spectrometer, we made a study of the inelastic scattering of cold neutrons in a sample of a disordered Ti-Zr alloy with a composition corresponding to a zero average value of neutron coherent scattering amplitude. The particulars of the phonon spectrum of a two-component disordered system are discussed on the basis of the results obtained.

ÉTUDE DE LA DIFFUSION INÉLASTIQUE DES NEUTRONS DANS L'ALLIAGE Ti-Zr. Au moyen d'un spectromètre à temps de vol, les auteurs ont étudié la diffusion inélastique des neutrons froids dans un échantillon d'alliage désordonné Ti-Zr dont les éléments formaient un ensemble correspondant à la valeur zéro de l'amplitude moyenne de la diffusion cohérente des neutrons. Sur la base des résultats obtenus, ils examinent les particularités que présente le spectre de phonons d'un système désordonné à deux éléments.

ИССЛЕДОВАНИЕ НЕУПРУГОГО РАССЕЯНИЯ НЕЙТРОНОВ. На нейтронном спектрометре методом времени пролета проведено исследование неупругого рассеяния холодных нейтронов образцом неупорядоченного сплава Ti-Zr с составом компонент, отвечающим нулевому значению средней амплитуды когерентного рассеяния нейтронов. На основе полученных результатов обсуждаются особенности фононного спектра двухкомпонентной неупорядоченной системы.

ESTUDIO DE LA DISPERSIÓN INELÁSTICA DE LOS NEUTRONES EN LA ALEACIÓN Ti-Zr. Mediante la determinación del tiempo de vuelo, los autores investigaron con el espectrómetro neutrónico la dispersión inelástica de neutrones fríos en una probeta de aleación no ordenada Ti-Zr, cuyos componentes están en la proporción que corresponde al valor nulo de la amplitud media de la dispersión neutrónica coherente. Basándose en los resultados obtenidos, analizan las características del espectro fonónico en las aleaciones binarias de estructura desordenada.

1. ВВЕДЕНИЕ

Исследование спектров колебаний разупорядоченных систем представляет большой интерес как в теории сплавов, так и в решении ряда других физических проблем: динамика вещества в аморфном состоянии, электронные свойства жидкостей и сплавов, влияние дефектов на динамику и т.д.

До последнего времени задача определения спектров колебаний разупорядоченных систем решалась, главным образом, теоретически, причем основная масса работ была посвящена динамике одномерных разупорядоченных систем [1], [2] и только недавно опубликованы работы, рассматривающие трехмерные системы [3]. Экспериментальные возможности решения указанной проблемы появились в последние годы в связи с развитием методов исследования неупругого рассеяния веществом тепловых и холодных нейтронов. Первое исследование

спектра неупруго рассеянных нейтронов на неупорядоченной системе - сплаве Mn - Co с содержанием компонент, сплава 42% Mn и 58% Co, отвечающим нулевой средней амплитуде когерентного рассеяния, было выполнено Стюартом и Брокхаузом [4].

Настоящая работа посвящена измерению спектра неупруго рассеянных нейтронов для другой двухкомпонентной неупорядоченной системы сплава Ti-Zr и анализу особенностей динамики такой системы. Оказывается возможным для общего случая связать измеряемое в нейтронном эксперименте сечение однофононного некогерентного рассеяния с функцией распределения частот колебаний. Для поликристаллического образца в частном случае $\frac{\sigma_n}{M_n} = \text{const}$, где σ_n - сечение некогерентного рассеяния n -ой компоненты, а M_n - масса ее ядра, можно восстановить частотную функцию $g(\omega)$ без модельных предположений. Если это соотношение не выполняется, экспериментальное сечение дает качественное представление о спектре и его сингулярностях, а количественное восстановление спектра можно произвести лишь вводя дополнительные предположения о поведении векторов поляризации.

2. ОБЩАЯ ТЕОРИЯ

Неупорядоченные сплавы имеют геометрически правильную кристаллическую решетку со случайным распределением атомов различных типов по ее узлам. Это не позволяет произвести обычное фононное разложение смещений атомов, для чего, как известно, требуется периодическое повторение набора атомов (элементарной ячейки). Поэтому в случае рассеяния на таких структурах неприменимы обычные выражения, полученные для упорядоченных кристаллов.

Однако, оказывается возможным получить связь между дважды дифференциальным сечением и энергетическим спектром решетки, не делая предположений о геометрической структуре и периодичности по массам. Рассмотрим систему ядер, связанных квазиупругими силами и совершающих малые колебания около положения равновесия $\vec{r}_n$. Как известно, движение такой системы описывается набором частот ω , которые находятся из решения задачи на собственные значения динамической матрицы. Смещения атомов даются разложением по нормальным координатам:

$$\vec{U}_n(t) = \sum_{\omega} \frac{\vec{C}_n(\omega)}{\sqrt{M_n}} q_{\omega}(t), \quad (1)$$

$$q_{\omega}(t) = i(2\omega)^{-\frac{1}{2}} [a_{\omega} e^{-i\omega t} - a_{\omega}^{\dagger} e^{i\omega t}] .$$

Здесь M_n - масса n -го ядра; a_{ω} и $a_{\omega}^{\dagger}$ - операторы поглощения и рождения кванта частоты ω ; $\vec{C}_n(\omega)$ - вектора поляризации, являющиеся собственными векторами динамической матрицы и удовлетворяющие условию нормировки:

$$\sum_n |C_n|^2 = 1. \quad (2)$$

Использование разложения (1) вместо обычного фононного удобно в случае некогерентного рассеяния, т.к. при этом процессе не сохраняется квазиимпульс фонона, а следовательно не проявляются его кинетические свойства. Для сечения рассеяния на описанной выше системе, являющейся, по существу, макромолекулой, можно воспользоваться следующим выражением [5]:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{k}{2\pi k_0} \sum_{nn'} e^{i\vec{k}(\vec{r}_n - \vec{r}_{n'})} a_n a_{n'}^+ \int e^{i\epsilon t} \langle \chi_{nn'} \rangle_T dt$$

$$\langle \chi_{nn'} \rangle_T = \prod_{\omega} \exp \left\{ - \left[\frac{(\vec{k} \vec{C}_n(\omega))^2}{M_n} + \frac{(\vec{k} \vec{C}_{n'}(\omega))^2}{M_{n'}} \right] (4\omega)^{-1} \coth \frac{\omega}{2k_B T} \right\} \times (3)$$

$$\times \sum_{n=-\infty}^{\infty} e^{in\omega t} e^{-n\omega/2k_B T} I_n \left[\frac{(\vec{k} \vec{C}_n(\omega)) (\vec{k} \vec{C}_{n'}(\omega))}{2\sqrt{M_n M_{n'}} \omega \operatorname{sh} \omega / 2k_B T} \right].$$

Здесь k_0 , k , κ - начальный, конечный и переданный нейтронный импульс;

ϵ - изменение энергии нейтрона;

a_n - длина рассеяния на n -ом ядре, $\hbar = 1$. Разлагая функцию Бесселя от малого аргумента в ряд и ограничиваясь одно-квантовым процессом, получим:

$$\langle \chi_{nn'}^{(1)} \rangle_T = e^{-(w_n + w_{n'})} \frac{(\vec{k} \vec{C}_n(\omega)) (\vec{k} \vec{C}_{n'}(\omega))}{2\sqrt{M_n M_{n'}}} \frac{e^{i\omega t}}{e^{\omega/k_B T} - 1}, \quad (5)$$

где

$$w_n = \sum_{\omega} \frac{(\vec{k} \vec{C}_n(\omega))^2}{M_n} \left(\frac{2}{e^{\omega/k_B T} - 1} + 1 \right), \quad (6)$$

w_n - фактор Дебая-Валлера.

Проводя обычное усреднение по спиновому состоянию рассеивателя, выделим некогерентное одноквантовое рассеяние:

$$\frac{d^2\sigma^{(1)}_{\text{incoh}}}{d\Omega d\epsilon} = \frac{k}{8\pi k_0} \sum_n \frac{\sigma_n}{M_n} e^{-2w_n} \sum_{\omega} \frac{(\vec{k} \vec{C}_n(\omega))^2}{\omega} \frac{\delta(\omega - \epsilon)}{e^{\omega/k_B T} - 1}, \quad (7)$$

где

$$\sigma_n = 4\pi [\langle a_n^2 \rangle - \langle a_n \rangle^2].$$

Используя квазинепрерывный характер спектра частот, запишем

$$\sum_{\omega} \rightarrow \int q(\omega) d\omega. \text{ Тогда получим, произведя интегрирование:}$$

$$\frac{d^2 \sigma^{(1) \text{ incoh}}}{d\Omega d\epsilon} = \frac{k}{8\pi k_0} \cdot \frac{1}{\epsilon} \cdot \frac{g(\epsilon)}{e^{\epsilon/k_B T} - 1} \sum_n \frac{\sigma_n}{M_n} e^{-2w_n} (\vec{\kappa} \vec{C}_n(\epsilon))^2. \quad (8)$$

В случае поликристаллов возможно дальнейшее упрощение выражения (8). Фактор Дебая-Валлера с достаточной точностью можно считать не зависящим от ориентации монокристалла, вычисляя его в Дебаевском приближении, тогда в (8) от ориентации монокристалла будут зависеть лишь вектора поляризации, жестко связанные с главными осями. Усреднение по положению главных осей в этом приближении эквивалентно усреднению по ориентации векторов $C_n(\epsilon)$. Проведем такое усреднение, используя $\overline{C_1 C_2} = \frac{1}{3} |\vec{C}|^2 \delta_{12}$.

Тогда

$$\frac{d^2 \sigma^{(1) \text{ incoh}}}{d\Omega d\epsilon} = \frac{k}{8\pi k_0} \cdot \frac{\kappa^2}{\epsilon} \cdot \frac{q(t)}{e^{\epsilon/k_B T} - 1} \sum_n \frac{\sigma_n}{M_n} e^{-2w_n} |\vec{C}_n(\epsilon)|^2. \quad (9)$$

(1) incoh

Угловая зависимость $\frac{d^2 \sigma}{d\Omega d\epsilon} \sim \kappa^2$ оказывается верной для произвольных поликристаллов (независимо от симметрии и числа атомов в элементарной ячейке). Для случая одинаковых атомов, используя (9) и (2) получим обычный результат [6]. То же для атомов с одинаковым отношением $\frac{\sigma_n}{M_n}$.

Описанный подход особенно удобен для рассмотрения некогерентного рассеяния на неупорядоченных сплавах, так как в некогерентное рассеяние все ядра дают аддитивные вклады, и поэтому усреднение по распределению атомов по узлам можно сделать непосредственно в выражении (9). При этом так как усреднение производится по ансамблю динамических матриц с данными концентрациями компонент, мы должны считать смещения атомов одного сорта одинаковыми.

Учитывая концентрации A_j -компонент, получим из (9) для сплава с j -компонентами

$$\frac{d^2 \sigma^{(1) \text{ incoh}}}{d\Omega d\epsilon} = \frac{\kappa}{8\pi k_0} \cdot \frac{\kappa^2}{\epsilon} \cdot \frac{q(t)}{e^{\epsilon/k_B T} - 1} \sum_j e^{-2w_j} A_j \frac{\sigma_j}{M_j} \overline{|\vec{C}_j(\epsilon)|^2} \quad (10)$$

и вместо (2) новое условие нормировки

$$\sum_j |\vec{C}_j(\epsilon)|^2 A_j = 1. \quad (11)$$

При рассмотрении рассеяния на поликристаллах большую трудность представляет отделение некогерентного рассеяния от когерентного. Однако для сплавов можно так подобрать концентрации, что когерентное сечение будет обращаться в нуль.

Действительно, из (3) и (5) найдем для когерентного одно-квантового сечения:

$$\frac{d^2\sigma^{(1)\text{coh}}}{d\Omega d\epsilon} = \frac{\kappa}{8\pi k_0} \sum_{nn'} e^{-(w_n + w_{n'})} e^{i\vec{k}(\vec{r}_n - \vec{r}_{n'})} \langle a_n \rangle \langle a_{n'} \rangle \times \\ \times \sum_{\omega} \frac{(\vec{\kappa} \vec{C}_n(\omega)) (\vec{\kappa} \vec{C}_{n'}(\omega))}{2\sqrt{M_n M_{n'}}} \cdot \frac{\delta(\omega - \epsilon)}{e^{\omega/k_B T} - 1} \quad (12)$$

В отличие от некогерентного рассеяния усреднение по случайным распределениям ядер по узлам надо производить сразу же, что даёт

$$\langle a_n \rangle = \sum_j A_j a_j. \quad (13)$$

Если в числе компонент сплава есть ядра с амплитудами рассеяния разных знаков, можно подобрать концентрации так, что $\langle a_n \rangle \equiv 0$

и $\frac{d^2\sigma^{(1)\text{coh}}}{d\Omega d\epsilon} = 0.$

ПРОВЕДЕНИЕ ЭКСПЕРИМЕНТА И ОБРАБОТКА РЕЗУЛЬТАТОВ

Образец сплава Ti-Zr был приготовлен дуговой плавкой компонент в атмосфере инертного газа с последующим естественным охлаждением. Состав сплава 62% Ti и 38% Zr, выбирался из соображений обеспечения полностью некогерентного рассеяния нейтронов. Действительно, используя значения $a_{\text{Ti}} = -0,38 \cdot 10^{-12}$ см и $a_{\text{Zr}} = 0,62 \cdot 10^{-12}$ см, получим $\langle a \rangle = 0$ и, следовательно, согласно (12) (13) сечение когерентного рассеяния равно нулю.

В целях проверки неупорядоченности сплава были проведены нейтронографические исследования образца сплава. Анализ нейтронограмм показал, что образец не дает когерентных максимумов, которые наблюдались бы при отражении от подрешеток Ti и Zr, если бы система была упорядочена.

Спектр неупруго рассеянных нейтронов исследовался на установке, описанной в [7]. Образец сплава в виде диска с диаметром ~ 10 см и толщиной 1 см устанавливался в вакуумной камере под углом 45° к падающему пучку. Пропускание образца для холодных нейтронов составляло $\sim 0,22$. Спектр рассеянных нейтронов измерялся в интервале энергий от $5 \cdot 10^{-3}$ до 10^{-1} эв, причем наиболее детально исследовался интервал энергий от $8 \cdot 10^{-3}$ эв до $5,5 \cdot 10^{-2}$ эв. Использовался прерыватель с шириной щели 0,08 см, и измерения приводились двумя сериями: в интервале от $1,5 \cdot 10^{-2}$ эв до $5,5 \cdot 10^{-2}$ при скорости вращения прерывателя 5000 об/мин и в интервале $8 \cdot 10^{-3}$ эв до $2,5 \cdot 10^{-2}$ эв при скорости вращения 3600 об/мин. При этом ширина каналов временного анализатора составляла 32 мксек.

В полученные таким образом в каждой из серий результаты вводилась поправка на деформацию спектра рассеянных нейтронов функцией пропускания прерывателя, а затем они "сшивались" друг с другом с учетом показаний мониторов установки. Суммарные результаты измерений спектра неупруго рассеянных нейтронов на сплаве Ti - Zr с учетом поправок на отклонение эффективности детектора от закона $1/v$ и ослабление рассеянных нейтронов воздухом, находящимся между прерывателем и детектором, приведены на рис.1.

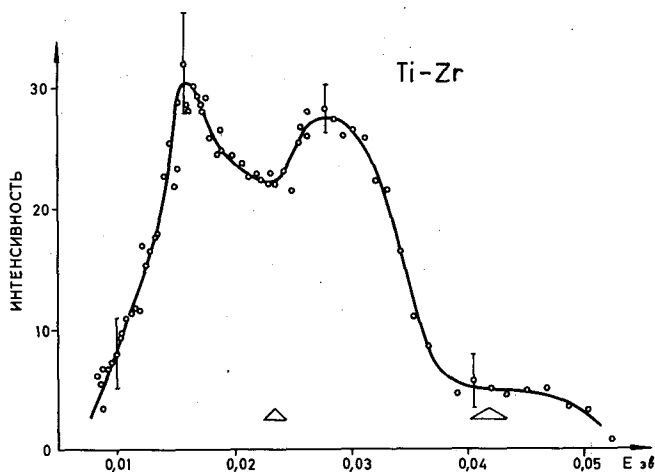


Рис.1

Экспериментальный спектр неупруго рассеянных нейтронов на сплаве Ti-Zr.

Прежде чем производить сравнение с выражением (10), в эти результаты необходимо внести поправки на деформацию спектров падающих и рассеянных нейтронов по толщине образца и учесть вклад многократных и многоквантовых процессов. Поскольку вклад от многоквантовых процессов нечувствителен к детальному виду спектра частот, его расчет проводился в приближении, в котором в качестве функции частотного распределения использовался спектр неупруго рассеянных нейтронов, исправленный на фактор Больцмана и на функцию $\frac{\kappa}{\kappa_0} \cdot \frac{\kappa^2}{\omega}$. Результаты указанной обработки приведены на рис.2.

Затем из этих данных с учетом полного разрешения установки восстанавливалась функция $g(\omega) \sum_j \frac{\sigma_j}{M_j} |C_j(\omega)|^2 A_j$.

Результаты приведены на рис.3. Подробности процедуры обработки экспериментальных результатов, аналогично использованной при восстановлении фононного спектра ванадия, описаны в работе [8].

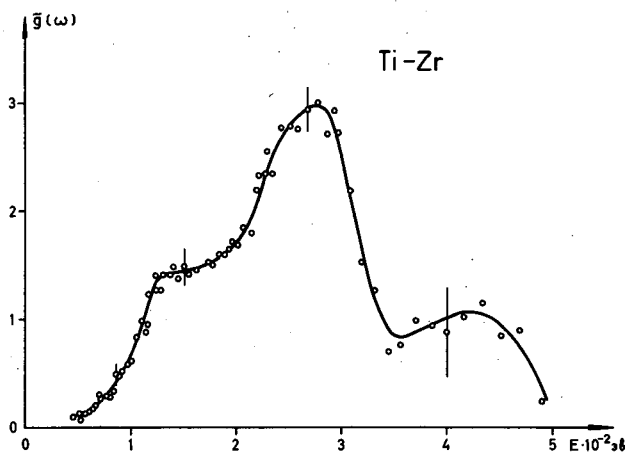


Рис. 2

Функция $\tilde{g}(\omega)$, восстановленная в предположении δ -функционального разрешения установки.

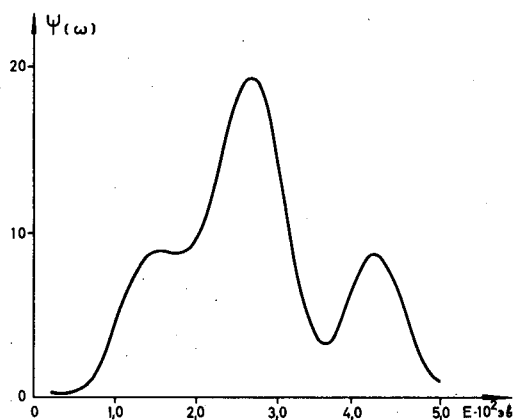


Рис. 3

Функция $\psi(\omega)$, восстановленная с учетом полной функции разрешения.

4. ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ

В результате описанной обработки экспериментальных данных получены значения величины:

$$\Psi(\omega) = g(\omega) \left\{ \frac{\sigma_{\text{Ti}}}{M_{\text{Ti}}} A_{\text{Ti}} \overline{|\vec{C}_{\text{Ti}}(\omega)|^2} + \frac{\sigma_{\text{Zr}}}{M_{\text{Zr}}} A_{\text{Zr}} \overline{|\vec{C}_{\text{Zr}}(\omega)|^2} \right\}. \quad (14)$$

Видно, что в этом случае строгое нахождение спектра частот $g(\omega)$ невозможно. Однако можно сделать некоторые качественные выводы о его характере: 1) есть основание предполагать, что зависимость $|\vec{C}(\omega)|^2$ от частоты ω - гладкая, поэтому сингулярности $\psi(\omega)$ совпадают с сингулярностями частотного спектра; 2) расчеты, проведенные для простейших моделей упорядоченных кристаллов [9], показали, что легкий атом колеблется в основном в оптической ветви, а тяжелый в акустической, причем квадраты смещений являются монотонными функциями частоты.

Перепишем выражение для $\psi(\omega)$ в следующем виде (используя (11)):

$$\Psi(\omega) = g(\omega) \left[\frac{\sigma_{Zr}}{M_{Zr}} + A_{Ti} \overline{|\vec{C}_{Ti}(\omega)|^2} \left(\frac{\sigma_{Ti}}{M_{Ti}} - \frac{\sigma_{Zr}}{M_{Zr}} \right) \right]. \quad (15)$$

Используя предыдущие рассуждения и тот факт, что $\frac{\sigma_{Ti}}{M_{Ti}} > \frac{\sigma_{Zr}}{M_{Zr}}$, получаем, что высокочастотная область спектра вносит завышенный вклад в $\psi(\omega)$, т.к. у титана масса атома меньше, а сечение рассеяния больше, чем у циркония. Определенный интерес представляет сравнение экспериментальных данных по функции $\psi(\omega)$ с результатами расчетов по спектрам разупорядоченных систем [2] и [3]. Очевидно, что такое сравнение может быть проведено только качественно.

На основании численного расчета спектра одномерной разупорядоченной системы из компонент А и В ($m_A \neq m_B$) Дином [2] показано, что спектр распределения частот колебаний разупорядоченной системы значительно отличается от спектра системы упорядоченной. Акустическая часть спектра частот деформируется при разупорядочении мало. Основные изменения происходят в запрещенной полосе и в оптической части спектра. При этом запрещенная полоса заполняется частотами, возникающими в результате разупорядочения, так что акустическая и оптическая части спектра сливаются, а сама оптическая часть спектра расщепляется на большое количество отдельных максимумов. К аналогичным выводам по отношению к исчезновению запрещенной полосы фононного спектра приходит и Брэдли [3] при анализе динамики двухкомпонентной разупорядоченной простой кубической решетки. Поскольку Брэдли использовал метод моментов, то расщепление высокочастотной части спектра колебаний им не было получено.

В этой связи представляется возможным на основании данных, приведенных на рис.3, сделать следующие заключения. Полного исчезновения запрещенных полос в спектре частот сплава Ti - Zr не наблюдается. Как в области низких, так и в области высоких частот в спектре наблюдаются относительно глубокие провалы, которые меньше провалов в спектрах упорядоченных решеток V и Ni [8,11], но, тем не менее, проявляются отчетливо. Не наблюдается также и предсказанное Динем расщепление оптической части спектра частот. Последнее возможно объясняется недостаточной разрешающей способностью установки, на которой проводились измерения.

Если же сравнивать данные по $\psi(\omega)$ с результатами расчета спектра частот гексагональной плотноупакованной решетки Mg, выполненного Гарлендом и Слуцким [10], то можно сказать, что в спектре неупорядоченной системы Ti - Zr особенности спектра частот как бы размыты: отношение ординат максимумов к ординатам минимумов меньше, ширины максимумов больше, чем в случае Mg. Такой результат, в противоположность результатам Дина, не является неожиданным.

В заключение авторы выражают свою благодарность М.И.Певзнеру за интерес, проявленный к данной работе, и участие в обсуждении результатов, Р.П.Озерову за предоставление образца и С.В.Киселеву за проведение нейтронографического исследования образца.

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DISCUSSION

B. MOZER: I would like to say that we have also considered doing completely incoherent scattering on alloys. We tried Ti-Zr among other things, and our results are in agreement with those of Dr. Tchernoplekov. We are beginning an experiment on the Ti-N system. For the incoherent scatterer the nitrogen concentration is $\approx 35\%$ and the mass ratio 1/3. The system has the disordered NaCl structure and should allow an easier impurity band if it exists.

SCATTERING LAW FOR METAL ATOMS IN CHEMICAL COMPOUNDS

P. A. EGELSTAFF AND G. HOLT

NUCLEAR PHYSICS DIVISION, AERE, HARWELL, DIDCOT, BERKS.
UNITED KINGDOM

Abstract — Résumé — Аннотация — Resumen

SCATTERING LAW FOR METAL ATOMS IN CHEMICAL COMPOUNDS. The motions of neutron absorbing atoms in chemical compounds can be studied by measuring the shape of neutron resonance absorption lines. If the independence of nuclear and atomic motions is assumed, the observed shape of a line is given by a convolution of a Breit-Wigner function with a scattering law which represents the motions of the atoms composing the sample. The scattering law is observed in this work with a resolution function equal to the natural width of the resonance. Although this is usually much wider than the experimental resolution of conventional scattering experiments, this method is, nevertheless, worthwhile because it has two advantages over the conventional one:

- (1) There are negligible interference effects in the observed quantity,
- (2) The motion of one atom (the species showing the resonance) can be observed in a compound containing many other atoms.

Since the scattering law function is non-symmetrical, the measured effect will be seen as an asymmetry in line shape. Also, the effect should be more significant for oxides than metals since the kinetic energy per atom is greater for the former, leading to a broader scattering law.

Measurements of line shapes have been made with the Dido fast chopper and the measured resonance lines are compared between Ta and Ta_2O_5 ; and Hf and HfO_2 . A detailed calculation of line shape has also been made for each case from an assumed frequency function and using the methods of EGELSTAFF and SCHOFIELD (NucLSci. Engng) with the programmes LEAP and LINESHAPE written by McLatchie. Finally, conclusions derived by this technique are compared with those obtained by conventional neutron scattering methods.

LOI DE DIFFUSION POUR LES ATOMES MÉTALLIQUES DES COMPOSÉS CHIMIQUES. On peut étudier les mouvements des atomes absorbant des neutrons dans les composés chimiques en mesurant la forme des raies d'absorption résonante des neutrons. Si on admet que les mouvements nucléaires et atomiques sont indépendants, la forme d'une raie peut s'exprimer au moyen de la convolution d'une fonction de Breit-Wigner avec une loi de diffusion qui représente les mouvements des atomes composant l'échantillon. Les auteurs ont constaté que la fonction de résolution de la loi de diffusion est égale à la largeur naturelle de la résonance. Bien que cette résolution soit d'ordinaire supérieure à celle qui est obtenue dans les expériences de diffusion classique, la méthode employée est quand même utile car elle présente, sur les méthodes habituelles, les avantages suivants:

1. Les effets d'interférences sont négligeables dans les quantités observées;
2. Le mouvement d'un atome (de l'espèce présentant une résonance) peut être observé dans un composé contenant plusieurs autres atomes.

La fonction de la loi de diffusion n'étant pas symétrique, l'effet mesuré se traduira par une asymétrie dans la forme de la raie. En outre, l'effet devrait être plus marqué pour les oxydes que dans les métaux étant donné que l'énergie cinétique par atome est supérieure dans les oxydes, ce qui donne lieu à une loi de diffusion plus large.

Les auteurs ont mesuré les formes spectrales à l'aide du sélecteur mécanique rapide du réacteur Dido et comparé les raies de résonance mesurées entre Ta et Ta_2O_5 ainsi qu'entre Hf et HfO_2 . Ils ont aussi procédé à un calcul détaillé de la forme des raies dans chacun des cas, en se fondant sur une fonction de fréquence hypothétique et en employant la méthode d'Egelstaff et Schofield dans les programmes LEAP et LINESHAPE établis par McLatchie. Enfin, ils comparent les conclusions que l'on peut tirer de cette technique à celles que l'on obtient à partir des méthodes de diffusion neutronique classique.

ЗАКОН РАССЕЯНИЯ АТОМОВ МЕТАЛЛОВ В ХИМИЧЕСКИХ СЛОЖНЫХ СОЕДИНЕНИЯХ. Движение поглощающих нейтронов атомов в химических сложных соединениях может быть изучено посредством измерения формы спектральных линий резонансного поглощения нейтронов. Если предположить, что ядра и атомы движутся независимо, то наблюдаемая форма спектральной линии получается из сопоставления функции Брейт-Вигнера с законом рассеяния, который описывает движение составляющих образцов атомов. В настоящей работе закон рассеяния анализируется с помощью функции разрешения, равной естественной широте резонанса. Хотя этот резонанс обычно гораздо более широк, чем экспериментальное разрешение при обычных опытах по рассеянию, тем не менее этот метод представляется ценным, имея следующие два преимущества над обычным методом:

- 1) в наблюдаемом явлении воздействия интерференции ничтожны;
- 2) движение единичного атома (вещества, обнаруживающего резонанс) может наблюдаться в сложном соединении, содержащем много других атомов.

Ввиду несимметричности функции закона рассеяния измеренное воздействие будет представляться в виде асимметрии формы спектральной линии. Поэтому воздействие должно быть более значительным для окисей, чем для металлов, так как кинетическая энергия, приходящаяся на каждый атом, более значительна для окисей, и это приводит к более широкому закону рассеяния.

Измерения формы спектральных линий были произведены при помощи селектора быстрых нейтронов на реакторе "Дидо"; измеренные резонансные спектральные линии сравниваются для Ta_2O_5 и для Hf и HfO_2 . Для каждого случая, исходя из предположительной функции частоты и метода Егелстаффа и Шюфильда, был произведен подробный расчет формы спектральной линии, для чего были использованы составленные Маклатчи программы LEAP и LINESHAPE. Выведенные на основании этих методов заключения сравниваются с результатами, полученными на основании обычных методов рассеяния нейтронов.

LEY DE DISPERSIÓN DE ÁTOMOS METÁLICOS EN COMPUESTOS QUÍMICOS. Los movimientos de los átomos que absorben neutrones en compuestos químicos pueden estudiarse midiendo la forma de las rayas de absorción de neutrones por resonancia. Si se supone que los movimientos nucleares y atómicos son independientes, la forma observada de una raya viene dada por la convolución de una función Breit-Wigner con una ley de dispersión que representa los movimientos de los átomos que componen la muestra. En este trabajo, la ley de dispersión se observa con una función resolutive igual a la amplitud natural de la resonancia. Si bien ésta suele ser mucho mayor que el poder de resolución alcanzado en los experimentos corrientes de dispersión, este método es útil porque respecto del tradicional presenta dos ventajas:

1. Los efectos de interferencia en la cantidad observada son despreciables,
2. El movimiento de un átomo (la especie que presenta la resonancia) puede observarse en un compuesto que contenga muchos otros átomos.

Como la función de la ley de dispersión carece de asimetría, el efecto medido se observa como asimetría en la forma de la raya. Asimismo, el efecto debe ser más marcado en los óxidos que en los metales, dado que la energía cinética por átomo es mayor en los primeros y, como consecuencia, la ley de dispersión es más amplia.

Los autores han efectuado mediciones de la forma de las rayas con el selector mecánico rápido del reactor Dido y comparan entre sí las rayas de resonancia medidas en el caso del Ta y del Ta_2O_5 , y en el caso del Hf y del HfO_2 . También han realizado un cálculo detallado de la forma de las rayas para cada caso utilizando una función hipotética de frecuencia y los métodos de Egelstaff y Schofield (Nuclear Science and Engineering), así como los programas LEAP y LINESHAPE elaborados por McLatchie. Por último, comparan las conclusiones obtenidas por este procedimiento con las deducidas conforme a los métodos corrientes de dispersión neutrónica.

1. INTRODUCTION

The frequency distribution of normal modes in diatomic crystals can be calculated theoretically (e.g. HARDY et al. [1]) and can be measured in some simple cases (e.g. SINCLAIR [2]). However in such studies the separate motion of atoms of each type is considered on simplified models because of the theoretical and experimental problems associated with the investigation of the motion of one type of atom only.

The object of the work described in this paper was to obtain some experimental information on the motion of metal atoms in oxides, since the technique of neutron resonance absorption can be used in this special case to isolate that part of the frequency distribution associated with the metal atoms. Briefly the technique is to compare the shape of the neutron absorption line in pure metal with that in the metal oxide. In both cases the unknown nuclear line shape will be distorted by the motion of the metal atoms, but the distortions will differ between the two cases. From this difference some information on the two frequency distributions may be deduced.

Neutron absorption line shapes in crystals have been discussed by LAMB [3], who showed that at sufficiently high temperatures the shape could be approximated by that due to a perfect gas at a fictitious temperature T' given by the average kinetic energy of an atom in the system. This model is valid when the following condition is satisfied:

$$\Gamma + P/A \gg \theta_D$$

where Γ is the nuclear width, P is the neutron momentum, A is the ratio of neutron to nuclear masses and θ_D is the Debye temperature. EGELSTAFF [4] discussed the limits of validity of this approximation and suggested that it was unlikely to be valid for oxides, so making them suitable for studies of the present type. Experimental work on this problem has been carried out by JACKSON *et al.* [5] on U_3O_8 who have demonstrated that in the optical mode the amplitude of the metal atom vibration is much less than that of the oxygen as expected. This was done by a comparison of the oxide experimental data with calculations based on a frequency distribution consisting of two δ -functions - one for acoustical and one for the optical modes. In the present work the metal and oxide shapes are carefully compared for three different cases, and the calculated shapes are based on a more general model. The conclusions will be based on the difference between a pair of measured curves and a pair of calculated curves.

The line shape is calculated from the assumption of the independence of nuclear and atomic motions. Thus the observed shape of a slow neutron resonance line is given in this case by a convolution of a Breit-Wigner function representing the nuclear motions with the "scattering law" representing the motions of the atoms composing the samples:

$$W(E_0) = \sigma_0 (\Gamma/2)^2 \int_{-\infty}^{+\infty} \frac{S_s(p, E)}{(E_0 - E_r - E)^2 + (\Gamma/2)^2} dE. \quad (1)$$

where σ_0 is the cross-section at the resonant energy E_r , Γ is the nuclear line width and E_0 the neutron energy. If a nucleus absorbs a neutron of energy E_0 , the momentum $p = \sqrt{2mE_0}$ is imparted to the atomic system, and the probability that energy $(E_0 - E)$ is available for nuclear excitation is $S_s(p, E)$. This function is the self part of the scattering function of VAN HOVE [6].

The function $S_s(p, E)$ is also studied in neutron scattering experiments but with much better resolution (i.e. with a resolution width $\ll \Gamma$). However, the neutron absorption method has two advantages. First there are no interference corrections to be made to the observations, and second the energies E_r for nuclear excitation are different for different nuclei, so that the motions of one type of atom can be observed in the presence of others. It can also be used for nuclei with large absorption cross sections (e.g. Hf) and hence unsuitable for scattering work.

Transmission measurements have been carried out on metals and oxides at room temperature, and the samples selected and the resonances examined are as follows: Ta/Ta₂O₅ at 4.28 eV - U/UO₂ at 6.68 eV - Hf/HfO₂ at 2.38 eV. Also preliminary measurements on Ta₂O₅ and UO₂ have been made at liquid nitrogen temperatures.

As was expected, the shape of the transmission dips measured using the metal samples is close to that calculated from the perfect gas approximation. The oxide transmission dips however do not fit this model and in particular are less deep than the metal curves. Calculations have been made with a frequency distribution consisting of a Debye spectrum for the acoustical modes and a narrow rectangle for the optical modes.

2. APPARATUS

(a) The neutron spectrometer

The measurements were carried out with the Dido multi-rotor fast chopper using three fibre-glass rotors (EGELSTAFF *et al.* [7]). A general arrangement of the system is shown in Fig. 1. The rotating collimators provide neutrons stopping material before and after the burst has been defined by the chopping rotor. For the experiments described the chopping

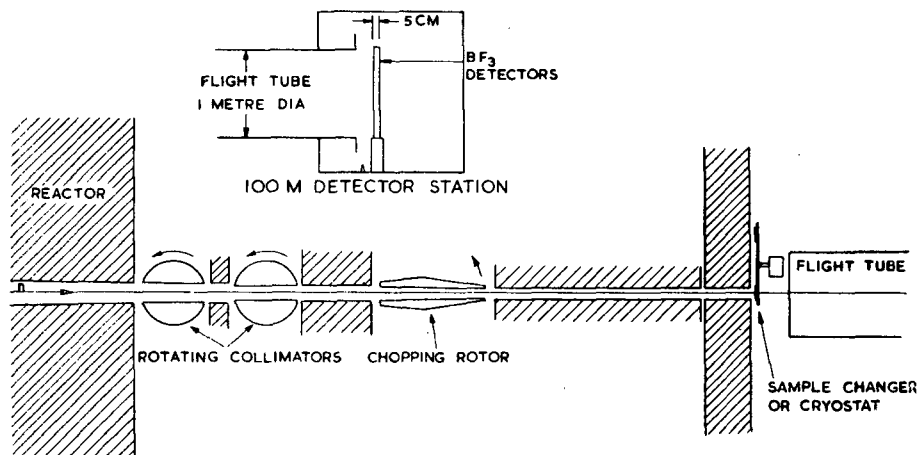


Fig. 1

Layout of neutron spectrometer.

rotor and rotating collimators were driven at speeds of 200 and 100 rev/s respectively. A bank of 80-1 atm pressure $B^{10}F_3$ detectors connected in parallel was used at the 50-m station for the measurements on uranium and at the 100-m station for the Ta and Hf measurements. Timing channels of $2.5\mu s$ were employed and at a 100-m flight path the resolution of the machine was $0.05\mu s/m$.

(b) The samples

Samples of Ta_2O_5 , UO_2 and HfO_2 were carefully prepared from spectroscopically pure oxide powders. In each case a sufficient quantity of oxide to give a peak transmission of between 0.2 and 0.4 was carefully weighed and all of it was well mixed with aluminium powder. A mechanically strong sample was prepared by placing the mixture in a die and applying a pressure of 15 t/m^2 . Aluminium was selected as a binder because of its suitable mechanical properties, low neutron absorption, and high thermal conductivity. After bonding each sample was radiographed to confirm that the oxide was evenly distributed throughout the aluminium. For each oxide sample, two further samples were pressed from the same batch of aluminium powder, both having equal mass of aluminium per unit area to that used in the oxide sample. Analysis showed that the aluminium powder used contained 0.1% oxide.

Ta, U and Hf metal samples were prepared from foil, by cold rolling technique, to have approximately equal number of atoms per cm^2 to the associated oxide sample. The difference in the number of metal atoms, in the metal foil as compared to the oxide was, typically, 2%. A correction for this small difference is easily made to the data before a comparison is made.

For the room temperature transmission measurements the samples were attached to a 3-position sample changer used in the position shown in Fig. 1. The metal samples were backed on to one of the aluminium blanks, and the second aluminium blank was fixed in the third position of the sample changer. These three samples were placed in the neutron beam in rotation for periods of six hours. Runs lasting 10 d were carried out on each combination to give an accurate comparison between metal and oxide.

During the measurements on Ta/ Ta_2O_5 the energy scale was checked by using a uranium monitor marker, and during the measurements on Ta/ Ta_2O_5 and U/ UO_2 , the background was continuously monitored at 3.35 eV and 11.14 eV by means of a thick terbium sample held over the beam. In addition the background was measured during separate runs at 4.28 eV and 6.68 eV using special thick Ta and U samples. For the data on Hf/ HfO_2 the background was measured at 2.334 eV by means of a thick tellurium sample in a separate experiment.

For the measurements at liquid nitrogen temperature a cryostat was installed in place of the 3-position sample changer. The Ta_2O_5 or UO_2 sample and blank were attached to a nylon cord and suspended in a bath of liquid nitrogen, the level of which was controlled automatically. So far an accurate comparison of the metal and oxide samples at the low temperature has not been made.

3. CALIBRATIONS

(a) Test of nuclear line shape

The nuclear absorption line shape is expected to be very close to that given by the Breit-Wigner formula. This shape can be observed if an absorption line having a large value of Γ is studied. A convenient example of this type is the 4.906 eV level in Au^{197} . Thus a careful examination of the shape of this line was made in order to test whether the equipment distorted the line.

Transmission measurements were made on samples of gold foil in the manner described above. The flight path used for this work was 50 m. Corrections for resolution width, Doppler broadening and background from distant levels were made by the methods discussed by EGELSTAFF *et al.* [8], and the '1/V' factor was removed. These corrections were of the order of 5%.

In order to examine the shape of the resonance the data was plotted in a form corresponding to the equation

$$(\sigma_0 / \sigma - 1)^{1/2} = (2/\Gamma) (E - E_r) \quad (2)$$

σ_0 is the value of the cross-section at the resonant energy E_r , and σ is the observed cross-section. This equation is the single level Breit-Wigner formula and in this representation a curve which exactly fitted this equation would appear as a symmetrical V.

The parameter σ_0 was determined from data within the range $E_r \pm \Gamma/10$ using an approximate value of Γ ; the value found being $\sigma_0 = 37360 \text{ b}$. A value of $\Gamma = 0.136 \text{ eV}$ is obtained by fitting Eq. (2) to the data in the range $E_r \pm \Gamma/2$. E_r corresponds to the peak of the resonance and its exact value is found by adjusting it to give a symmetrical V-plot. The V-plot for the resonance is given in Fig. 2. The central V is the region used to find the value of Γ and the outer V shows the fit of Eq. (2) to the remainder of the data, from which it is seen that the shape corresponds to a single level Breit-Wigner resonance.

(b) Energy calibration

An accurate energy calibration was carried out using the 6.672 eV resonance in U^{238} . Similar arrays of BF_3 detectors were installed at the 50-m and 100-m detector stations, and the outputs were fed into the time analyser, which was arranged to cover the arrival time of the 6.67 eV neutrons at both stations. Thus the flight time of neutrons of the resonance energy over the distance between the two stations could be easily measured and the energy of the resonance determined. Great care was taken to measure the distance between the stations. The distance between two reference points, one at the 50-m station and another at the 100-m station, was measured by surveying techniques to an accuracy of 1 part in 500 000. The distance from each reference point to an identical point on the appropriate counter bank

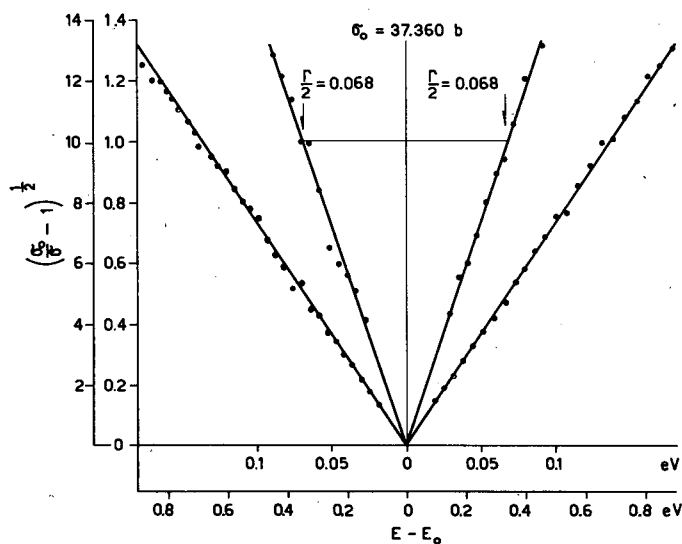


Fig.2

V-plot for 4.906 eV resonance of gold showing fit of line shape to Breit-Wigner formula.

was measured to ± 0.5 mm, so that this distance (49.993 m) is known to a greater accuracy than other factors.

The minima of the two transmission curves were $1399 \pm 1 \mu\text{s}$ apart which gave an inverse neutron velocity of $27.99 \mu\text{s/m}$. Thus the resonance energy was determined to be 6.672 ± 0.010 eV, and all other energy measurements were made relative to this value. This energy corresponds to the peak of the resonance observed in room temperature metal. Using Lamb's perfect gas approximation the true resonance energy is 6.644 ± 0.010 eV. The energy of this resonance has been measured by other workers to be 6.68 ± 0.06 eV [9].

4. THEORY AND COMPUTED LINE SHAPES

In order to assess the effect different frequency distributions have on the observable line shape, a series of calculations have been carried out using an IBM 7090 computer. These calculations were based on the parameters of the 4.28 eV resonance of Ta¹⁸¹.

First the function $S_s(p, E)$ is calculated from the frequency distribution by the method of EGELSTAFF and SCHOFIELD [10] using the computer programme LEAP devised by McLatchie. The integral at Eq. (1) can be evaluated numerically with a computer and the programme LINESHAPE of McLatchie was used for this purpose. Finally the transmission of hypothetical samples having the same thickness as the tantalum samples used in these experiments was calculated from the computed cross-sections. The frequency distributions used consisted of a Debye distribution for the acoustic part and a rectangle for the optical part. The position and width of the

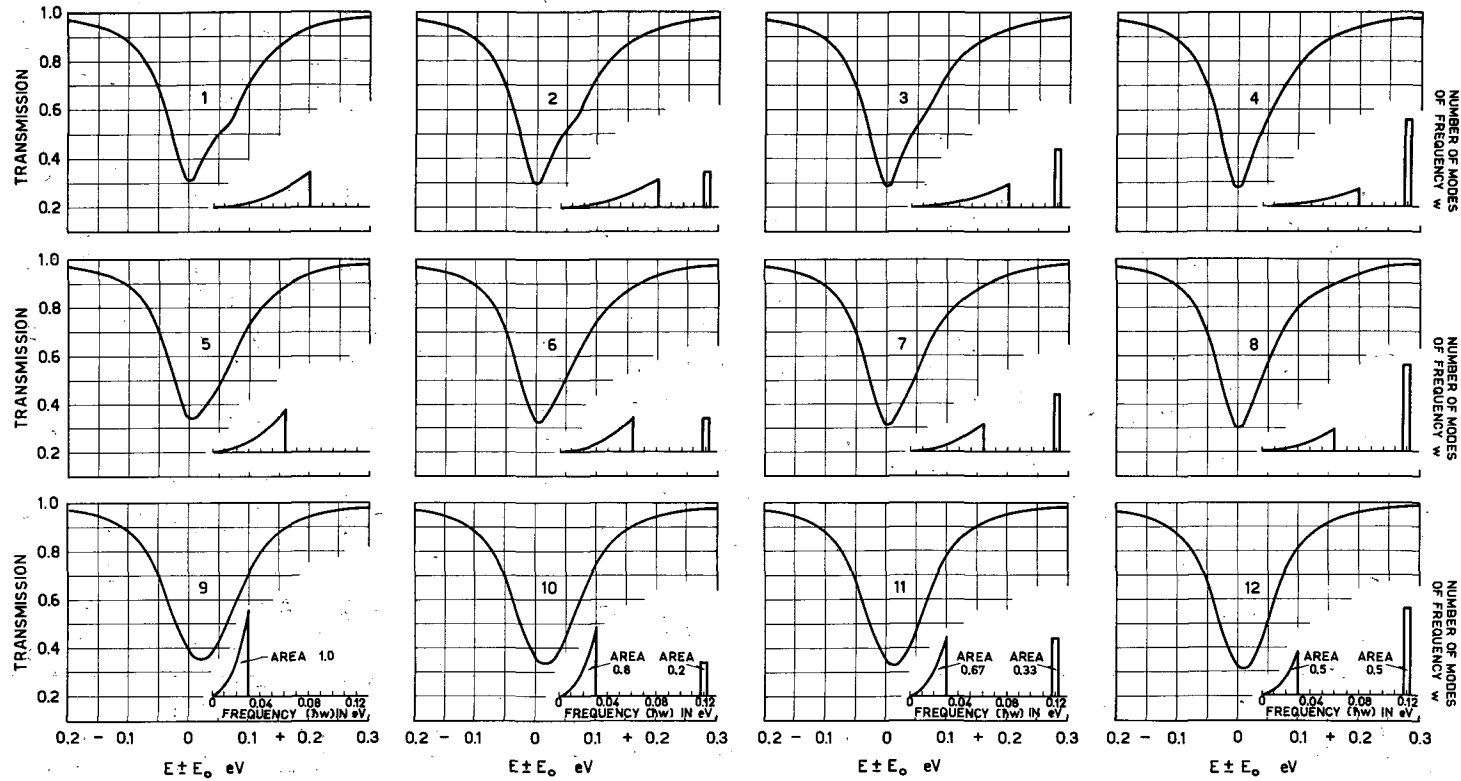


Fig. 3

Transmission dips calculated for 4.26 eV resonance of Ta using various frequency distributions.
The frequency distributions are shown as insets to each diagram.

optical part was fixed arbitrarily at 0.12 eV and 0.005 eV respectively, and the area of both parts added together was normalized to unity. Two factors were varied; the Debye cut-off and the amplitude of the optical modes.

The results of twelve calculations are given at Fig. 3, and the frequency distribution employed is given as an inset to each curve. A correlation of shape with distribution is clear although the effects are not large. To complete the picture further calculations are required in which the position of the optical mode is varied.

Several interesting facts can be seen from these curves. The most important is that it is difficult to draw unambiguous conclusions from one curve; for example cases 9 and 11 look alike and could be matched by perfect gas curves (of differing nuclear width) although the frequency distributions are not alike. Since the nuclear width is not known *a priori*, this situation is ambiguous. However a pair of curves is sufficient to identify the position in the family and hence the relative types of frequency distributions. For this reason the relative shape of metal and oxide curves is of greatest importance. Another fact is that the minimum depth is obtained for

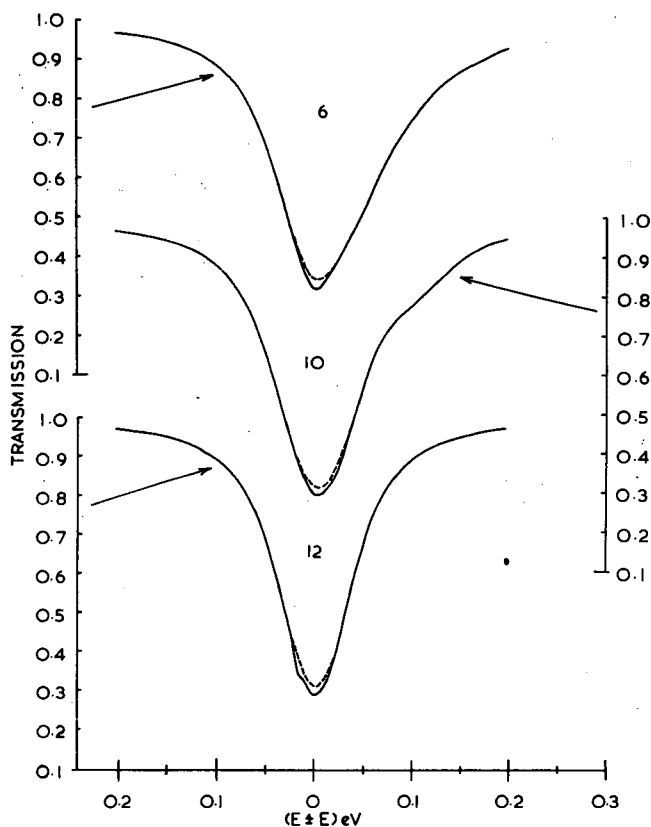


Fig. 4

Examples of the effect of the experimental resolution at a 50m flight path on the calculated curves in Fig. 3.

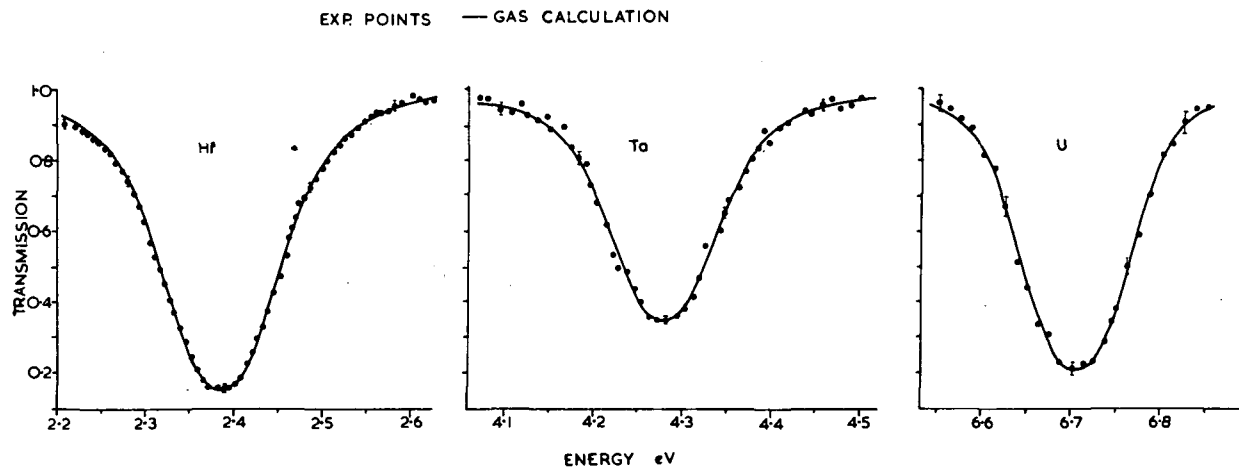


Fig. 5

Comparison of room temperature metal transmission measurements with calculations based on a perfect gas.

case 9, which is the nearest to the perfect gas (i. e. it has zero optical mode and is nearest to zero Debye cut-off). This curve is in fact indistinguishable from that due to a perfect gas. An increase in either the Debye cut-off or the size of the optical mode leads to an increase in the depth of the transmission curves. In this respect these calculations behave in an opposite manner to the effective temperature (perfect gas) approximation of LAMB [3]. The reason for this is that Lamb's approximation gives an average shaped curve of the correct area; the true curves are sharper in the centre but broader in the wings due to the behaviour of the Debye-Waller factor.

Finally, the computer programme SLOP devised by Hall was used to make numerical convolutions of the curves of Fig. 3, with the resolution function of the spectrometer. Three examples are given in Fig. 4 for the resolution appropriate to a 50-m flight path. The effect is small and roughly the same in all three cases and hence is unlikely to affect the analysis. In the case of calculations for the 100-m flight path the distortion due to resolution was negligible.

5. RESULTS AT ROOM TEMPERATURE

The experimental transmission dips for the three metal samples at room temperature are given in Fig. 5 compared with the calculated shapes for a perfect gas. Nuclear widths (Γ) have been chosen to make this calculation fit the data (this is the normal procedure used in the analysis of slow neutron resonance data). Reasonably good fits are obtained as would be expected from Lamb's treatment for samples with low Debye temperatures.

Observed transmission dips for the oxide samples are compared to the metal data in Fig. 6. Ta and Hf data were taken at the 100-m flight path. The smooth lines in this figure are the fitted curves of Fig. 5. It can be seen that in all cases the metal sample gives a deeper transmission curve than the oxide. In addition the oxide curve is less symmetric than the metal one.

In deducing the number of tantalum atoms in the oxide samples they were assumed to be of stoichiometric composition. At the conclusion of this work they will be chemically analysed to test this assumption. However the relative shapes of the curves in Fig. 5 (i. e. roughly equal area for metal and oxide) suggests that the samples are good.

6. RESULTS AT 80°K

Some preliminary data has been taken on the uranium and tantalum oxide samples at 80°K. These results are shown in Fig. 7. The flight path was 50-m and so far the required comparison with metal has not yet been made. Consequently these data will be compared to curves calculated from the data of Fig. 5 using Lamb's approximation. The results of Jackson *et al.* suggest that this procedure may be fairly reliable. These calculations are given in Fig. 7, and the correction to the calculation for the experimental resolution at 50-m is also given.

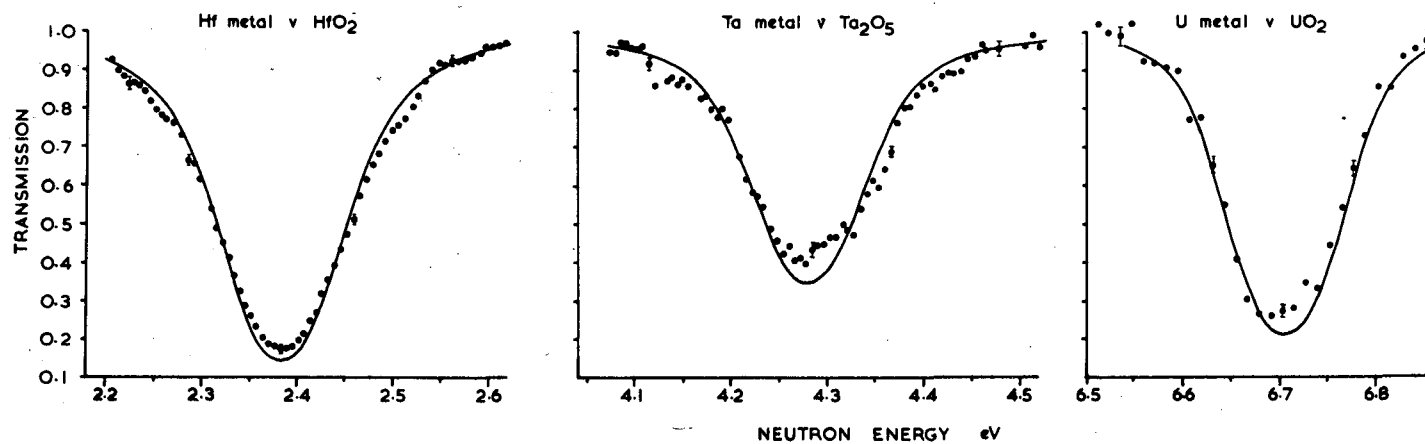


Fig. 6

Comparison of metal and oxide data at room temperature.
The solid lines are the calculated curves given in Fig. 5.

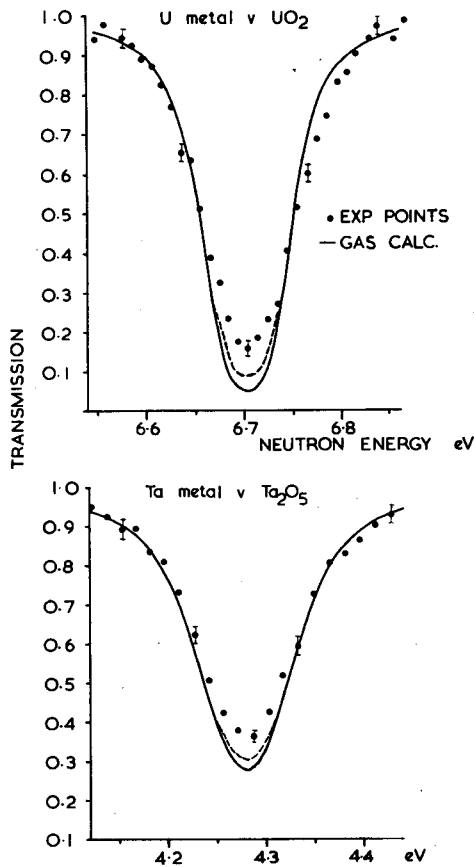


Fig. 7

Comparison of metal and oxide data at 80°K. The solid lines are calculated from the gas approximation of LAMB [3], using nuclear widths derived from the data of Fig. 5, and Debye temperatures of 245°K for Ta and 160°K for U. The dotted line shows the correction to the calculation for experimental resolution.

7. DISCUSSION

The comparison of the calculated curves of Fig. 3, with those of Fig. 6 shows that the difference in depth of the oxide and metal curves cannot be explained if the metal is assumed to behave like a perfect gas. Thus although the perfect gas curves (see Fig. 5) are of the right shape that must be fortuitous. The only pairs of curves of the right shape are those in which the oxide spectrum is much softer than that of the metal, and this seems inconsistent with other data (e.g. specific heat).

It is unlikely that the metal will have a low Debye temperature and also a weak mode at 0.12 eV as illustrated in Fig. 3. However a small peak in the distribution at ~ 0.05 eV and the remainder of it concentrated at low energies could be consistent with the observed Debye temperatures. In this

case the oxide distribution would need to have a weak optical mode at 0.05 eV and a lower Debye cut-off than the metal. The ratio of areas in the optical and acoustical modes can be calculated by the effective mass technique of SACHS and TELLER [11], and this gives values consistent with the above choice of frequency distribution.

Comparison of the experimental data with the curves of Fig. 3 shows that a strong optical mode cannot be present in the oxide case and from this point of view our data are consistent with Jackson *et al.* A study of their results shows that the difference between metal and oxide curves reported here can also be seen in their work and that their calculations do not adequately describe this difference.

If the distributions are of the proposed type there will be significant effects as a function of temperature. The preliminary data show that the resonances get deeper as the temperature is lowered and that the difference between oxide and metal is of the same magnitude at 80°K as at room temperature.

It is concluded that significant differences between metal and oxide transmission curves can be observed which are difficult to explain theoretically.

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DISCUSSION

B. MOZER: Have you tried doping a light atom lattice with your heavy absorbing atoms? You should see a large Debye-Waller factor.

P.A. EGELSTAFF: Well, that's the next thing I want to try. I've no explanation for the effects, but I would like to put some of these heavy metals into an alloy with a light metal. If the technique is really feasible there's an extraordinarily interesting range of experiments to be done here. To some extent the technique is parallel with the Mössbauer effect of course.

B. MOZER: Calculations on impurities show that you get a rather enhanced effect if you put this heavy atom in a light lattice.

P.A. EGELSTAFF: Well, there's no question but that the technique is very difficult; the effects are small and you have to be very careful to see the thing accurately, just because the levels are so wide.

I. WALLER: May I ask if you can also use this method for rather dilute solutions of impurities?

P. A. EGELSTAFF: Yes, I should say the probable limit is about 10^{-4} . It depends upon the cross-section for the resonance absorber, but they are all extraordinarily high, these resonance absorption cross-sections, so that it is really quite sensitive.

P. SCHOFIELD: Another point is that, in a molecular crystal, the Debye-Waller factor for one type of atom is not determined solely by the frequency distribution, but also depends on the amplitudes associated with the atomic displacements. This works in the right direction since the heavy atoms have most of their amplitude associated with the low-frequency modes.

P. A. EGELSTAFF: If I understand your point correctly you are saying that the effective Debye temperature for the metal atoms in the oxide could be much less than for the case of the parent metal. If this were the case it would help to explain these results.

I. WALLER: And this weighted frequency distribution can certainly be very different from the Debye spectrum.

P. A. EGELSTAFF: Yes, I agree.

H. PALEVSKY: I should like to make a statement which is probably obvious to most of those present. It is important to realize that this method is inherently insensitive because of the natural width of the nuclear levels. As Egelstaff has pointed out, this only allows one to observe the general features of the thermal motions, through a convolution integral. The chances of obtaining unique spectra by an inverse transform are very small. This is in marked contrast to scattering experiments discussed in the last two days, where some details in the frequency spectra have been observed experimentally.

P. EGELSTAFF: This is quite true, but I would like to point out again that in another sense this method is much more sensitive than the scattering method, namely for the detection of the motion of one type of atom in the presence of other types (e.g. an impurity in a host lattice). If the explanation of our results which Schofield has just given is correct, that would be an example of a result obtained by this method which could not have been obtained solely by the scattering method.

K. S. SINGWI: As you yourself have indicated, the theory you have outlined is essentially contained in LAMB'S famous paper [Phys. Rev. 55 (1939) 190], and Bollinger at Argonne was the first to demonstrate the effect of crystalline binding on the resonance adsorption of neutrons by uranium nuclei in a U_3O_8 lattice. The reason why no experiments were done on these between 1939 and 1961 is, I think, - and here I must agree with Palevsky - that this method you have suggested for determining the scattering law is, for obvious reasons, insensitive and cannot surpass the conventional neutron scattering method.

THE NEUTRON SCATTERING LAW AND THE FREQUENCY DISTRIBUTION OF THE NORMAL MODES OF BERYLLIUM AND BERYLLIUM OXIDE*

R.N. SINCLAIR**

ATOMIC ENERGY OF CANADA, LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

THE NEUTRON SCATTERING LAW AND THE FREQUENCY DISTRIBUTION OF THE NORMAL MODES OF BERYLLIUM AND BERYLLIUM OXIDE. The scattering of neutrons by phonons in polycrystalline specimens of beryllium and beryllium oxide has been studied using the phased rotor neutron time-of-flight spectrometer at the NRU reactor, Chalk River. The differential scattering cross-section was measured for several incident neutron energies between 0.015 eV and 0.132 eV using eleven detectors in the range of scattering angle from 12° to 150° . The cross-sections have been expressed in terms of dimensionless energy transfer and momentum transfer units as the scattering law $S(\alpha, \beta)$. Frequency distributions and the functions $p(\beta)$, have been deduced from the scattering law after the elimination of interference effects, the effects of multiple phonon scattering and the Debye-Waller factor. The regenerative process described in an accompanying paper has demonstrated the accuracy of the application of these corrections.

The frequency distribution of beryllium shows a high frequency cut-off corresponding to a Debye temperature of 940°K . The main deviation from a Debye model distribution is a peak at 0.050 eV which corresponds to the transverse optical vibrations.

Two peaks occur in the frequency distribution of beryllium oxide corresponding to modes of energy 0.040 eV and 0.086 eV. These probably correspond to the maximum energies of the acoustical and optical vibrations.

LA LOI DE DIFFUSION DES NEUTRONS ET LA DISTRIBUTION DES FRÉQUENCES DES MODES NORMAUX DU BÉRYLLIUM ET DE L'OXYDE DE BÉRYLLIUM. L'auteur a étudié la diffusion des neutrons par des phonons dans des échantillons polycristallins de béryllium et d'oxyde de béryllium à l'aide du spectromètre neutronique à temps de vol à rotor de phase, situé au réacteur NRU à Chalk River. Il a mesuré la section efficace différentielle de diffusion pour des énergies de neutrons incidents variant entre 0,015 eV et 0,132 eV, en utilisant onze détecteurs disposés aux angles de diffusion compris entre 12° et 150° . Il a exprimé les sections efficaces en fonction d'unités de transfert d'énergie et de transfert d'impulsion sans dimension, sous forme d'une loi de diffusion $S(\alpha, \beta)$. Les distributions de fréquences et les fonctions $p(\beta)$ ont été déduites de la loi de diffusion, après l'élimination des effets d'interférence, des effets de la diffusion des phonons multiples et du facteur de Debye-Waller. Le processus de régénération décrit dans un autre mémoire démontre la précision de l'application de ces corrections.

La distribution des fréquences du béryllium présente une coupure de haute fréquence correspondant à une température de Debye de 940°K . L'écart principal par rapport à la distribution modèle de Debye est constitué par un pic à 0,050 eV qui correspond aux vibrations optiques transversales.

ЗАКОН РАССЕЯНИЯ НЕЙТРОНОВ И РАСПРЕДЕЛЕНИЕ ЧАСТОТ НОРМАЛЬНЫХ КОЛЕБАНИЙ В БЕРИЛЛИИ И ОКСИД БЕРИЛЛИЯ. В Исследовательском центре Чок Ривер изучалось рассеяние нейтронов фононами в поликристаллических образцах бериллия и окиси бериллия с использованием сфокусированного вращающегося спектрометра нейтронов по времени пролета. Было измерено дифференциальное поперечное сечение рассеяния для некоторых энергий бомбардирующих нейтронов между 0,015 и 0,132 эв с использованием одиннадцати детекторов с углом рассеяния от 12° до 150° . Поперечные сечения были выражены с уче-

* Joint project between AECL, Chalk River and AERE, Harwell.

** Research carried out while a National Research Council of Canada Fellow. Present address: AERE, Harwell.

том безразмерной передачи энергии и единиц передачи импульса как закон рассеяния $S(\alpha, \beta)$. Распределения частот и функций $p(\beta)$ выводились из закона рассеяния после исключения эффектов интерференции, эффектов многократного рассеяния фононов и коэффициента Дебая-Уоллера. Регенеративный процесс, описанный в сопутствующем докладе, продемонстрировал точность применения этих поправок.

Распределение частот для бериллия указывает на высокую частоту обрезания, соответствующую дебаевской температуре 940°K. Главным отклонением от распределения по модели Дебая является максимум при 0,050 эв, который соответствует поперечным оптическим колебаниям.

Два максимума встречаются в распределении частот для окиси бериллия, соответствующих колебаниям с энергией 0,040 и 0,086 эв. Они, вероятно, соответствуют максимальным энергиям акустическим и оптическим колебаниям.

LEY DE DISPERSION NEUTRONICA Y DISTRIBUCION DE FRECUENCIAS DE LOS MODOS NORMALES DEL BERILIO Y DEL ÓXIDO DE BERILIO. El autor ha estudiado la dispersión de neutrones por fonones en muestras policristalinas de berilio y de óxido de berilio utilizando el espectrómetro neutrónico de tiempo de vuelo con rotor en fase instalado en el reactor NRU de Chalk River. Ha medido la sección eficaz diferencial para una serie de energías de los neutrones incidentes comprendidas entre 0,015 eV y 0,132 eV, utilizando 11 detectores colocados en ángulos de dispersión que varían entre 12° y 150°. Ha expresado las secciones eficaces como ley de dispersión $S(\alpha, \beta)$ en unidades adimensionales de transferencia de energía y de cantidad de movimiento. Después de eliminar los efectos de interferencia, los efectos de la dispersión de fonones múltiples y el factor de Debye-Waller, ha deducido las distribuciones de frecuencia y las funciones $p(\beta)$ basándose en la ley de dispersión. El proceso regenerativo descrito en otra memoria también presentada en este Simposio demuestra el grado de precisión que se alcanza al aplicar esas correcciones.

La distribución de frecuencias en el caso del berilio presenta la frecuencia de corte más alta para una temperatura de Debye igual a 940°K. La principal discrepancia respecto de una distribución según el modelo de Debye es un pico a 0,050 eV, que corresponde a las vibraciones ópticas transversales.

En la distribución de frecuencias del óxido de berilio aparecen dos picos correspondientes a los modos de energía 0,040 eV y 0,086 eV, que a su vez corresponden sin duda a las energías máximas de las vibraciones acústicas y ópticas, respectivamente.

INTRODUCTION

The vibration spectra in beryllium and beryllium oxide at 293°K have been determined from measured partial differential scattering cross-sections. The analysis was carried out using the scattering law notation. $S(\alpha\beta)$ is derived from the differential scattering cross-section by the relation [1]

$$\frac{\delta^2 \sigma}{\delta \Omega \delta E} = \frac{\sigma_0}{4\pi} \cdot \frac{k'}{k} e^{-\beta/2} S(\alpha\beta) \quad (1)$$

where

$$\alpha = \frac{\hbar^2 Q^2}{2Mk_B T}, \quad \beta = \frac{\hbar\nu}{k_B T}.$$

The cross-section describes the scattering process in which the incident neutron energy is changed by $\Delta E = \hbar\nu$ and the incident neutron wave vector k becomes k' . Q represents the wave vector change ($k - k'$) and, for a random polycrystalline specimen, may be regarded as a scalar quantity. M is the mass of the scattering atom. The scattering law has the same value for neutron energy gain and energy loss processes and the temperature dependence is related only to changes in the energy levels of the scattering system.

The frequency distribution of the normal modes of vibration in crystalline materials is of prime importance in the calculation of specific heat,

resistivity and other macroscopic phenomena. The distribution is determined by the combined effects of both the interatomic forces (which may extend over a long range of neighbouring atoms) and the crystal structure. Direct measurement from studies of incoherent inelastic scattering has been possible only in the few cases where interference effects in the scattering are negligible. VAN HOVE [2] discussed slow neutron scattering with reference to a "self" term corresponding to the motion of a single atom and a term involving the interference effects. The information concerning the dynamical properties of the scattering system is most easily derived from the "self" part of the scattering law S_d . The removal of the interference term S_d from the scattering law presents the most difficult problem in the determination of the frequency distribution. A satisfactory calculation of the term is difficult since S_d itself depends upon the distribution of normal modes. Methods have recently been proposed [3] whereby S_d may be calculated from an assumed frequency distribution. A reiterative procedure has been adopted in this work to fit the data at those high values of α at which S_d may be neglected. The procedure also extrapolates the measured scattering law to regions of high α and β which are unattainable by experiment but essential for the calculation of the scattering kernel for neutron thermalization work.

EXPERIMENT

The phased rotor time-of-flight spectrometer [4] at the NRU reactor was used to measure partial differential cross-sections for beryllium and beryllium oxide at 293°K. Monoenergetic neutrons were selected by two curved slit rotors and two collimating rotors of fibreglass construction were phased to remove fast neutrons from the beam. The neutron beam was monitored by three fission monitors separated by known distances. Time sorting the counts in these monitors gave the time-of-flight of the beam incident on the sample. The sample was oriented at 45° to the incident beam and the scattered intensity was observed in a ring of detectors. Eleven scintillation detectors were placed at scattering angles in the range from 12.5° to 155.4° at a distance of 1.296 m from the sample.

The time-of-flight of the scattered neutrons, using a reference pulse from a rotor, and the detector number were written on magnetic tape [5]. The scattering in each detector was analysed into 270 time channels of length 6 μ s or 4.63 μ s/m.

The background at the detectors was measured as a function of time by alternating the sample and an empty sample holder with a 30-min cycle. The background correction was applied after allowing for any variation in the intensity of the incident beam. The normalization of the background is very satisfactory over the period of time immediately before the opening of the rotor system when the thermal neutron scattering from the sample can be considered to be zero. The repetition rate of 400 counts/s precluded any overlap correction.

Several incident neutron energies in the range from 0.015 eV to 0.132 eV were used for each sample and each gave results in overlapping ranges of the variables α and β .

The determination of the detector efficiencies is described in a later section. The number of neutrons incident upon the sample was determined from the total number of counts in a fission monitor in the monoenergetic beam. The transmission of the sample as measured by a fission monitor was used to deduce the effective number of atoms in the sample. The accuracy of the absolute scale of the scattering law $S(\alpha\beta)$ is strongly dependent upon this transmission measurement together with the measurement of the absolute efficiencies of the detectors.

The total cross-section deduced from the measured distributions can provide a check on the absolute scale of S derived by the above method. This involves interpolation between the integrated scattering points to complete the angular distribution. In this experiment most of the scattering occurred in the coherent elastic scattering peaks and the interpolation cannot be reliably performed because of the limited number of detectors.

THE DETECTOR CALIBRATION

The 4 3/4-in square scintillation detectors were composed of Li^6F in zinc sulphide [6]. The effective absolute efficiencies of the eleven detectors (including a geometry factor) at a chosen energy were determined from the angular variation of the total elastic and inelastic scattering from a vanadium sample. The scattering from vanadium may be regarded as totally incoherent and the total scattering cross-section for an incoherent scattering sample is given as a function of angle by the relation [7]

$$\delta\sigma/\delta\Omega = (\sigma_b/4\pi) [1 - \frac{2}{A} (1 - \cos\phi)]. \quad (2)$$

σ_b is the bound atom cross-section, A is the mass of the scattering atom in terms of the neutron mass and ϕ is the angle of scattering. Measurement of the angular cross-section thus enables the absolute efficiencies of the counters to be determined. The values obtained in this manner at 0.035 eV were compared to values found by subtracting the inelastic scattering from the measured energy distributions and using the relation

$$(\delta\sigma_{el}/\delta\Omega) = (\sigma_b/4\pi) e^{-a\lambda} \quad (3)$$

where λ is a function of the physical temperature and the Debye temperature of the sample. Agreement between the two methods was satisfactory. The mean efficiency of the detectors at 0.035 eV is 22.0%.

The efficiencies of the detectors have been determined by the two methods over a wide range of energies and an expression has been fitted to the accumulated data of the following form [8]

$$\epsilon_r = B\tau e^{-\mu} [(e^{\mu-\sigma'} - 1)/(\mu - \sigma')]. \quad (4)$$

σ' is the known cross-section of the $(n\alpha)$ reaction in the scintillator material and μ is the unknown absorption cross-section for the photons in

the scintillator. B is a scaling factor and ϵ_r the detector efficiency for neutrons of time-of-flight τ μ s/m. This expression provides the basis for the interpolation and extrapolation of the measured detector efficiencies as a function of energy.

The efficiencies of the detectors were verified for the incident neutron energy before and after each experimental run by a vanadium measurement.

RESULTS

A typical neutron energy distribution is shown in Fig. 1 and is the neutron intensity resulting from the scattering by beryllium oxide of 0.132 eV neutrons through 121.1° . The scattering resulting from creation and annihilation of phonons is on the wings of the Bragg scattering peak. The time dependent background has been subtracted by the method previously described.

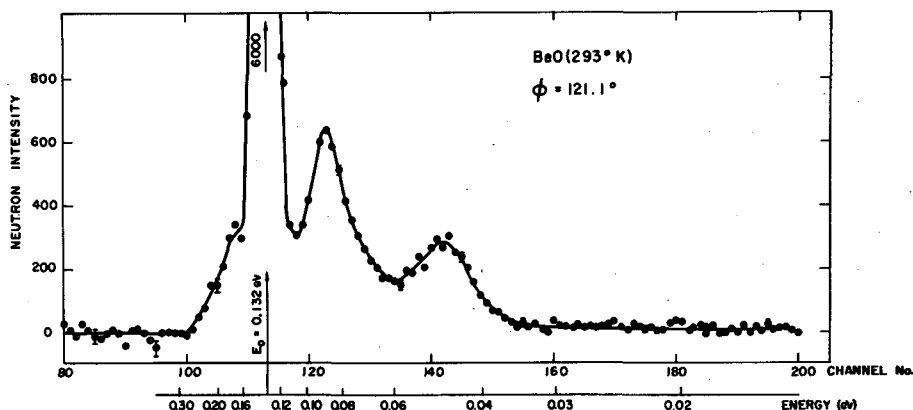


Fig. 1

A typical energy distribution of neutrons of incident energy 0.132 eV after scattering by beryllium oxide at room temperature.

The data in the figure (including a background measurement) was accumulated in about 100 h of counting time. The differential cross-sections derived from the corrected intensities were expressed as the scattering law through Eq.(1). Each experimental run at a single incident neutron energy produced about a thousand useful points in the $S(\alpha\beta)$ plane. The resolution of some was spoilt by the time-of-flight scale of the experiment. This can be seen in the neutron energy gain scattering in Fig. 1 which does not show the structure of the energy loss scattering.

Fig. 2 demonstrates the form of the scattering law as deduced from a single energy distribution of the scattering by beryllium of neutrons of incident energy 0.124 eV. $\beta = h\nu/kT$ is defined as positive for scattering events in which the neutron gains energy.

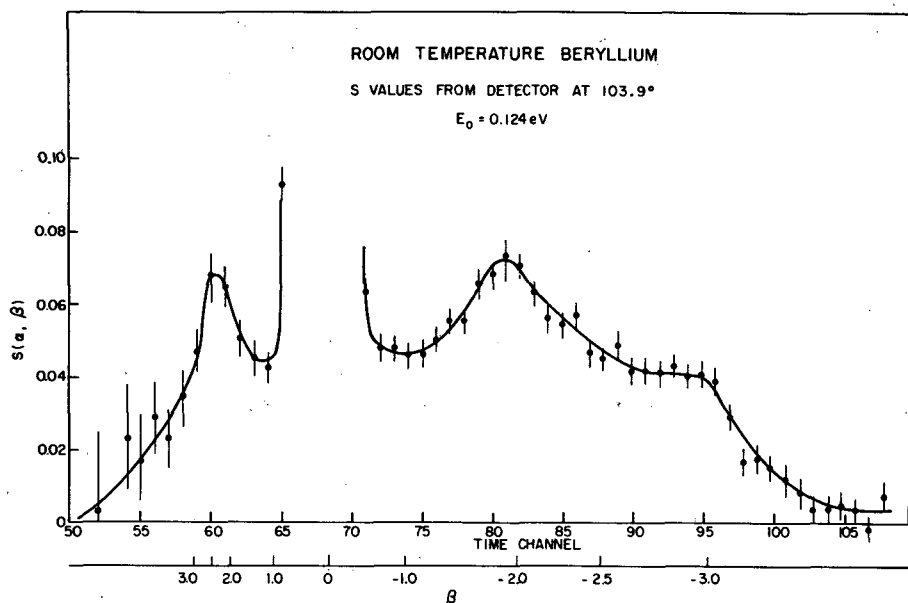


Fig. 2

The scattering law $S(\alpha\beta)$ for beryllium as measured in a detector at 103.9° to the incident beam.

The width of the effective resolution varies in a complicated manner [9] with the incident and scattered neutron times-of-flight owing to the velocity and time spread in the neutron burst produced by the rotor system.

A true resolution correction involves fitting simple analytical expressions to distribution such as that of Fig. 1 and the application of a correction with the markedly varying resolution function. The results presented in this paper have only been corrected for resolution effects in that certain neutron energy gain points have been omitted from the analysis. Also the lower limit on the range of β used in the analysis was set by the spread of the wings of the elastic scattering.

The scattering from beryllium at 293°K has been measured with incident neutron energies of 0.0375 eV and 0.124 eV. Each energy gave results in overlapping ranges of α and β . The transmission of the sample used at the low energy was 0.817 and at the high energy 0.867. The error bars shown on the typical energy distribution in Fig. 2 represent only the error due to the statistics of the neutron count. Although the curve does not show $S(\alpha\beta)$ at a constant value of α , the square of the momentum transfer, the main features of the phonon spectra are apparent. The distribution of neutrons on the low energy side of the elastic peak suggests a Debye cut-off corresponding to $\beta \approx 3.2$ or 940°K . This value agrees well with other neutron measurements and estimates made from the specific heat. The peak in $S(\alpha\beta)$ at $\beta = 2.0$ can be correlated with the phonon frequency-wave number relationship for the normal modes in beryllium [10]. The peak probably corresponds to the rather flat transverse optical branch which, in

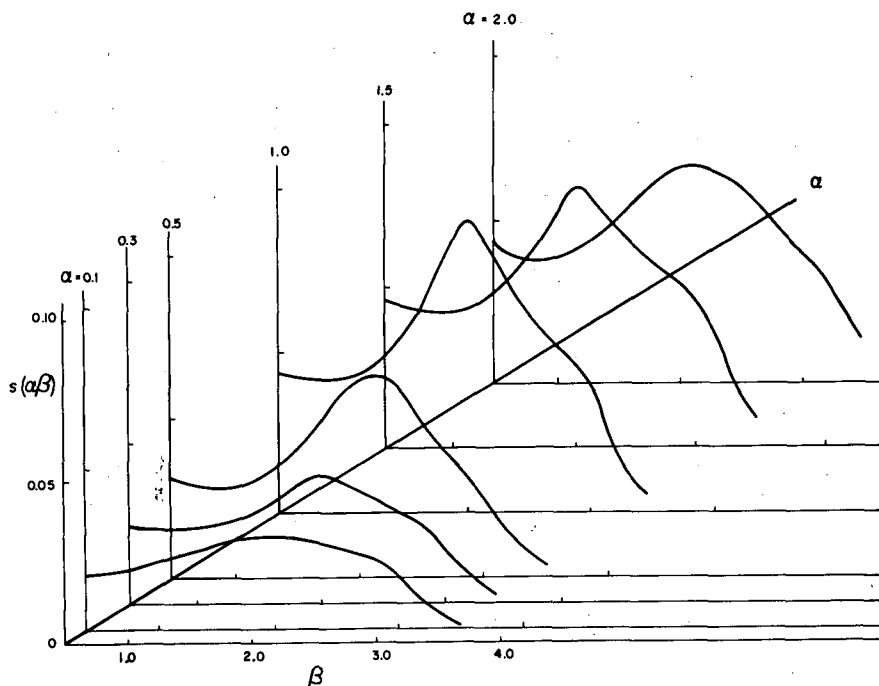


Fig. 3

The scattering law for beryllium at 293°K.
The contours are not corrected for experimental resolution.

the [100] direction, centres about a value of $\beta = 2.0$. The high energy cut-off at a value of $\beta \approx 3.2$ corresponds to the highest energy reached by the longitudinal optical branch in the lattice direction which has been investigated.

The scattering law represented in Fig. 3 shows contours through all the available data for beryllium. The normal presentation of the scattering law by lines of constant β is unsuitable for these measurements since it does not clearly display the important structure in the variation with energy. The value of β corresponding to the peak value of $S(\alpha, \beta)$ and to the rapid decrease in intensity above $\beta = 3.0$ is almost independent of the value of α . The limit of the range in α was determined by the highest incident energy and the limit in β was governed by the finite width of the elastic scattering peaks in the low incident energy experiment.

The inelastic scattering from samples of beryllium oxide was studied at three incident neutron energies. At the incident energy of 0.0980 eV a sample of transmission 0.91 gave a low counting rate so at 0.0165 eV and 0.132 eV a thicker sample of transmission 0.81 was placed in the beam. The high energy transfer processes could only be observed satisfactorily as neutron energy loss with the highest incident energy.

Fig. 1 shows the neutron intensity in a detector after background subtraction and again the main features of the phonon spectrum are apparent. The peaks correspond to values of $\beta = -1.6$ and $\beta = -3.4$. The two peaks

were also observed in neutron energy gain processes in the 0.0165 eV experiment. There was no indication of any other vibrational levels up to energies of 0.125 eV or $\beta \approx 5.0$.

Beryllium oxide has a zincite ZnO type of structure in which the beryllium atoms are interstitially located in an array of close packed oxygen atoms. The bonding is ionic and, considering the atomic weights of both atoms, the optical vibrations would be expected to occur at energies around 0.09 eV.

The full width at half-height of the peak at $\Delta E \approx 0.086$ eV is 0.012 eV. Expressions in [9] give the width of the resolution function in terms of the incident and scattered neutron time-of-flight and the spectrometer parameters. The value for this level is found to be 0.004 eV. The observed peak due to the optical vibrations is thus broadened in energy by about 10%. If a Debye temperature can be defined from the high energy limit of the phonon spectrum then Θ_D is 1070°C.

The mass used in the definition of α and the value σ_b in the calculation of the scattering law for a diatomic system is determined only by convention. In this instance the beryllium mass and bound atom cross-section were chosen. The measured scattering law is shown in Fig. 4 and the range of α was such that even with an incident energy of 0.132 eV the maximum in $S(\alpha\beta)$ could not be reached for any value of β . The experimental agreement between values of S derived from experiments with thick and thin samples indicated that the multiple scattering introduced by the thicker sample was not significant at least for the values of $\beta < 2.5$ at which the comparison was possible.

ANALYSIS

The two problems in the determination of the vibration spectra from the measured partial differential cross-section are the removal of the interference effects and the correction for the multiple phonon scattering processes in the remaining "self" or incoherent term. The separation of the interference term was achieved in the first instance by considering only the scattering in the region of high momentum transfer where the term S_d is believed to be small [11]. The effect of the term may be seen in Fig. 3 for beryllium where $S(\alpha\beta)$ remains almost constant as α falls below 0.1. The separation has previously been effected for graphite [12] by subtraction of S_d when $S(\alpha\beta)$ was expressed as the ratio S/α in terms of α and a similar procedure has been adopted here for both beryllium and beryllium oxide.

It has been shown [13] that the frequency distribution is related to S_s through the relation

$$\rho(\beta) = 2\beta \sinh \beta/2 \lim_{\alpha \rightarrow 0} \left(\frac{S_s}{\alpha} \right). \quad (5)$$

The limit of S_s as α tends to zero is taken to eliminate the multiple phonon effects which depend upon the fourth and higher even powers of the

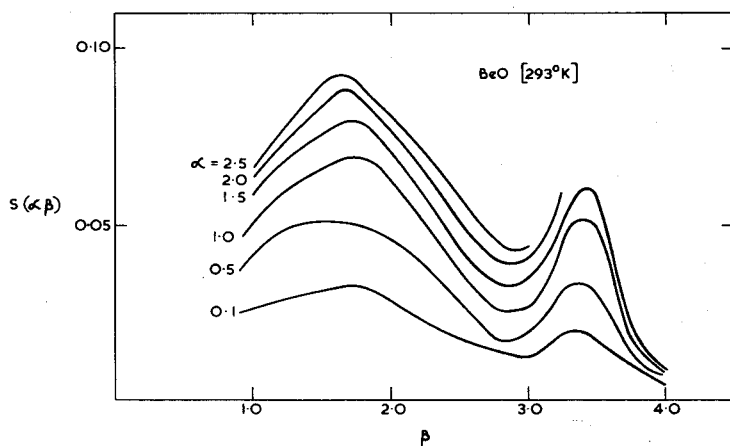


Fig. 4

The scattering law for beryllium oxide at 293°K.

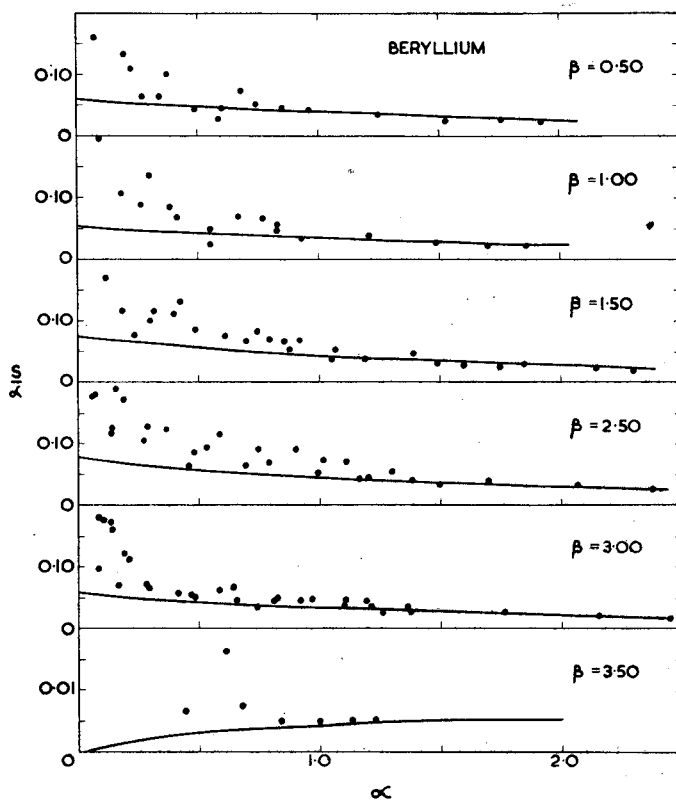


Fig. 5

Typical plots of S/a against a for beryllium.
The curves are derived from the distribution shown in Fig. 7.

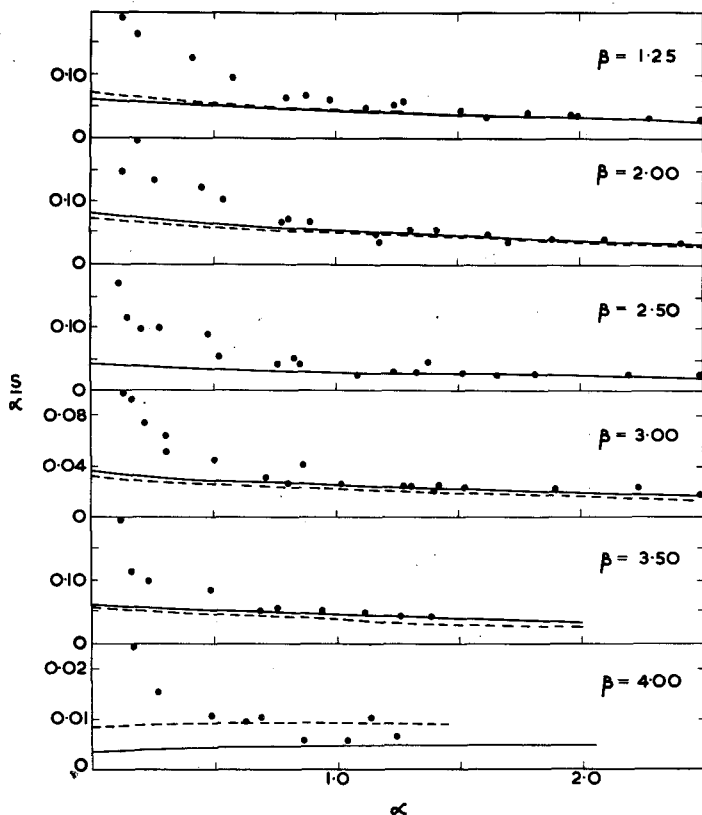


Fig. 6

Plots of S/α against α for beryllium oxide.
The dashed and continuous lines are derived from the
corresponding frequency distributions shown in Fig. 7.

momentum transfer, and to make the effective Debye-Waller factor equal to unity.

Figs. 5 and 6 show the form of the experimental points expressed as S/α . The interference effects cause a rise in S/α at low α for both materials. In the first instance an extrapolation to zero α of the form predicted by calculations of the self term for a Debye solid [14] was fitted to the experimental points above a value of α of 0.8. The Debye temperature was assumed from the observed high energy limit of the single phonon scattering. Frequency distributions were then found by use of Eq. 5.

A method has been proposed [3] whereby the self term of the scattering law may be calculated from the frequency distribution. It is assumed that the atoms move in a symmetrical parabolic potential or that the self correlation function is Gaussian in shape. A reiterative procedure has been based on the assumption to derive the frequency distribution which gives the best fit to the experimental points. The starting point for iteration was the distribution obtained from the Debye assumption as outlined above. A condition was applied from the definition of the distribution $\rho(\beta)$.

$$\int_0^{\infty} \rho(\beta) d\beta = 1. \quad (6)$$

In the case of the diatomic beryllium oxide the reiteration was based on the supposition that the same $\rho(\beta)$ was applicable both to the beryllium and oxygen atoms. The scattering law, as defined previously, may be written [11] in terms of two self terms corresponding to the motions of each type of atom and interference terms.

$$S_{OB} = S_1(\alpha) + \frac{P_2}{P_1} \cdot \frac{\sigma_2}{\sigma_1} S_2 \left(\frac{M_1}{M_2} \alpha \right) + \text{interference terms} \quad (7)$$

where $P_1 P_2$ are the abundances of the atoms and $\sigma_1 \sigma_2$ and $M_1 M_2$ represent the bound atom cross-sections and the masses respectively. On these definitions, the area under the observed frequency distribution is given by

$$\left(\int_0^{\infty} \rho(\beta) d\beta \right)_{\text{Observed}} = 1 + (P_2 / P_1) (\sigma_2 / \sigma_1) \quad (8)$$

The curves in Fig. 5 are the result of the first iteration for beryllium and are seen to give a reasonable fit of the data above a value of α of about 1.2. The frequency distribution to which these curves correspond is shown

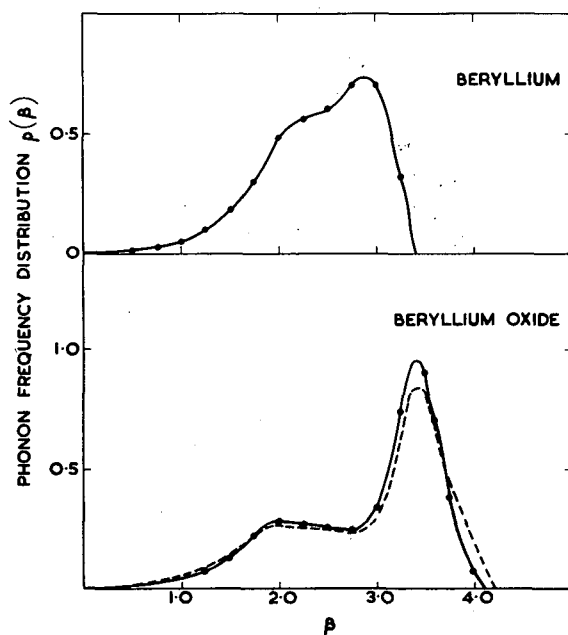


Fig. 7

The phonon frequency distributions for beryllium and beryllium oxide. The dashed and continuous lines for beryllium oxide correspond to the first and second iterations (see Fig. 6). The points denote the values of β at which the reiterative process has been tested.

in Fig. 7. The points signify only the values of β at which comparisons such as those in Fig. 5 have been made.

A sample of the results for beryllium oxide is given in Fig. 6. The broken curves correspond to the first iteration and the continuous lines to the second. The sensitivity of the method is demonstrated in Fig. 7 by the two corresponding phonon frequency distributions. The agreement between the second iteration and the experimental points is good in the range of α greater than 1.3.

DISCUSSION

The derivation of the frequency distributions described in this paper cannot be considered to be complete without a similar computation of the interference term S_d which we assumed to be negligible at high values of α . Recent calculations [11] have shown that, as is to be expected, S_d contains a high degree of structure. The angular resolution of these experiments was not sufficient to detect any peaks in the scattering law at low values of α . The degree of validity of the Gaussian approximation upon which the reiteration procedure is based cannot be determined from this data until the ability of the procedure to explain the whole scattering law has been demonstrated. However it is already clear that the derived frequency distributions must show all the important features of the vibration spectra. The room temperature frequency distributions are now being used in calculations of the variation of lattice specific heat with temperature. The distribution for beryllium shows that the average energies of the optical and acoustical modes of vibration are very close. The optical vibrations in beryllium oxide dominate the frequency distribution and the mean energy of the vibration is almost twice that of the acoustic branches. The narrow width of the peak at 0.086 eV implies that the frequency of the phonons in at least one of the optical branches is almost independent of the wave number.

ACKNOWLEDGEMENTS

The author is indebted to B. C. Haywood, I. M. Thorson and the other members of the Chalk River Scattering Law Group for assistance in all facets of the experiment. Acknowledgment is also made to P. A. Egelstaff for helpful discussions and computational assistance.

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DISCUSSION

K.E. LARSSON: Your figures show a coherence contribution at $\beta = 1$. Doesn't that correspond to about 0.025 eV ?

B. HAYWOOD (on behalf of R.N. Sinclair): Yes, that is correct.

K.E. LARSSON: Well, beryllium is a coherent scatterer so that would mean that in all the cases where you have a coherent scatterer you would have a coherence correction stretching out over the whole spectrum. I was just thinking, for instance, of the data we saw this morning on nickel.

B. HAYWOOD: I agree, the point needs considering.

SCATTERING LAW FOR UO_2 *

I.M. THORSON AND B.C. HAYWOOD**

ATOMIC ENERGY OF CANADA, LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

SCATTERING LAW FOR UO_2 . The scattering law for UO_2 at 22°C has been measured using the Chalk River thermal neutron analyser. Partial differential cross-sections were measured over the range of energy transfer of 0.01 eV to 0.1 eV and of momentum transfer 0.01 eV to 0.8 eV. The results are presented in $S(\alpha, \beta)$ notation. Extrapolations of S/α versus α as $\alpha \rightarrow 0$ have given an initial estimate of the generalized frequency distributions $p(\beta)$.

LA LOI DE DIFFUSION POUR UO_2 . Les auteurs ont mesuré la loi de diffusion pour UO_2 à la température de 20°C en employant l'analyseur des neutrons thermiques de Chalk River. Ils ont mesuré les sections efficaces différentielles partielles dans une gamme de transferts d'énergie allant de 0,01 eV à 0,1 eV et pour des transferts d'impulsion variant entre 0,01 eV et 0,8 eV. Les résultats sont présentés sous la forme $S(\alpha, \beta)$. Les extrapolations de la courbe représentant S/α en fonction de α , lorsque $\alpha \rightarrow 0$ ont fourni une première estimation des distributions de fréquences généralisées $p(\beta)$.

ЗАКОН РАССЕЯНИЯ НЕЙТРОНОВ ДЛЯ UO_2 . Проверился закон рассеяния нейтронов для UO_2 при 22°C с использованием анализатора тепловых нейтронов в Исследовательском центре Чок Ривер. Парциальные дифференциальные сечения измерялись в области передачи энергии (0,01 - 0,1 эв) и области передачи импульса (0,01 - 0,8 эв). Результаты представлены в выражении $S(\alpha, \beta)$. Экстраполяции S/α при $\alpha \rightarrow 0$ дали первоначальную оценку обобщенных распределений частот $p(\beta)$.

LEY DE DISPERSIÓN DEL UO_2 . Los autores han determinado la ley de dispersión correspondiente al UO_2 a 22°C utilizando el analizador de neutrones térmicos de Chalk River. Han medido las secciones eficaces diferenciales parciales en el intervalo de transmisión de energía de 0,01 eV a 0,1 eV y de transmisión de cantidad de movimiento de 0,01 eV a 0,8 eV. Exponen los resultados con la notación $S(\alpha, \beta)$. Las extrapolaciones de S/α en función de α cuando $\alpha \rightarrow 0$ permiten calcular en primera aproximación las distribuciones de frecuencia generalizadas $p(\beta)$.

I. INTRODUCTION

The inelastic scattering of thermal neutrons by UO_2 is of direct interest in reactor spectra calculations. Although the primary interest for reactor physics is in the energy transfer kernel $K(E_0 \rightarrow E)$

$$K(E_0 \rightarrow E) dE = \int_{4\pi} \frac{d^2 \sigma(E_0 \rightarrow E, \theta)}{d\Omega dE} d\Omega dE$$

the most satisfactory method of studying the problem is by measuring the double differential cross-section $d^2 \sigma(E_0 \rightarrow E, \theta)/dE d\Omega$. The dynamics of the UO_2 crystals must be studied in interpreting the cross-sections measured and this is useful not only for fundamental interest but also as an aid in the

* Joint project between AECL, Chalk River and AERE, Harwell.

** From AERE, Harwell at present at Chalk River.

extrapolation of the cross-section to regions of E_0 , E and θ where experimental measurements are very difficult.

The crystal structure of UO_2 in its stoichiometric form is quite well established [1] as face-centred cubic CaF_2 type structure with the oxygen at the $(1/4, 1/4, 1/4)$, $(1/4, 1/4, 3/4)$, $(1/4, 3/4, 1/4)$ etc., positions. Data on the dynamics of UO_2 are very limited but qualitatively one expects the oxygen motions to be more important in their effects on the inelastic neutron scattering than the uranium motions. Diffraction studies [2] give a ratio ~ 2.5 for the mean square vibration amplitude for the oxygen atoms to that for the uranium atoms.

The scattering from UO_2 is predominantly coherent since both oxygen and uranium are zero spin nuclei and so have unique neutron scattering lengths. Thus the analyses of the data to determine the average dynamics of UO_2 crystals may be complicated by the interference effects. It appears possible, however, to interpret the measured inelastic cross-sections in terms of direct scattering by individual nuclei over wide enough ranges of energy and momentum transfer to employ EGELSTAFF's extrapolation procedure [3] to derive the frequency distribution. This function can then be used to compute the direct, inelastic neutron scattering cross-section for any momentum or energy transfer.

The results presented here were taken with the phased rotor velocity selector time-of-flight apparatus at the NRU reactor at Chalk River [4, 5]. The incident neutron energies used (0.184 eV, 0.126 eV and 0.038 eV) enabled the cross-sections to be measured over an energy transfer range of 0.007 to 0.09 eV and a momentum transfer of approximately $0.05 (\text{eV} \times \text{amu})^{1/2}$ to $0.70 (\text{eV} \times \text{amu})^{1/2}$ ($Q = 2(\text{\AA})^{-1}$ to $15(\text{\AA})^{-1}$). The higher energy transfer data are more restricted in momentum change since the experiments yield good quality data only from events in which the neutron loses energy. The cross-sections for elastic scattering are not presented here

II. THEORY

It has been shown [6, 7] that the partial differential neutron cross-section for a system of identical particles may be written

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{E}{E_0}\right)^{1/2} N \left[\langle a \rangle^2 \mathcal{S}^c(k, \epsilon) + \left(\langle a^2 \rangle - \langle a \rangle^2 \right) \mathcal{S}^i(K, \epsilon) \right] \quad (1)$$

where the coherent and incoherent parts are given directly by the terms $\mathcal{S}^c$ and $\mathcal{S}^i$ respectively and the average of the scattering lengths are taken in the indicated manner. K and ϵ are the momentum and energy transferred in the interaction.

Van Hove further showed that $\mathcal{S}^i(K, \epsilon)$ and $\mathcal{S}^c(K, \epsilon)$ are the Fourier transforms of the time dependent self and total correlation functions $G_s(r, t)$ and $G(r, t)$ where $G(r, t) = G_s(r, t) + G_d(r, t)$ and $G_d(r, t)$ is his pair correlation function. For studies of the structure of matter Eq. (1) is a suitable starting point but if the dynamics of a system are of primary interest the cross-section is better written

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{E}{E_0}\right)^{1/2} N \left[\langle a^2 \rangle \mathcal{F}^i(K, \epsilon) + \langle a \rangle^2 \left(\mathcal{F}^c(K, \epsilon) - \mathcal{F}^i(K, \epsilon) \right) \right] \quad (2)$$

The first term is now the direct scattering by individual nuclei and does not involve correlations of other atoms except as they affect the motion of a single nucleus. The second term, the interference term, involves explicitly the correlation of positions of other particles through the Fourier transform of the $G_d(r, t)$ function. For predominantly incoherent scatters $\langle a \rangle^2$ is small relative to $\langle a^2 \rangle$ and it is adequate to retain the first term only. However for UO_2 where $\frac{\langle a \rangle^2}{\langle a^2 \rangle} \sim 1$ the second term is important for values of K and ϵ where $\mathcal{F}^d(K, \epsilon) = \mathcal{F}^c(K, \epsilon) - \mathcal{F}^i(K, \epsilon)$ is not negligible. The range of K and ϵ for which $\mathcal{F}^d(K, \epsilon)$ is significant is not easily established. The interference is expected to cause oscillations in the cross-section especially as $K \rightarrow 0$. This problem will be discussed in Section V.

For UO_2 a further complication enters because of the two types of scattering nuclei, the U^{238} and the O^{16} . The total expression for the cross-section is then a sum of direct scattering terms for the uranium and for the oxygen with the scattering lengths of uranium and oxygen respectively, plus four interference scattering terms which arise from correlations in position and time of the various combinations of type of atoms.

Over the range of K and ϵ for which the interference effects are negligible the partial differential cross-section for one UO_2 molecule may be written

$$\frac{d^2\sigma}{d\Omega d\beta} = \frac{(k_B T)^{-1}}{4\pi} \left(\frac{E}{E_0}\right)^{1/2} e^{-\beta/2} \left((\sigma_u \mathcal{F}_u^i(\alpha, \beta) + 2\sigma_o \mathcal{F}_o^d(\alpha, \beta)) \right) \quad (3)$$

σ_u and σ_o are the bound atom cross-sections for the uranium and oxygen respectively,

E_0 and E are incident and scattered neutron energies,

$$\beta = (E_0 - E)/k_B T = \epsilon/k_B T$$

$$\alpha = (E_0 + E - 2\sqrt{E_0 E} \cos \theta)/k_B T = K^2/2mk_B T,$$

m is the neutron mass*

Since $\sigma_u = 2\sigma_o$ to an accuracy of $\pm 5\%$ Eq. (3) may be written

$$\frac{d^2\sigma}{d\Omega d\beta} = \frac{(k_B T)^{-1}}{4\pi} \left(\frac{E}{E_0}\right)^{1/2} e^{-\beta/2} \sigma_u \mathcal{F}_{\text{UO}_2}^d(\alpha, \beta). \quad (4)$$

For a lattice of one type of atom, the frequency distribution of the normal modes of vibration can be derived from the scattering cross-sections by [8]

$$\rho(\beta) = 2\beta \sinh \beta/2 \lim_{\alpha \rightarrow 0} \frac{A S_i(\alpha, \beta)}{\alpha} \quad (5)$$

where A is the ratio of the mass of a scattering nucleus to the mass of the

* The neutron mass is used here, as the mass of the scattering nucleus is not unique.

neutron. The first energy moment condition of PLACZEK [9] which at $\alpha = 0$ is equivalent to the unit area normalization of the frequency distribution is given by

$$\int_0^{\infty} 2\beta \sinh \beta/2 S(\alpha, \beta) d\beta = \alpha / A \quad (6)$$

and in the limit of $\alpha \rightarrow 0$ can be written

$$\int_0^{\infty} 2\beta \sinh \beta/2 \lim_{\alpha \rightarrow 0} (S/\alpha) d\beta = 1/A. \quad (6a)$$

From the experimental UO_2 data the frequency distributions for the oxygen and uranium atoms are not directly separable but both S_u^1 and S_o^1 from Eq. (3) satisfy Eq. (6a). Thus if the data are analysed on the basis of Eq. (4) the frequency distribution so derived is the sum of the frequency distribution for one uranium atom and one oxygen atom and should have a total area normalization of $1/238.1 + 1/16.00 = 0.0667$.

III. EXPERIMENTAL MEASUREMENTS

The differential scattering cross-sections were measured using the Chalk River phased rotor neutron velocity selector time-of-flight apparatus. This apparatus is described briefly in a companion paper [10] and elsewhere [4, 5]. For these experiments the velocity selector gave bursts of neutrons of approximately Gaussian distribution in time of arrival at the scattering specimen position with $\sigma_t = 5.9 \mu\text{s}$. The reciprocal velocity distribution for neutrons in the bursts has a standard deviation of $\sigma_r = 2.2 \mu\text{s}/\text{m}$. These parameters were only slightly dependent on the reciprocal neutron velocity being selected, thus the fraction resolution $\Delta t/t$ is approximately proportional to the neutron velocity.

The pulsed neutrons were scattered by plane slab specimens of UO_2 . The scattered neutrons were detected 1.30 m from the specimen by eleven scintillation detectors placed at scattering angles between 12.5° and 155.4° to the incident beam direction. The events from each detector are sorted into $6 \mu\text{s}$ time channels according to elapsed time since the incident neutron arrived at the scattering specimen. The instabilities on the start of the time channel gates are small ($\pm 2 \mu\text{s}$) relative to the instantaneous position of the neutron burst and the time channel widths are fixed by a 1 Mc crystal controlled oscillator. To measure the incident neutron flux and fix the velocity scale for the scattered neutrons two thin foil fission chamber monitors are operated in the beam. The counts from these monitors are time sorted in an identical manner to those from the detectors. The distributions and the geometry factors gave the neutron velocity scale directly and the shape of the monitor distributions gave an estimate of the neutron velocity selector stability when data were being taken.

The results from several days operation are required to give the modest statistical accuracy obtained and it was necessary to interleave periods of

data accumulation with the scattering specimen in and out of the pulsed beam to compensate adequately for detector background. These data were accumulated separately and combined in the data processing to give the net specimen scattering. The specimen transmission was determined from the monitor totals for the sample in and out of the beam. Published total cross-section measurements [11] were then used to calculate the number of UO_2 molecules per cm^2 of beam. The detector efficiencies relative to the monitor efficiencies were determined from auxiliary measurements using a vanadium-scattering specimen [5].

No corrections were applied for the effects of multiple scattering, but the correction should be negligible for most of the data since the specimen transmissions were approximately 0.88. No corrections for velocity resolution of the apparatus were applied as the statistical accuracy of the data does not warrant it. Fission and delayed neutrons from the U^{235} in the specimen were not detected by the scintillator counters due to the low detection efficiency of these counters for high energy neutrons.

The scattering specimens were natural uranium, pressed and sintered powder slabs of stoichiometric UO_2 . The slab thickness was 0.20 cm and the specimen normal direction was 45° to the incident beam, giving a transmission of approximately 0.88.

IV RESULTS

Data were taken using three different incident neutron energies $E_0 = 0.184$ eV, 0.126 eV and 0.038 eV. The background and detector efficiency corrections were applied as in Eq. (3) of [10] and the resulting cross-sections reduced to the $S(\alpha_{ij}, \beta_i)$ notation by evaluation of Eqs. (4), (5) and (6) of [10]. The parameters used for σ_b and M were $\sigma_b = 9.0$ b and $M = 1.009$ amu, i. e. the neutron mass.

Fig. 1 shows the net neutron counts versus reciprocal velocity for a detector at a scattering angle of 138.2° and an incident neutron energy of 0.038 eV. The counts from adjacent pairs of time channels have been averaged to improve the statistical accuracy of the points; the line is only a guide to the points and does not represent any calculated fit to the data. Data taken at higher incident energies generally exhibit much more inelastic scattering than is shown in Fig. 1, but these data are shown to indicate the structure in the cross-section at an energy transfer of ~ 0.012 eV. This structure is not resolved in data taken with a higher incident neutron energy.

Figs. 2, 3 and 4 give the scattering law results for UO_2 at 20°C in the form of S/α versus α for discrete values of β . More results were taken than are shown in Figs. 2, 3 and 4 but the results at intermediate values of β can be found to within the experimental accuracy by linear interpolation of these plots. The errors shown in Fig. 2 are from the counting statistics only with no allowance for any systematic errors. No errors are shown in Figs. 3 and 4 for the sake of clarity, but since the results are taken under different experimental conditions the spread of the points is an indication of the overall consistency of the data. The spread of the experimental points in Figs. 3 and 4 is only slightly larger than expected from the counting statistics indicating that no significant systematic errors exist.

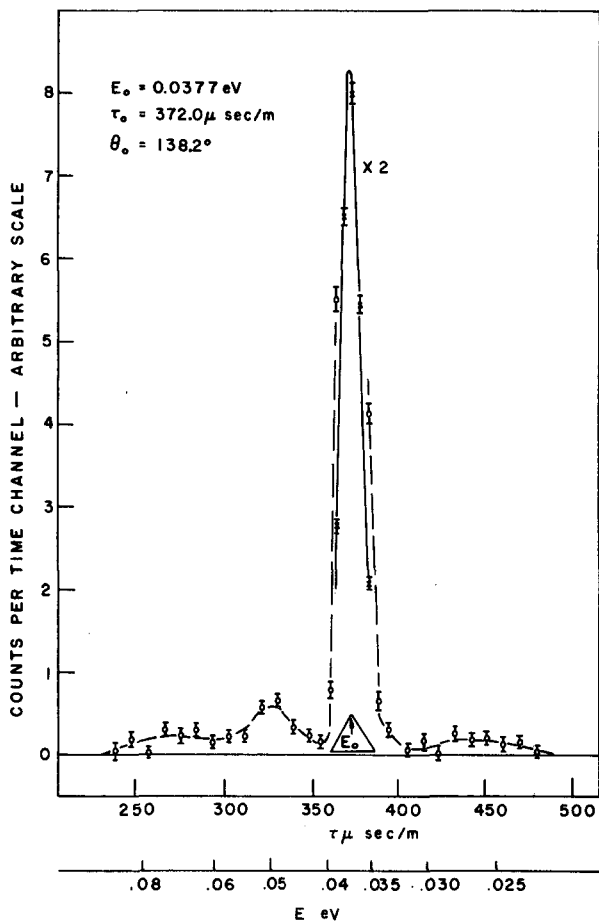


Fig. 1

The measured time-of-flight distribution of neutrons scattered from UO_2 at 20°C for an incident neutron energy of 0.0377 eV at a scattering angle of 138.2° . The structure at $E \sim 0.05$ eV gives the bump in the $\rho(\beta)$ curve at $\beta \sim 0.05$.

The results are presented in the form shown since the extrapolation of S/α to $\alpha = 0$ is done on the semi-logarithmic plots. Also the results are readily available at constant β as a time channel represents the same neutron energy for all detectors.

The results of Figs. 3 and 4 are extrapolated linearly to $\alpha = 0$, ignoring all points below $\alpha \sim 3$ for reasons discussed below. The results on Fig. 2 and other results for $\beta < 1$ were extrapolated to $\alpha = 0$ by using a line of the same slope as was used for the $\beta = 1.10$ results. This arbitrary procedure was necessary since the results at low β did not extend to high enough α to establish this slope. The extrapolation lines are shown in Figs. 2, 3 and 4. These values of $\lim S/\alpha$ and the equation

$$\alpha \rightarrow 0$$

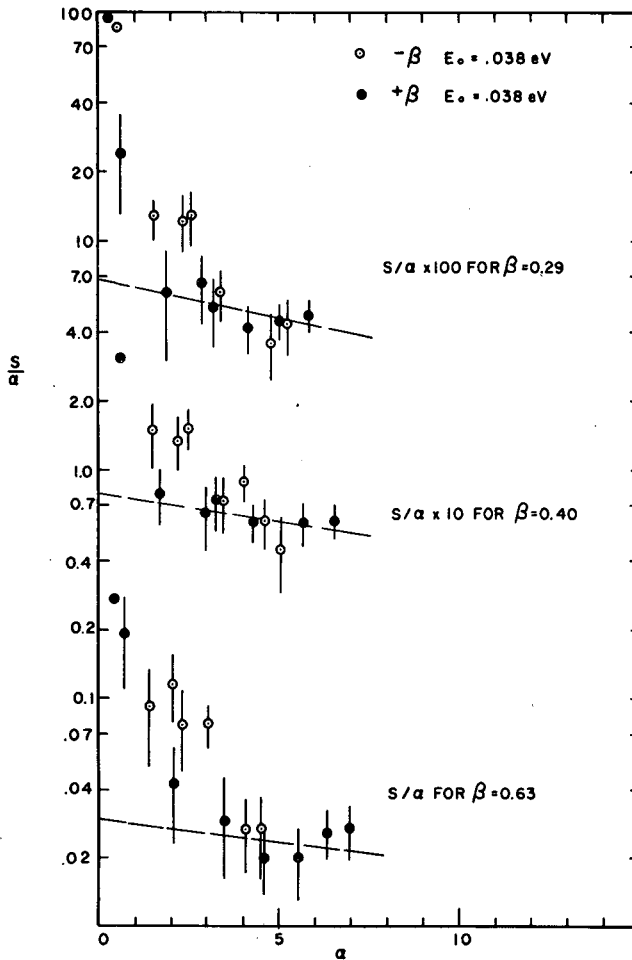


Fig. 2

Scattering law results for UO_2 at 20°C in the form S/a versus a at three values of β .

$$\rho(\beta) = 2\beta \sinh \beta/2 \lim_{\alpha \rightarrow 0} (S/\alpha)$$

give the $\rho(\beta)$ in Fig. 5.

V DISCUSSION OF RESULTS

The sharp rise in the measured S values as $\alpha \rightarrow 0$ is probably due mostly to multiple scattering effects. The low α region has small cross-section and so any measured contributions from multiple scattering events contribute

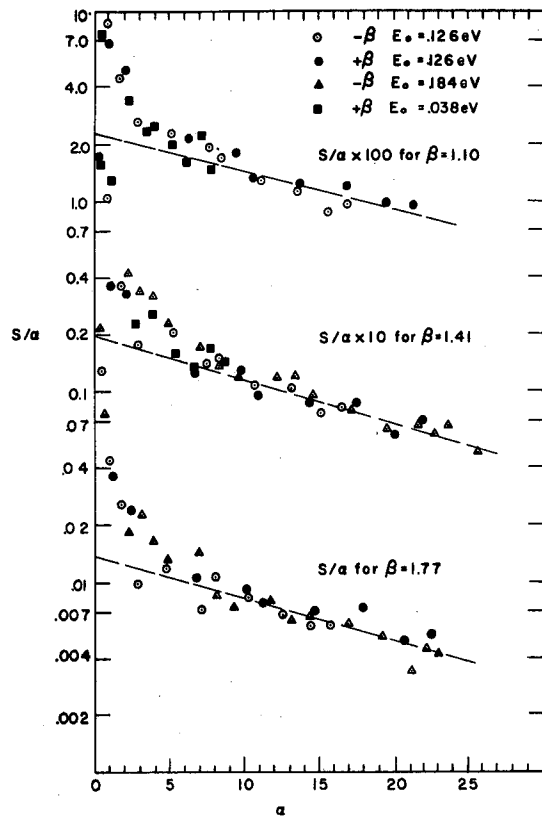
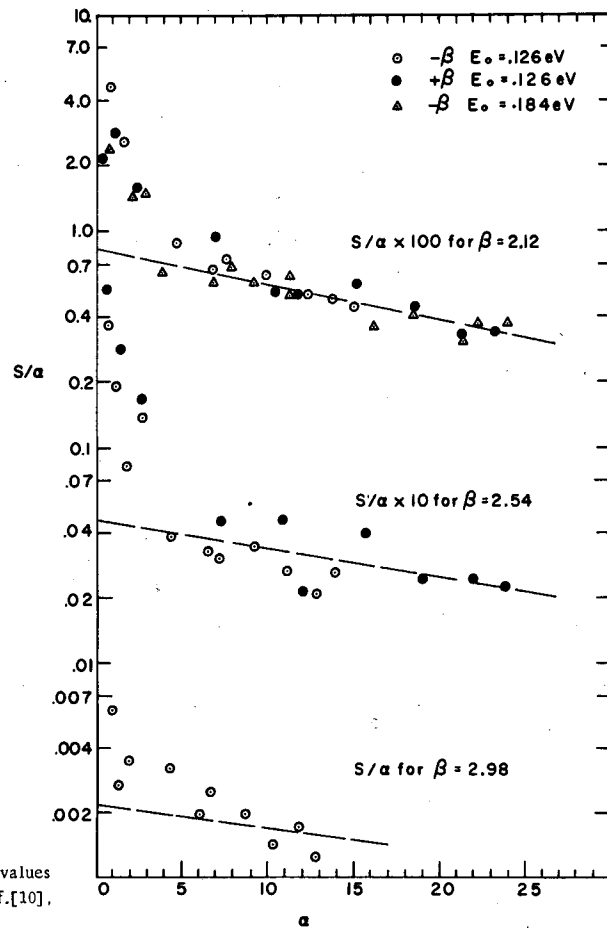


Fig. 3 and 4

Scattering law results for UO_2 at 20°C in the form S/a versus a for fixed values of β . Definition of S , a and β is given by Eqs. (3), (4), (5) and (6) of Ref. [10], where $\sigma_b = 9.0 \text{ b}$ and $M = 1.009 \text{ amu}$.



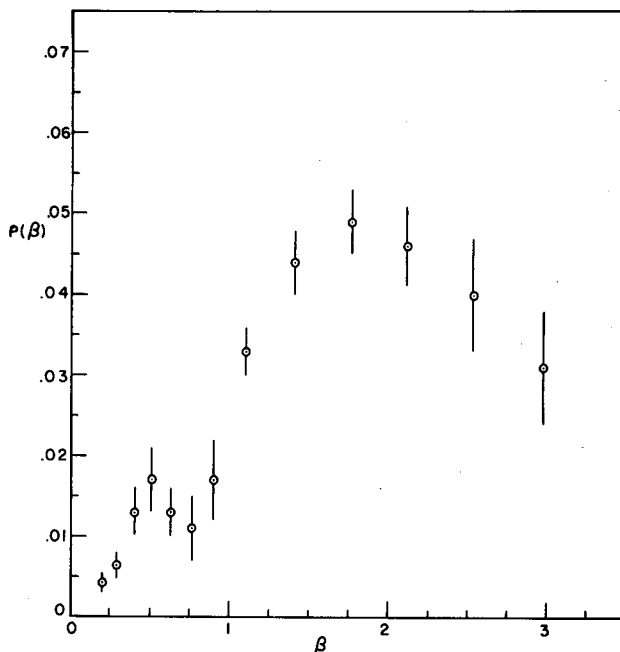


Fig. 5

Experimental frequency distribution of one uranium atom and one oxygen atom based on Eqs. (4) and (5) of the text with $A = 1$.

a significant fraction of the total. Anharmonic forces in the UO_2 crystals and interference effects may also contribute to this sharp rise but probably less than the multiple scattering. Interference effects at $\beta = 0$ makes S as a function of α follow the structure factor. At small α and $\beta \neq 0$ the interference effects probably make S_d oscillate about $S_d = 0$, the oscillation following the structure factor but damped as β increases. This does not show up consistently in the results, however; this absence may be due to poor resolution in $\Delta\alpha/\alpha$ at low α where the interference effects are expected. For $\alpha \geq 5$ ($Q = 8(A)^{-1}$) (See Figs. 2, 3 and 4) the effect of crystal orientation should be negligible, i. e. the neutron "sees" only one nucleus at a time, thus $S = S_s$ only.

The slopes of the lines in the extrapolation of S/α versus α were constrained to be a smooth function of β . This may smooth the $\rho(\beta)$ function more than is warranted but the statistical accuracy makes this procedure necessary. The errors indicated on the $\rho(\beta)$ points in Fig. 5 represent approximately one standard deviation assuming the slope of the line used in the extrapolation is correct.

The contributions of the oxygen and the uranium to the area under $\rho(\beta)$ in Fig. 5 are by Eq. (6a) 0.063 and 0.004 respectively. The total area to $\beta = 3.0$ of the experimental $\rho(\beta)$ is approximately 0.086. This discrepancy is slightly larger than the probable error of $\sim 25\%$ on the absolute cross-

section scale, especially since more area above $\beta = 3.0$ is indicated. Multiphonon effects are probably important above $\beta \sim 2$ and may not be adequately removed by the extrapolation procedure. This effect would raise the measured $\rho(\beta)$ for $\beta > 2$ and possibly account for the normalization discrepancy.

Finally it is interesting to note that ratios of the mean energies and areas of the peaks at $\beta = 0.5$ and $\beta = 1.8$ are roughly those indicated by a crude model which assumes identical but uncoupled forces on the uranium atoms and the oxygen atoms. This would then imply that the peak at $\beta = 0.5$ is due to uranium atom motions and the one at $\beta = 1.8$ is due to oxygen atom motions.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. P. A. Egelstaff for discussions and comments on the results presented here. They would like to thank C. Duffil, B. Marlow and R. B. Werden for technical assistance and I. Baksys, H. Greenspan and R. J. Royston of the Argonne National Laboratory for the data processing of some of these results.

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DISCUSSION

G. DOLLING: Should the $p(\beta)$ curve you showed have some particular area? If so, what is it and does it agree with the theoretically expected value?

I. M. THORSON: The area should be 0.067 and experimentally we find 0.086. This is just on the limits of our error. There may be multiphonon effects here as well.

D. T. GOLDMAN: Might there exist a higher energy oscillation of the oxygen atoms about the uranium? This could influence your results in the high energy transfer range.

I. M. THORSON: I think the mass of oxygen is too large for this ZrH-like energy distribution to be probable at relatively high energies.

B. N. BROCKHOUSE: I would like to suggest that the function $p(\beta)$ be given some other name than frequency distribution. Except for very simple monatomic crystals $p(\beta)$ is not the frequency distribution as ordinarily defined. Perhaps "spectral function" or some similar term might be better.

P. SCHOFIELD: When there is more than one type of atom present $p(\beta)$ is not even the spectral function of Singwi, but some combination of the spectral functions of each type of atom. This may well be the reason why the normalization condition is violated in such cases.

FRÉQUENCES DE VIBRATIONS OPTIQUES DANS LA FLUORINE CaF_2

D. CRIBIER, B. FARNOUX ET B. JACROT
CENTRE D'ÉTUDES NUCLÉAIRES DE SACLAY
FRANCE

Abstract — Résumé — Аннотация — Resumen

FREQUENCY OF OPTICAL VIBRATIONS IN FLUORITE (CaF_2). The authors studied the optical vibration frequencies of fluorite. Particular attention was paid to determining the frequencies at $q \approx 0$. The use of a time-of-flight basis of 8,30 m and a resolution of $6 \mu\text{s/m}$ permitted the frequencies to be determined to an accuracy of 1%. The findings were as follows: Raman frequency $\nu_R = 9,66 \times 10^{12}$ c/sec infra-red absorption frequency (transverse vibration) $\nu_T = 7,75 \times 10^{12}$ c/sec; longitudinal infra-red frequency $\nu_L = 14,36 \times 10^{12}$ c/sec. Within experimental errors, the Lyddane-Sachs-Teller correlation was verified.

FRÉQUENCES DE VIBRATIONS OPTIQUES DANS LA FLUORINE CaF_2 . On a étudié les fréquences de vibration optique de la fluorine. Un soin particulier a été apporté à la détermination des fréquences à $q \approx 0$. L'utilisation d'une base de temps de vol de 8,30 m et d'une résolution de $6 \mu\text{s/m}$ a permis de déterminer les fréquences avec une précision de 1%. On trouve: fréquence Raman $\nu_R = 9,66 \cdot 10^{12}$ c/s; fréquence d'absorption infra-rouge (vibration transversale) $\nu_T = 7,75 \cdot 10^{12}$ c/s; fréquence infra-rouge longitudinale $\nu_L = 14,36 \cdot 10^{12}$ c/s. La relation de Lyddane-Sachs-Teller est vérifiée aux erreurs d'expérience près.

ЧАСТОТА ОПТИЧЕСКИХ КОЛЕБАНИЙ ВО ФЛЮРИТЕ (CaF_2). Авторы изучали частоты оптического колебания флюорита. Особое внимание было уделено установлению частот $q \approx 0$. Использование времени пролета расстояния 8,3 м и разрешающей способности $6 \mu\text{сек/м}$ дало возможность установить частоты с точностью до 1%. Были обнаружены: частота Раман $\nu_R = 9,66 \cdot 10^{12}$ колебаний в секунду; частота инфракрасного поглощения поперечное колебание $\nu_T = 7,75 \cdot 10^{12}$ колебаний в секунду; частота продольного инфракрасного поглощения $\nu_L = 14,36 \cdot 10^{12}$ колебаний в секунду. Формула Lyddane-Sachs-Teller правильна в пределах экспериментальных погрешностей.

FRECUENCIAS DE VIBRACIÓN ÓPTICA EN EL FLUORURO DE CALCIO. Los autores han estudiado las frecuencias de vibración óptica del fluoruro de calcio. Han prestado especial atención a la medida de las frecuencias para $q \approx 0$. La utilización de una base de tiempo de vuelo de 8,30 m y de una resolución de $6 \mu\text{s/m}$ ha permitido determinar las frecuencias con una precisión del 1%. Los resultados son: frecuencia Raman $\nu_R = 9,66 \cdot 10^{12}$ Hz; frecuencia de absorción infrarroja (vibración transversal) $\nu_T = 7,75 \cdot 10^{12}$ Hz; frecuencia infrarroja longitudinal $\nu_L = 14,36 \cdot 10^{12}$ Hz. La validez de la relación de Lyddane-Sachs-Teller se ha verificado dentro del margen de error experimental.

1. INTRODUCTION

Une longue étude expérimentale conduit à préciser les valeurs des fréquences «principales» du cristal et à ébaucher les courbes de dispersion des phonons pour les directions [100] et [111]. Les fréquences «principales» des ondes qui polarisent électriquement le cristal sont dans le rapport prévu par Lyddane, Sachs et Teller.

2. EXPÉRIENCES

Le cristal de fluorine a trois atomes par motif cristallin. Donc dans la représentation des phonons en courbes de dispersion, à chaque direction

du vecteur d'onde $\underline{q}$ seront associées neuf courbes de dispersion; si la direction du vecteur $\underline{q}$ est parallèle à un axe de symétrie [100] ou [111], les vibrations de polarisation mécanique transversale sont dégénérées deux par deux; il reste six courbes de dispersion: deux courbes de dispersion des phonons «acoustiques», quatre courbes de dispersion des phonons «optiques».

Pour les petites valeurs du vecteur d'onde ($|\underline{q}| < 1/10 |\underline{q}|_{\text{max}}$) les phonons «optiques» se classent en deux types, suivant le mode de vibration du motif cristallin: le premier type de vibration induit une modulation à la fréquence caractéristique du phonon, du tenseur de polarisabilité du motif cristallin; il est responsable de l'effet Raman observé dans la fluorine [1]; les ondes de ce type de polarisation mécanique transversal ou longitudinal ont même fréquence ν_R ; le second type polarise électriquement le milieu et ces ondes de polarisation électrique ont des fréquences ν_L et ν_T différentes suivant que la vibration est longitudinale ou transversale; les ondes transversales sont responsables de l'absorption du rayonnement infra-rouge par le cristal. LYDDANE, SACHS et TELLER [2] prévoient que, pour ce type d'onde et pour ce cristal qui peut être alors assimilé à un cristal biatomique, $\nu_L/\nu_T = (\epsilon_0/n^2)^{1/2} = 1,82$; ϵ_0 est la constante diélectrique statique; elle est connue à 2% [3]; n est l'indice de réfraction pour la lumière visible, il est défini à mieux que 0,5% [4].

Nous avons tenté de mesurer avec une précision comparable ν_L et ν_T et ν_R souvent appelés fréquences «principales» du cristal. Le tableau I ré-

TABLE I

COMPARAISON DE FRÉQUENCES MESURÉES PAR LES NEUTRONS
ET PAR D'AUTRES TECHNIQUES

Fréquence	Autres Techniques	Diffusion inélastique des neutrons
ν_R	Effet Raman $9,66 \cdot 10^{12}$ c/s ($321,5 \pm 1 \text{ cm}^{-1}$)	$9,67 \cdot 10^{12} \pm 0,10 \text{ c/s}$
ν_T	Absorption infra-rouge [5] $51,5 \mu$	$7,75 \cdot 10^{12} \pm 0,07 \text{ c/s}$ (40μ)
ν_L	Diffusion des rayons X [6] $7,6 \cdot 10^{12}$ c/s.	$14,36 \cdot 10^{12} \pm 0,20 \text{ c/s}$

sume les résultats obtenus comparés aux valeurs données par les autres techniques de mesures.

Le rapport ν_L/ν_T des valeurs des fréquences obtenues par diffusion des neutrons est égal à 1,85. La relation de Lyddane, Sachs et Teller est donc bien vérifiée aux erreurs d'expérience près.

Pour mesurer avec précision ces phonons de grande énergie, nous avons utilisé un spectromètre à temps de vol; l'énergie des neutrons incidents était de $4,5 \cdot 10^{-3} \pm 3 \cdot 10^{-4}$ eV; les neutrons diffusés avaient des énergies de l'ordre de $3 \text{ à } 6 \cdot 10^{-2}$ eV; énergies mesurées par temps de vol sur une base de 830 cm; la résolution étant de $6 \mu\text{s/m}$.

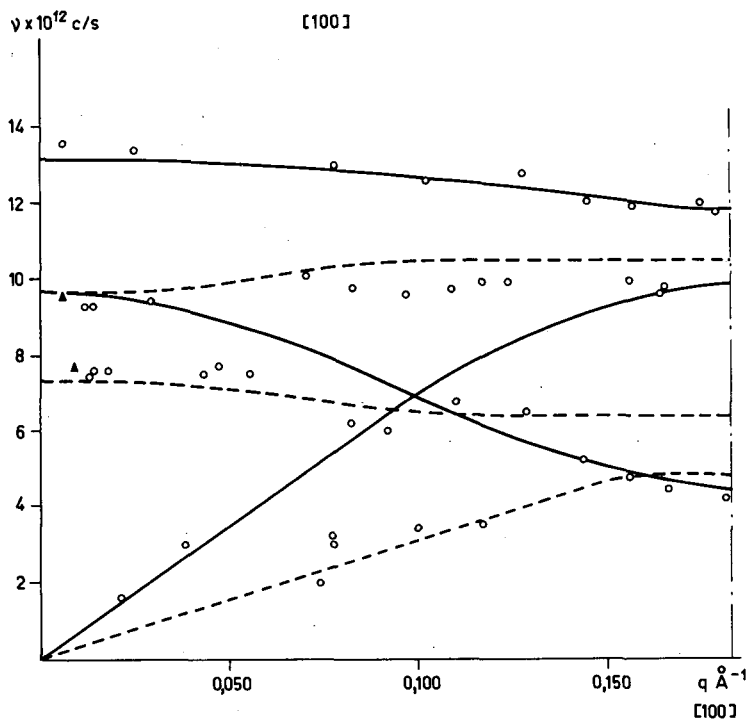


Figure 1

Courbes de dispersion dans la direction $[100]$ dans CaF_2 .

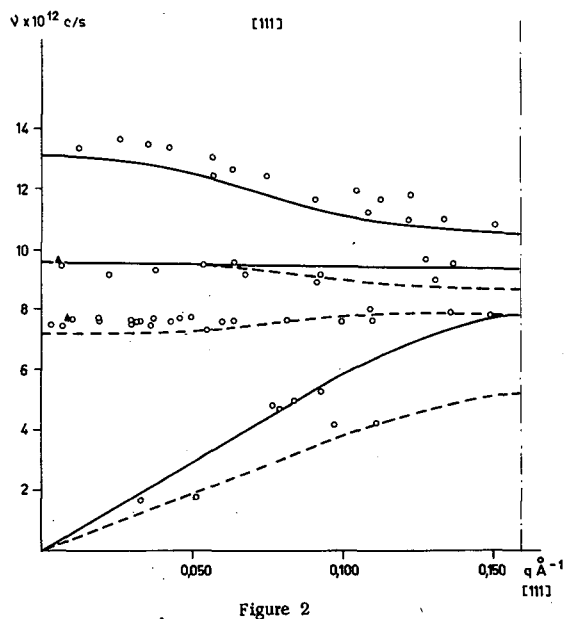


Figure 2

Courbes de dispersion dans la direction $[111]$ dans CaF_2 .

Cette haute résolution conduit à des temps d'expérience très grands, même en utilisant une source froide de neutrons [7]. Aussi pour tracer les courbes de dispersion, nous avons utilisé une base de temps de vol de 400 cm environ, une résolution de 25 μ s/m, sacrifiant la précision à l'intensité.

Les figures 1 et 2 donnent les points expérimentaux comparés aux courbes données par GANESAN et SHRINIVASAN [8]. Ces courbes de dispersion sont calculées à partir d'un modèle de champ de force cristallin qui décrit les interactions entre proches voisins à l'aide de tenseurs dont les composantes sont ajustées pour rendre compte des valeurs des constantes élastiques et des fréquences «principales» connues; les interactions coulombiennes à grande distance sont décrites en affectant à chaque ion une charge effective dont la valeur est aussi ajustée sur les données expérimentales.

Les fréquences «principales» choisies par Ganesan et Shrinivasan pour ajuster leur modèle avaient des valeurs plus faibles que celles déterminées par nos expériences. Mais il semble que ce modèle simple soit, dans le cas de la fluorine, une bonne approximation pour calculer le spectre de vibration du réseau.

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THE TEMPERATURE DEPENDENCE OF SOME NORMAL MODES IN STRONTIUM TITANATE

R. A. COWLEY*

ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

THE TEMPERATURE DEPENDENCE OF SOME NORMAL MODES IN STRONTIUM TITANATE. The frequency/wave vector dispersion curves have been measured for some of the normal modes in strontium titanate along [100]. The experiments were performed using the triple axis spectrometer at Chalk River, usually with the constant Q technique. Of particular interest is the temperature dependence of the lowest transverse optical branch, which has been studied at two temperatures. The frequencies (units 10^{12} cycles/s) at $q = 0$ are 1.27 ± 0.05 at 90°K and 2.73 ± 0.05 at 296°K . The dispersion curves have maximum frequencies (4.2 at 90°K , 4.4 at 296°K) near the middle of the zone; at the zone boundary the frequencies are about 3.5. The anomalous temperature dependence of the $q = 0$ mode has been predicted by Cochran, and the magnitude of the change with temperature, which may be obtained from the temperature dependence of the dielectric constant, is in good agreement with the theory. The non-infrared active mode has been observed and has a frequency at $q = 0$ of 7.95 ± 0.15 .

VARIATIONS DE CERTAINS MODES NORMAUX DANS LE TITANATE DE STRONTIUM, EN FONCTION DE LA TEMPÉRATURE. L'auteur a mesuré les courbes de dispersion fréquence/vecteur d'ondes pour certains modes normaux dans le titanate de strontium, le long de la direction [100]. Les expériences ont été faites à Chalk River en employant le spectromètre triaxial et en se fondant sur la méthode du Q constant. Les variations en fonction de la température qui présentent un intérêt particulier sont celles de la branche optique transversale inférieure, qui ont été étudiées à deux températures différentes. Les fréquences (en unités de 10^{12} cps) pour $q = 0$ sont de 1.27 ± 0.05 à 90°K et de 2.73 ± 0.05 à 296°K . Les courbes de dispersion présentent des maxima de fréquences (4,2 à 90°K et 4,4 à 296°K) au voisinage du milieu de la zone; aux limites de zone, les fréquences sont d'environ 3,5. L'anomalie dans les variations en fonction de la température pour le mode $q = 0$ a été prévue par Cochran et la grandeur de cette anomalie en fonction de la température, que l'on peut obtenir grâce aux variations de la constante diélectrique en fonction de la température, est en bon accord avec la théorie. Le mode d'activité non infrarouge a été observé et il possède une fréquence de 7.95 ± 0.15 pour $q = 0$.

ЗАВИСИМОСТЬ НЕКОТОРЫХ НОРМАЛЬНЫХ СОСТОЯНИЙ В ТИТАНАТЕ СТРОНЦИЯ ОТ ТЕМПЕРАТУРЫ. Были измерены кривые рассеяния вектора "частота/волна" для некоторых нормальных состояний в титанате стронция вдоль оси 100. Опыты были проведены при помощи имеющегося в Чок Ривере трехосевого спектрометра обычно по методу постоянного Q . Особый интерес представляет зависимость от температуры нижней поперечной оптической кривой, которая была изучена при двух температурах. Частоты (в единицах 10^{12} циклов в секунду) при $q = 0$ равны 1.27 ± 0.05 при 90°K и 2.73 ± 0.05 при 296°K . Кривые рассеяния имеют максимальные частоты (4,2 при 90°K и 4,4 при 296°K) вблизи средней части зоны; по краям зоны частоты составляют приблизительно 3,5. Аномальная температурная зависимость для состояния $q = 0$ была предсказана Кохраном, а величина изменения в зависимости от температуры, которая может быть получена на основании зависимости диэлектрической константы от температуры, хорошо согласуется с теорией. Наблюдалось также неинфракрасное активное состояние с частотой, равной 7.95 ± 0.15 при $q = 0$.

INFLUENCIA DE LA TEMPERATURA SOBRE ALGUNOS MODOS NORMALES EN EL TITANATO DE ESTRONCIO. El autor ha medido en el titanato de estroncio las curvas de dispersión frecuencia/vector de onda para

* Visitor from the Cavendish Laboratory, Cambridge.

algunos modos normales en la dirección [100]. Efectuó los experimentos con el espectrómetro triaxial de Chalk River, en general según el método de Q constante. Ofrece particular interés la variación de la rama óptica transversal más baja en función de la temperatura, que se ha estudiado para dos valores de ésta. Las frecuencias (tomando 10^{14} Hz como unidad) para $q = 0$ son $1,27 \pm 0,05$ a 90°K y $2,73 \pm 0,05$ a 296°K . Las curvas de dispersión presentan frecuencias máximas ($4,2$ a 90°K , $4,4$ a 296°K) hacia el centro de la zona. En el límite de ésta las frecuencias son de 3,5, aproximadamente. La anómala influencia de la temperatura sobre el modo $q = 0$ ha sido prevista por Cochran, y la magnitud de la variación con la temperatura, que puede deducirse de la modificación de la constante dieléctrica en función de la temperatura, concuerdan satisfactoriamente con los valores calculados teóricamente. Se ha observado el modo activo no infrarrojo, que tiene una frecuencia de $7,95 \pm 0,15$ para $q = 0$.

I. INTRODUCTION

Measurements have been made, by neutron spectrometry, of the frequency wave-vector dispersion relations in a material, strontium titanate, whose properties are very similar to those of a ferroelectric. In particular, the lowest frequency transverse optic mode has been studied at several different temperatures. COCHRAN [1] has associated this mode with the temperature dependence of the static dielectric constant, and these measurements are in good agreement with the dielectric constants measurements [2] as interpreted by the theory.

Strontium titanate was chosen as a suitable crystal in which to study the lattice dynamics of a ferroelectric for several reasons:

- (1) The static dielectric constant is large and follows the familiar Curie Law temperature dependence about 70°K . The Curie temperature (about 35°K) enables a considerable change in the frequency of the lowest transverse optic mode to be observed at easily accessible temperatures.
- (2) The nuclear and chemical properties are good.
- (3) The structure, perovskite, is cubic and quite simple compared with that of most ferroelectrics.
- (4) Excellent single crystals were provided by the Titanium Division of the National Lead Company.

II. EXPERIMENTAL DETAILS AND THE DISPERSION CURVES

The crystal, which was used for most of the experiments, was a 150 carat boule of strontium titanate with the [100] axis along the length of the boule. It was mounted with this axis vertical in a metal cryostat, and was either cooled or heated from above.

The triple axis crystal spectrometer [3] at the NRU reactor at Chalk River was used for the experiments. The spectrometer was mainly employed in the "constant Q " mode of operation [3]. Energy distributions are taken while the wave vector transfer Q is kept constant, and the frequencies ν and reduced wave vectors q are given by the conservation equations, $h\nu = E_0 - E'$, and $Q = k_0 - k'$. E_0 and E' are the energies, and k_0 , k' the wave vectors of the incoming and outgoing neutrons respectively, while $Q = 2\pi\tau - q$, and τ is a reciprocal lattice vector.

A few neutron groups were obtained by an alternative procedure [3]; the energy transfer is kept constant, and the wave vector transfer $\underline{Q}$ is varied so that the reduced wave vector $\underline{q}$ is always in a desired direction, in this case along the direction [100] in the reduced zone. This method was particularly useful for those branches where frequency changes rapidly with the wave vector.

Strontium titanate has five transverse branches along the symmetric [100] direction. The dispersion curves of four of these branches have been measured at 90°K and are shown in Fig. 1. The accuracy of the measure-

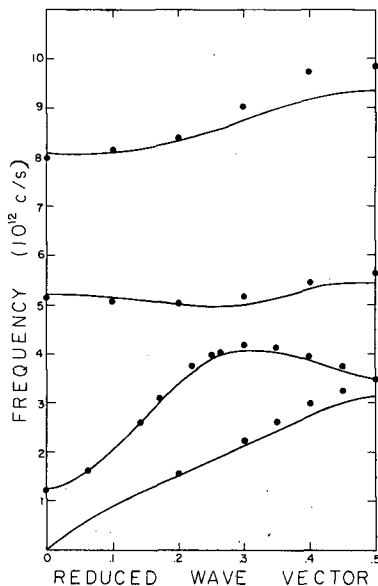


Fig. 1

The transverse dispersion relations along [100] at 90°K. The solid line shows the calculated dispersion relations of a rigid ion model.

ments is probably about the size of the points in the figure. The measurements suggest that the transverse acoustic and lowest transverse optic branches are degenerate at the zone boundary, within the accuracy of the experiments. We do not however, believe that this is a symmetry requirement of the perovskite structure.

The frequencies, at $\underline{q} = 0$, of the two lowest transverse optic modes have been measured by infra-red techniques [4, 5] and are in good agreement with the measurements described here. The highest transverse optic mode shown in Fig. 1 is the degenerate mode at $\underline{q} = 0$, and its frequency cannot be obtained from infra-red measurements. The fifth transverse branch has not been observed using neutrons, but infra-red measurements show a mode with a frequency of $16.4 \cdot 10^{12}/s$.

Some longitudinal modes have also been studied but the measurements are not yet complete, and are not presented in this paper.

III. THE TEMPERATURE DEPENDENCE OF THE LOWEST TRANSVERSE OPTIC MODE

A study has been made of the temperature dependence of the lowest transverse optic mode. Fig. 2 shows the dispersion relations of the whole branch at 90°K and 296°K. At the zone boundary, the frequency is almost the same at both temperatures.

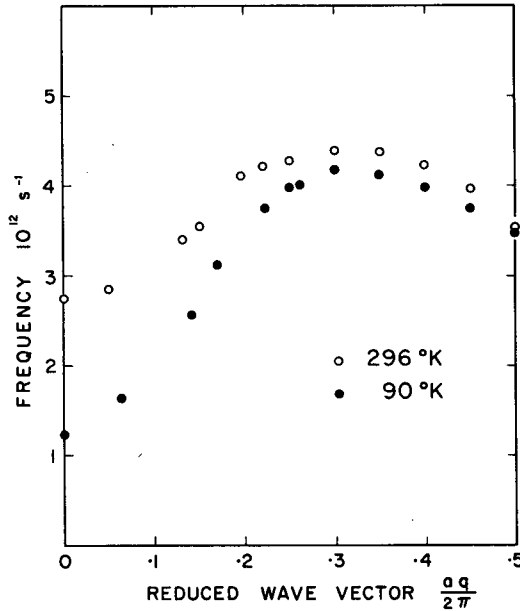


Fig. 2

The dispersion curve of the lowest frequency transverse optic branch along [100] at 90°K and 296°K.

The LYDDANE, SACHS and TELLER formula [6], connecting the frequencies of the optical modes at $q = 0$ and the dielectric constants of the crystal, has been extended by COCHRAN [1], to cubic crystals with more than two atoms in the unit cell. The ratio of the static dielectric constant, ϵ_0 , to the high frequency dielectric constant, ϵ , is given by

$$\frac{\epsilon}{\epsilon_0} = \prod_i \left(\frac{\omega_T^i}{\omega_L^i} \right).$$

ω_T^i and ω_L^i are the frequencies at $q = 0$ of the transverse and longitudinal modes of the i th optical branch, and the product is taken over all the optical branches. The static dielectric constant follows a Curie Law,

$$\epsilon_0 = C/T - T_c,$$

so that if only the lowest transverse optic mode is temperature dependent, then

$$\omega_T^2 = K(T - T_c) .$$

At the ferroelectric transition $\omega_T = 0$, and the crystal is unstable against this mode of vibration.

Fig. 3 shows a plot of the frequencies squared against temperature for the lowest frequency transverse optic branch at $q = 0$. The straight line

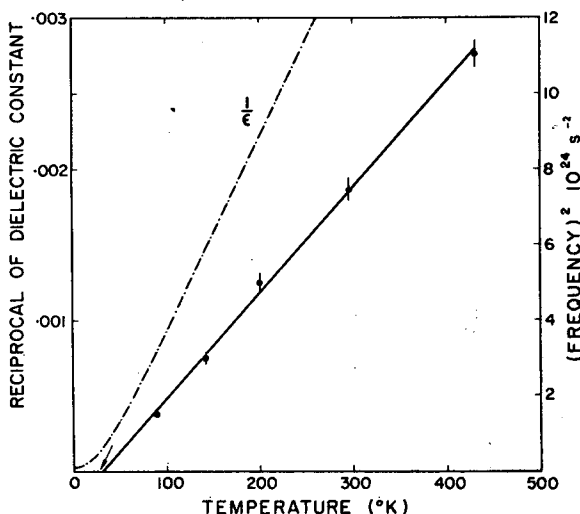


Fig. 3

A plot of the square of the frequency of the lowest $q = 0$ transverse optic mode against temperature. The solid line is a linear regression line through the points and gives a Curie temperature of $32 \pm 5^\circ\text{K}$. The other line shows the reciprocal of the dielectric constant from the measurements

of MITSUI and WESTPHAL [2].

gives a Curie temperature of $32 \pm 5^\circ\text{K}$. Measurements of the dielectric constant [2] give a Curie temperature of 28°K and of dielectric loss [7] a temperature of 37°K .

IV. A RIGID ION MODEL OF STRONTIUM TITANATE

Models have been obtained which give reasonable agreement with the measurements of the transverse dispersion relations at 296°K and 90°K . These models are rigid ion models in which the ions interact through long-range electrostatic forces and short-range repulsive forces.

The electrostatic forces are calculated by means of Coulomb coefficients; these dimensionless coefficients were first introduced by KELLER-MANN [8] and calculated for the alkali halides. The corresponding coefficients for the perovskite structure have been calculated [9] using the Edsac II computer at the Cambridge University Mathematical Laboratory.

The short-range forces were introduced between neighbouring ions, titanium and oxygen, strontium and oxygen, and the different types of oxygen ion. Two parameters were used to specify each of these interactions; they were defined as the force constant parallel and perpendicular to the line joining the interacting ions.

This model then includes eight arbitrary parameters, which were fitted to experimental measurements of the elastic constants [10], and to the neutron measurements. There are very few linear relations between the force constants and these measurements; in general the frequencies of the normal modes are eigen-values of a (5×5) matrix so that analytic solutions cannot easily be obtained. The fitting was therefore performed largely by trial and error using the Datatron computer at Chalk River.

The models are shown by the solid lines in Figs. 1 and 4 and the agreement with experiment is fairly satisfactory. However, there are consider-

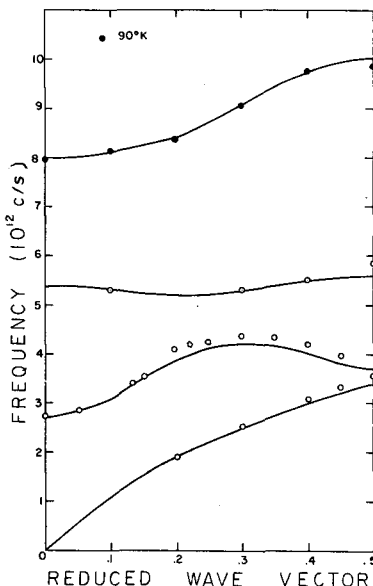


Fig. 4

The transverse dispersion relations along [100] at 296°K.
The solid line shows the dispersion relations which were calculated
using a rigid ion model.

able discrepancies with the longitudinal modes, and with the infra-red measurement of the fifth transverse optic branch at $q = 0$. These discrepancies are not surprising because the models neglect the polarizability of the ions, and it has been shown [11] that this polarizability must be included to obtain realistic models of the lattice dynamics of ionic crystals.

The parameters of the model give the ionic charge on the strontium ion as 2 electronic charges, while that on the titanium ion is about 1.3 electronic charges, much lower than the formal charge of 4. The anomalous behaviour

of the lowest transverse optic mode is obtained by increasing the titanium-oxygen interaction by about 10% at 90°K.

V. DISCUSSION

The measurements which have been described demonstrate that the temperature dependence of the static dielectric constant is associated with the temperature dependence of the lowest frequency transverse optic mode. A suitable approach to study the problem of ferroelectricity is therefore, in terms of the lattice dynamics of the crystal.

The modes suggest that the lowest frequency transverse optic mode at $q = 0$ is a vibration of the titanium ion against the oxygen octahedra and strontium ion; the displacements [12] of the ions in the transition of barium titanate suggest that a similar mode is associated with the transition in that crystal. The ferroelectric properties of both crystals may therefore be associated with the temperature dependence of the titanium oxygen short-range interaction.

The problem of obtaining a model of strontium titanate from the neutron measurement emphasizes the importance of measuring the intensities of the neutron groups. The eigenvectors and the elements of the dynamical matrix may then be calculated as described by BROCKHOUSE et al. [13].

It is hoped to continue both the experimental and theoretical work on strontium titanate in the hope of obtaining a more realistic model of this crystal and of the phenomenon of ferroelectricity in these titanates.

ACKNOWLEDGEMENTS

I am grateful to both Drs. W. Cochran and B. N. Brockhouse, for their help and encouragement throughout this work, to the Titanium Division of the National Lead Company for providing the crystals, and to the Department of Scientific and Industrial Research for the award of a maintenance grant.

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DISCUSSION

H. PALEVSKY: I don't understand the calculation by which you made your theoretical lines match your points. Did you use any data other than the neutron data?

R. A. COWLEY: The model was an eight-parameter rigid ion model. The parameters were chosen to fit the elastic constants and the measured dispersion curves by using a trial-and-error method.

H. PALEVSKY: Did you get a reasonable fit?

R. A. COWLEY: Yes, we did. However, the whole purpose of the calculation was to give some idea of the order of magnitude involved. We realized that polarizability as an important factor and this cannot be taken into account if only a rigid ion model is used.

B. JACROT: Have you observed any critical scattering as you approach the Curie point?

R. A. COWLEY: No, we have not, although we have not looked into this matter. However, if you will examine Fig. 4 for example, I think you will agree it would be extremely difficult to see any critical scattering, because it would get lost in the acoustic modes.

W. COCHRAN: Prior to the experiment just described by Cowley, an unsuccessful attempt was made at Cambridge to observe the scattering of X-rays by the transverse optical mode in barium titanate. I believe that the scattering by the T. O. mode is just another way of describing critical scattering in this case. Critical scattering of X-rays by other ferroelectric crystals has been detected by Mitsui.

LATTICE DYNAMICS OF SOME AMMONIUM SALTS BY INVERTED FILTER METHOD

K. MIKKE AND A. KROH

INSTITUTE FOR NUCLEAR RESEARCH, LABORATORY IB, SWIERK
POLAND

Abstract — Résumé — Аннотация — Resumen

LATTICE DYNAMICS OF SOME AMMONIUM SALTS BY INVERTED FILTER METHOD. Energy distributions of initially monochromatic neutrons scattered inelastically at 90° for ammonium halides and ammonium nitrate were measured by the inverted filter (beryllium and graphite) method.

At room temperature two sharp peaks were obtained for NH_4Br and NH_4Cl in the range 10 - 110 meV. For NH_4F three peaks were observed in this range, and this was confirmed by a separate measurement on the cold neutron facility. For NH_4I and NH_4NO_3 only a broad distribution was obtained. The result for NH_4I seems to be consistent with the assumption of a free rotation of an ammonium ion in this crystal at room temperature.

Measurements at -20°C , -60°C and -150°C were also made for these samples. For NH_4I sharp peaks appear at temperatures lower than -20°C . For NH_4NO_3 at -60°C the distributions are still like those at room temperature. Temperature variations of intensities for several of the observed peaks were also measured and compared with some theoretical predictions. Additional peaks appear for all halides at lower temperatures, and their nature is being investigated.

The results are compared with other data obtained indirectly by other methods, and an attempt to give a qualitative explanation is made.

ÉTUDE DE LA DYNAMIQUE DES RÉSEAUX DE QUELQUES SELS D'AMMONIUM PAR LA MÉTHODE DU FILTRE INVERSÉ. L'auteur a mesuré, par la méthode du filtre inversé (béryllium et graphite), les distributions en énergie de neutrons initialement monochromatiques diffusés inélastiquement à 90° dans des halogénures d'ammonium et dans du nitrate d'ammonium.

À la température ambiante, il a obtenu deux pics aigus pour NH_4Br et NH_4Cl dans la gamme des énergies allant de 10 à 110 meV. Pour NH_4F il a observé trois pics dans cette même gamme d'énergie; cette observation est confirmée par une mesure faite à l'aide de neutrons froids. Pour NH_4I et NH_4NO_3 , l'auteur n'a obtenu qu'une distribution large. Le résultat obtenu pour NH_4I semble être en bon accord avec l'hypothèse de la rotation libre d'un ion d'ammonium dans le cristal à la température ambiante.

L'auteur a fait également des mesures sur les échantillons pour des températures de -20°C , -60°C et -150°C . Dans NH_4I , des pics aigus apparaissent aux températures inférieures à -20°C . Dans NH_4NO_3 , à la température de -60°C , les distributions ressemblent encore à celles qui ont été obtenues à la température ambiante. Les variations d'intensité en fonction de la température pour quelques-uns des pics observés ont été mesurées et comparées aux prévisions théoriques.

D'autres pics apparaissent pour tous les halogénures aux basses températures; on en étudie actuellement la nature.

L'auteur compare les résultats avec d'autres données obtenues indirectement par d'autres méthodes et il essaie de donner une explication qualitative.

ОПРЕДЕЛЕНИЕ ДИНАМИКИ РЕШЕТКИ НЕКОТОРЫХ СОЛЕЙ АММОНИЯ МЕТОДОМ ИНВЕРТИРОВАННОГО ФИЛЬТРА. Распределение энергии первоначально монохроматических нейтронов, неупруго рассеянных под углом 90° , было измерено для галлидов аммония и нитрата аммония по методу инвертированного фильтра (из бериллия и графита).

При комнатной температуре были получены два резких пика для NH_4Br и NH_4Cl в диапазоне энергий от 10 до 110 мэв. Для NH_4F в этом диапазоне наблюдалось три пика, что было подтверждено независимым измерением на установке по получению холодных нейтронов. Для NH_4I и NH_4NO_3 было получено лишь приблизительное распределение. Результат для NH_4I , по-видимому, соответствует гипотезе свободного вращения ионов аммония в этом кристалле при комнатной температуре.

Для этих образцов были произведены также измерения при -20 , -60 и -150°C . Для NH_4J резкие пики появляются при температурах менее -20°C . Для NH_4NO_3 при -60°C распределения все еще аналогичны распределениям при комнатной температуре. Для ряда наблюдавшихся пиков были измерены также интенсивности изменений в зависимости от температуры, и эти изменения были сравнены с некоторыми теоретическими прогнозами.

При более низких температурах для всех галлоидных солей появляются дополнительные пики, характер которых исследуется в настоящее время.

Полученные результаты сравниваются с другими данными, полученными косвенным образом другими методами, и делается попытка дать им качественное объяснение.

ESTUDIO DE LA DINÁMICA RETICULAR DE ALGUNAS SALES DE AMONIO POR EL MÉTODO DEL FILTRO INVERTIDO. Los autores han medido, por el método del filtro invertido (berilio y grafito), las distribuciones energéticas de neutrones inicialmente monocromáticos dispensados inelásticamente a 90° en haluros de amonio y nitrato de amonio.

A la temperatura ambiente, han obtenido dos picos pronunciados para el NH_4Br y el NH_4Cl en el intervalo $10 - 110 \text{ meV}$. Los tres picos observados en ese intervalo en el caso del NH_4F han sido confirmados por medición independiente en el aparato de neutrones fríos. En el caso del NH_4I y del NH_4NO_3 , han registrado solamente una distribución amplia. El resultado referente al NH_4I parece compatible con la hipótesis de la rotación libre a temperatura ambiente de un ion amonio en este cristal.

Los autores han efectuado asimismo mediciones a -20°C , -60°C y -150°C con esas muestras. En el caso del NH_4I , aparecen picos muy acusados por debajo de -20°C . En lo que respecta al NH_4NO_3 , las distribuciones a -60°C siguen siendo análogas a las observadas a temperatura ambiente. También han medido, para algunos de los picos observados, las variaciones de la intensidad en función de la temperatura y las han comparado con algunas previsiones teóricas.

A temperaturas más bajas todos los haluros presentan otros picos cuya naturaleza se está investigando.

Los autores comparan esos resultados con otros datos obtenidos indirectamente por métodos distintos del citado y procuran explicarlos cualitativamente.

1. PHASE TRANSITIONS AND LATTICE DYNAMICS IN AMMONIUM HALIDES

Discontinuities of several properties like specific heat, dielectric constant, coefficient of expansion and piezoelectric effect are known to appear in ammonium halides at certain temperatures. The general classification of the phases occurring in ammonium halides was given recently by STEPHENSON [1]. The generalized phase diagram given in [1] is shown in Fig. 1, and the transition temperatures are listed in Table I.

In attempts to understand these phase transitions the explanation was put forward that motion [2] or orientation [3] of ammonium ion plays the decisive role in these transitions. While the transition from phase α to phase β seems to involve the change from free (phase α) to hindered (phase β) rotation [4, 5], the transitions $\beta - \gamma$, $\beta - \delta$ and $\gamma - \delta$ are thought to be due to the orientational ordering of NH_4^+ tetrahedra. As the tetragonal structure in the phase γ of ammonium halides is only a slight deformation of CsCl-type structure and seems to play a secondary role as compared with the ordering phenomena, the CsCl-type lattice is usually assumed for β , γ and δ phases and the same will be done in this paper. The two possible orientations of NH_4^+ tetrahedra within the CsCl cell are as shown in Fig. 2. The disordered β phase is characterized by the random distribution of orientations of ammonium ions. In the ordered γ and δ phases they align into antiparallel (γ phase) or parallel (δ phase) of the ammonium tetrahedra throughout the lat-

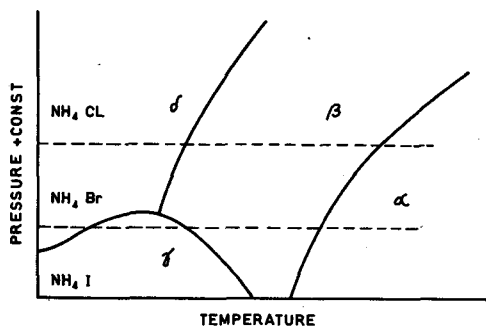


Fig. 1

Schematic generalized phase diagram showing the outline of the general correlation among the phases of the ammonium halides. If in a given halide the volume under pressure is decreased its behaviour becomes similar to that of another halide with an initially smaller molecular volume.

TABLE I

ATMOSPHERIC PRESSURE TRANSITION TEMPERATURES
OF THE AMMONIUM HALIDES
(the symbols in brackets mean the lattice types)

	$\alpha \rightarrow \beta$ (NaCl) (CsCl)	$\beta \rightarrow \gamma$ (CsCl) (Tetrag)	$\beta \rightarrow \delta$ (CsCl) (CsCl)	$\gamma \rightarrow \delta$ (Tetrag) (CsCl)
NH ₄ Cl	185°C		- 30°C	
NH ₄ Br	134°	- 38°		- 173°
NH ₄ I	-16°	- 42°		

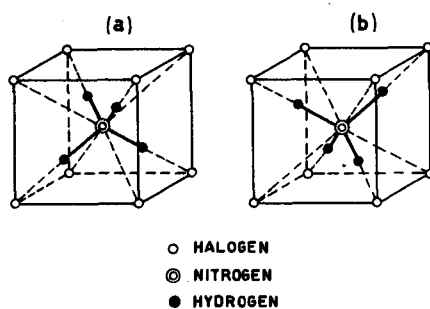


Fig. 2

Two possible orientations (a) and (b) of ammonium ion in a CsCl-type ammonium halide lattice. In the α phase the ammonium tetrahedra are oriented parallel from cell to cell, in the γ phase, anti-parallel, and in the β phase, at random.

tice. These views are supported by infra-red [4], neutron diffraction [5] and NMR [6] data.

For α phase the neutron diffraction [5] and infra-red [4] data seemed to support the "single approach" or "one-dimensional rotation" model in which one of the protons forms a strong bond to one of the surrounding halide atoms and the N-H-X axis become the axis of rotation of the whole ion. On the other hand the very recent extensive infra-red studies of NH_4I in phase α [7] indicate, however, that ammonium ion motions cannot be described in α phase either as fully free* rotation, or as the rotation of the ion around a N-H-X axis.

The first attempt to obtain some information on the dynamics of ammonium halides by neutron scattering was that of RUSH et al. [8], who have measured the total sub-thermal neutron cross section of ammonium halides as a function of neutron energy. It can be expected that the total neutron cross section in that neutron energy region is governed mainly by the inelastic processes, but the information on their nature cannot be extracted directly from this kind of data. Nevertheless the results obtained in [8] seem to confirm the assumption of a free rotation in ammonium iodide (α phase at room temperature, at which the measurements were made) and highly-hindered rotation in other ammonium halides (β phase at room temperature).

In the present work the methods of neutron spectrometry were applied for the direct investigation of the lattice dynamics of ammonium halides and ammonium nitrate. Eighteen peaks were found altogether at -150°C . The measurements were also made at -65°C , -20°C and at $+20^\circ\text{C}$. These results are listed in Table I. The obtained data also allowed the estimation of the temperature variations of the peak positions and widths. The observations of the temperature variations of the intensities of several peaks were also done.

Most of the determined transitions were either unknown before or known only in an indirect way from combination bands in infra-red and Raman effect studies. Use of neutron spectrometry in these investigations has all the advantages of an essentially new method. First, it is possible to check the known facts in a new way. But in addition some new facts can be revealed as neutrons are a tool which is not sensitive to restrictions inherent to infra-red and Raman techniques.

The application of neutron spectrometry for the studies of the dynamics of ammonium halides was initiated by BROCKHOUSE [9] whose measurements were, however, limited to the case of ammonium chloride only. Our preliminary data were presented in [10].

2. EXPERIMENT

The scattered neutron spectra were measured by the inverted filter (beryllium [9] and graphite) technique. Neutrons of definite energy E_0 and momentum k_0 were obtained by reflection from the (111) plane of an Al single

* The term "fully free rotation" will be used here to describe the rotation with 3° of freedom.

crystal*. After scattering from the sample by 90° they passed through a 15 cm thick beryllium filter or alternatively through a 15 cm thick graphite filter (interleaved with cadmium sheets) before entering the bank of BF_3 counters. Because of the high fast neutron background the fullest possible use of the advantages of this method was to be made. Thus a large detector solid angle (the scattered beam had a divergence of ca. 12°) and low pressure, not enriched BF_3 counters were used. In this way the detector efficiency for background neutrons was reduced appreciably without affecting its efficiency for cold neutrons transmitted by the filter.

The experimental set-up was basically the double crystal neutron spectrometer described in [11]. Some modifications were, however, necessary in order to avoid the excessive background and to meet the special requirements of the method.

Background considerations did not allow the use of the main spectrometer table either as a monochromator table or as the sample table. A remotely-controlled monochromator was therefore placed inside a large shield at the reactor beam hole and an additional rotary arm with the specimen table (rotating around its axis) was mounted on the main spectrometer arm. A thin monitor counter placed close to the sample was used both for measuring the incident monochromatic neutron intensity and (as an indicator) for incident neutron wavelength determination.

All samples were contained in airtight thin-walled Al containers. The measured transmission of the samples was in the range from 70% to 95%.

A cryostat constructed of expanded polystyrene (with Al multiple windows for incident and scattered beams) was used for low temperature measurements. To prevent moisture condensation on the sample and on the Al windows, a small stream of the evaporating cooling substance was directed into the volume containing the sample and was allowed to leak out via tiny holes in Al windows. The moisture condensing on the outer windows was blown away with a fan. A thermocouple for measuring the sample temperature was provided.

Considerable improvement of the resolution can be expected if the beryllium filter is replaced by a graphite one. Development of this modification of the method seemed to be desirable for more detailed investigations in the cases of fluoride and iodide where some indication of unresolved peaks was found and also for the measurements of the temperature variations of the peak widths. The expected resolution expressed in half width of the peak is of the order of 1 meV. The resolution actually obtained was estimated from the distribution for librational peak of ammonium bromide at -150°C , for which the intensity was highest. The results are shown as a dashed line inside the highest peak in Fig. 5. The half-width of this peak is ca. 3 meV. This figure compares well with the resolution measured in nearly identical conditions by means of the scattering from vanadium on a triple axis spectrometer. This shows that the main factor limiting the resolution is in our case the energy spread of the incident beam. The scattered intensity is reduced, however, by a factor of about 5 if a graphite filter is employed. The improved energy resolution of the incident beam would result in further inadmissible reduction of the scattered intensity. Thus no other improve-

* Kindly prepared by Mr. A. Modrzejewski of this laboratory.

ments were made and even in this case only a limited number of measurements with a reasonable statistics could be completed. The measurements are still under way.

3. RESULTS AND DISCUSSION

The measured angular distributions were converted into energy distributions and the corrections for room and fast neutron background applied. The slow neutron contamination of the monochromatic beam could be neglected for the energy range studied as checked by measuring the scattered intensity with the monochromator turned off the Bragg position.

The obtained neutron intensity versus incident neutron energy curves for NH_4I , NH_4Br , NH_4Cl , NH_4F and NH_4NO_3 are shown in Figs. 3-7. The

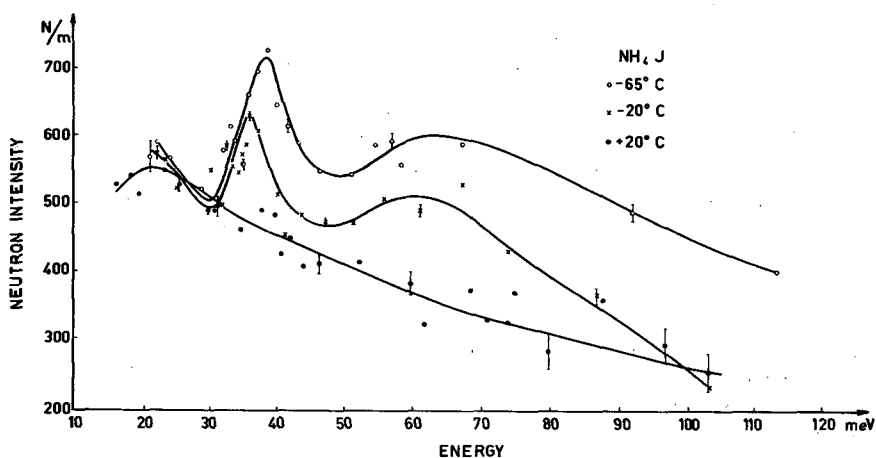


Fig. 3a

Energy distributions of neutrons scattered by ammonium iodide at various temperatures. Thick sample. The distributions at $+20^\circ\text{C}$ (filled circles), at -65°C (open circles) and at -20°C (crosses).

energy transfer is given by $\hbar\omega = E_0 - 3 \text{ meV}$, where E_0 is the incident neutron energy and 3 meV is the assumed value of the average energy of scattered and beryllium filtered neutrons. The energies corresponding to the peaks in the obtained distributions are collected in Table II.

Ammonium iodide

Ammonium iodide is the only ammonium halide which is in phase α at room temperature while other halides are in phase β at room temperature. It is expected that free rotation of NH_4^+ ion takes place in α phase and in β phase the motion of ammonium ion is librational in character. The evident difference in the shape of the room temperature distribution for ammonium iodide as compared with other halides indicates clearly that the NH_4^+ ion in

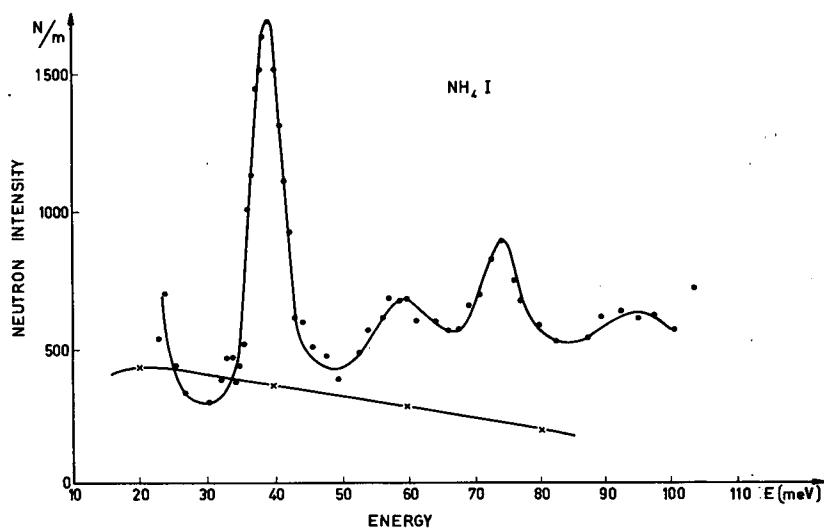


Fig. 3b

Energy distributions of neutrons scattered by ammonium iodide at various temperatures. Thick sample. The distribution at -150°C (filled circles). For comparison the distribution at $+20^\circ\text{C}$ is also plotted (crosses).

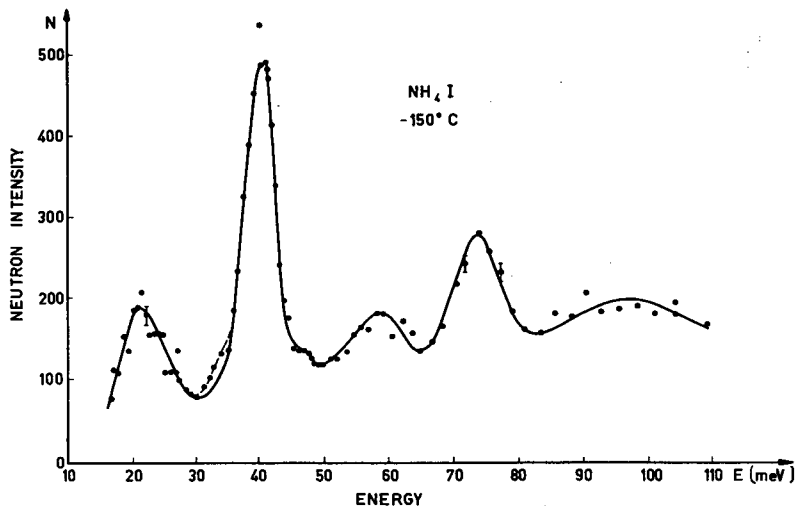


Fig. 3c

Energy distributions of neutrons scattered by ammonium iodide at various temperatures. Thin sample. The distribution at -150°C .

NH_4I possesses much higher freedom of motion than it has in other halides at that temperature.

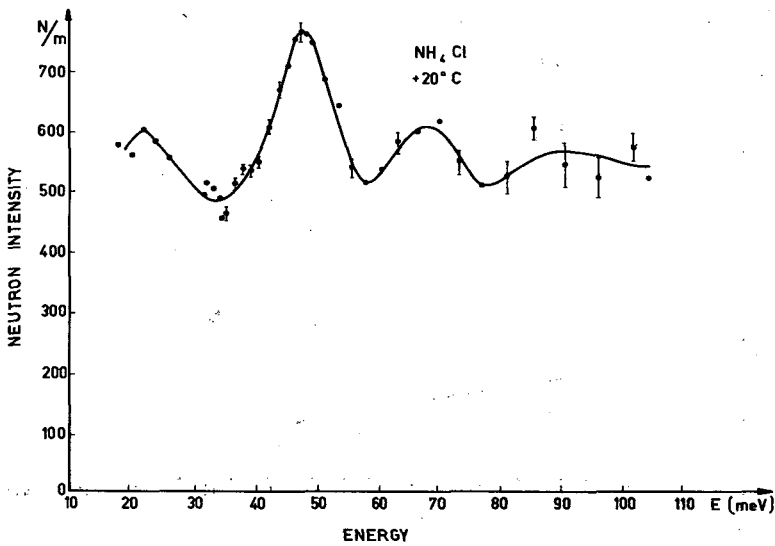


Fig. 4

Energy distribution of neutrons scattered by ammonium chloride at +20°C.

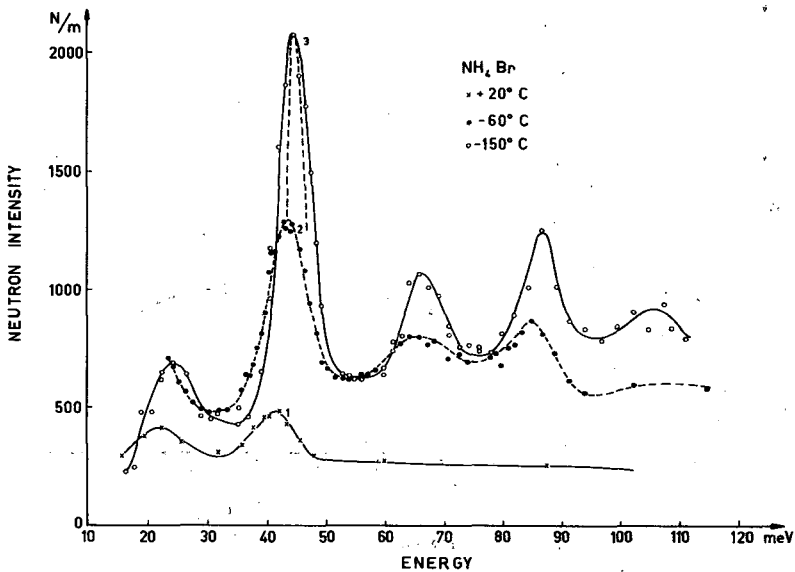


Fig. 5

Energy distributions of neutrons scattered by ammonium bromide at +20°C (crosses), at -65°C (filled circles) and at -150°C (open circles). The dashed line inside the highest peak is the distribution obtained with the graphite filter.

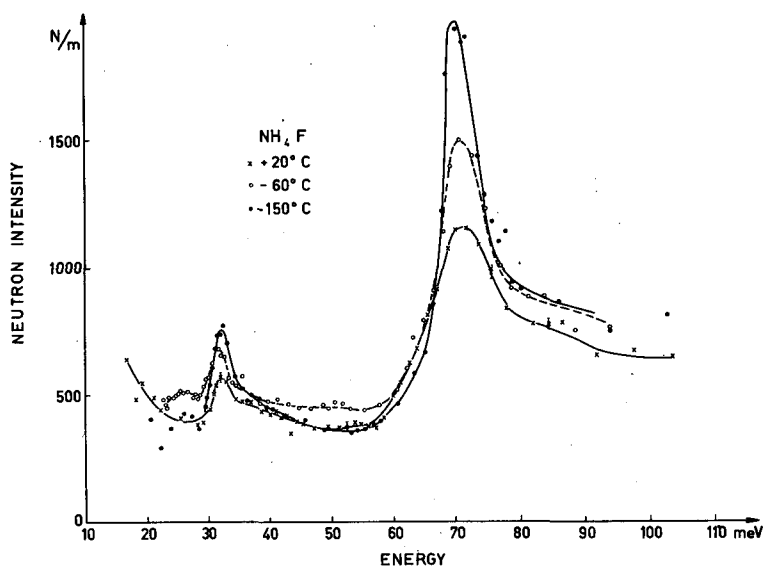


Fig. 6a

Energy distributions of neutrons scattered by ammonium fluoride at $+20^\circ\text{C}$ (crosses), at -65°C (open circles) and at -150°C (filled circles) measured by beryllium-shielded detector method.

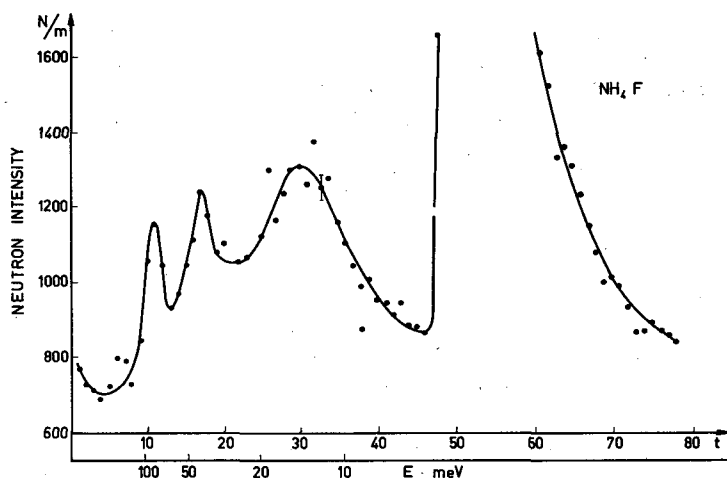


Fig. 6b

Energy distribution of beryllium-filtered neutrons after scattering by 90° by ammonium fluoride at $+20^\circ\text{C}$. The distribution was measured by chopper and time-of-flight method.

The restrictions acting at room temperature in other ammonium halides should appear in NH_4I while passing to β phase or to γ phase. This, in fact, was observed as can be seen from energy distributions at various tempera-

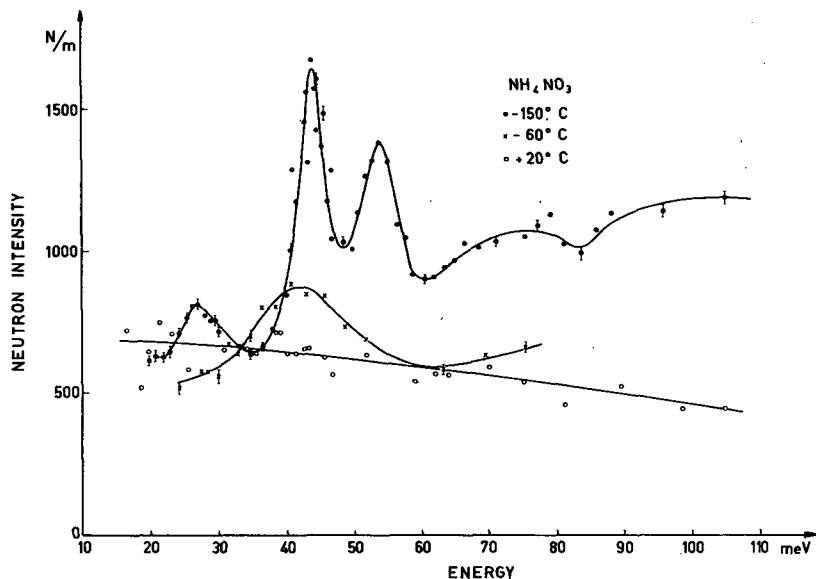


Fig. 7

Energy distributions of neutrons scattered by ammonium nitrate at 120°C (open circles), at -65°C (crosses) and at -150°C (filled circles).

tures shown in Fig. 3a, b and c. The α - β transition takes place in NH_4I at -16°C . Our distribution measured at -20°C shows a badly defined but quite evident peak at $\sim 270\text{ cm}^{-1}$. With decreasing temperature (distributions at -65°C and -150°C) its intensity increases rapidly and it becomes very well resolved. Some indication of the other peaks can be noticed in the distribution at -65°C and at -20°C . At -150°C the peaks at 145 cm^{-1} , 295 cm^{-1} , 445 cm^{-1} , 565 cm^{-1} and $\sim 750\text{ cm}^{-1}$ were resolved. No direct evidence of these transitions was reported before. Only the hindered rotation frequency (295 cm^{-1}) was computed from combination lines obtained by infra-red spectroscopy at -150°C [12]. 1685 cm^{-1} and 1916 cm^{-1} bands reported in [12] were assigned as $\nu_4 + \nu_6$ and $\nu_2 + \nu_6$, where ν_2 and ν_4 are the bending modes and ν_6 is the hindered rotation mode. The values derived in this way for ν_6 are 261 and 266 cm^{-1} in reasonable agreement with our value (295 cm^{-1}). The general similarity of the shape of the energy distributions for iodide below -20°C and those for bromide and chloride at room temperature is obvious. This clearly shows that the transition from β phase to α phase in ammonium halides is connected with the onset of the free rotation of the NH_4^+ ion. Our result is consistent with those of [12], where the 1685 and 1916 cm^{-1} bands were reported to be absent in α phase. Both our results and [12] contradict the earlier NMR and dielectric data which seemed to indicate the onset of free rotation at the λ -point, which for NH_4I lies at -42°C .

There remains the nature of other peaks best resolved at -150°C to be explained. The peak at 145 cm^{-1} is most probably the optical lattice mode of NH_4^+ analogous to those occurring in chloride and bromide. It was never

TABLE II

THE PEAK FREQUENCIES (IN cm^{-1}) OF THE SCATTERED NEUTRON SPECTRA FOR AMMONIUM HALIDES AND AMMONIUM NITRATE AT VARIOUS TEMPERATURES (IN $^{\circ}\text{C}$)

	+20 $^{\circ}\text{C}$	-20 $^{\circ}\text{C}$	-65 $^{\circ}\text{C}$	-150 $^{\circ}\text{C}$		+20 $^{\circ}\text{C}$	-65 $^{\circ}\text{C}$	-150 $^{\circ}\text{C}$
NH_4I				145	NH_4NO_3			
		270	285	295				195
				445			325	335
				565				420
				750				
NH_4Br	160		180	180				
	315		330	340				
			510	515				
			660	680				
			870	870				
NH_4Cl	155							
	355							
NH_4F	70							
	230		240	240				
	555		555	560				

reported before. The peaks at 445, 565 and 750 cm^{-1} could result from multiple scattering or they could be the combination frequencies of the optical and librational modes. In order to check the first possibility measurements with a "thin" sample (95% transmission, i. e. ca. 5 times less in comparison with standard samples) were made at -150°C . The distribution for this case is shown in Fig. 3c. It can be easily checked that this distribution is nearly identical with that obtained for the thick sample. Thus we must conclude that most likely these additional peaks are combination bands of the two peaks at 145 cm^{-1} and 295 cm^{-1} caused by multiphonon processes.

It can be seen from Fig. 3 that between -65°C and -150°C the librational peak shifts by about 1 meV and its width decreases from $\sim 8,5\text{ meV}$ to $\sim 5\text{ meV}$. More accurate measurements of the width versus temperature variations are under way.

Some measurements with the graphite filter were done for ammonium iodide at -150°C as there seemed to be some indication of unresolved peaks at the sides of the librational peak. These measurements did not reveal any fine structure and it was found that the small but definite bumps on the sides of the librational peak (Fig. 3c) were caused by improper correction for parasitic reflections from the monochromator crystal.

Ammonium bromide

The general pattern of transitions in ammonium bromide is similar to that of ammonium iodide at lower temperatures and of ammonium chloride [9]. At -150°C peaks at 180, 340, 515, 680 and $\sim 870\text{ cm}^{-1}$ were resolved. The width of the librational peak increases from $\sim 6\text{ meV}$ at -150°C to $\sim 7\text{ meV}$ at -65°C and $\sim 10\text{ meV}$ at $+20^{\circ}\text{C}$. There is also a shift of the peak position by about 3 meV between -150°C and $+20^{\circ}\text{C}$. The librational peak was not observed directly before but its frequency could be computed from combination bands in infra-red spectra. The value given in [12] for this frequency is 310 cm^{-1} at $+20^{\circ}\text{C}$ in good agreement with our value (315 cm^{-1}). The optical peak (180 cm^{-1}) was observed previously in Raman spectra at low temperatures [12]. The peaks at higher energies can be treated as combination bands of two lower peaks.

Ammonium fluoride

The case of NH_4F is much more complicated. NH_4F has a wurtzite-type structure in which each NH_4^+ ion forms four tetrahedral N-H-F bonds to surrounding F^- ions (which also form four tetrahedral N-H-F bonds to surrounding NH_4^+ ions). Nevertheless at higher pressures this structure collapses into the cubic one and for this reason it is claimed that fluoride should fit the general pattern proposed for the ammonium halides in [1].

The presence of the H-bond in NH_4F affects not only its structure but also the librational frequency of the NH_4^+ ion and this is in fact reflected in our distributions. The room temperature distribution (Fig. 6a) exhibits the likelihood to those for bromide and chloride. The librational frequency is, however, much higher (555 cm^{-1}). This transition was neither detected by Raman effect nor by infra-red spectroscopy at room temperature but some indirect indication of this mode was found at lower temperatures. This will be discussed below.

As in the case of NH_4Cl and NH_4Br there is another peak at room temperature in NH_4F (at 230 cm^{-1}) which is shifted to higher energies in comparison with lower peaks in other halides as is the librational peak. The nature of this peak has not been elucidated so far. In addition a slight indication of a third peak at still lower energy was found at room temperature. This energy range was not available for our inverted filter technique. Therefore a separate experiment on the cold neutron facility was performed and the obtained distribution is displayed in Fig. 6b. The third peak is clearly resolved there and it corresponds to ca. 70 cm^{-1} . It should be mentioned that a band at 1484 cm^{-1} reported in [12] but not given any assignment may be explained as the combination of our 70 cm^{-1} line with the ν_4 bending mode at 1410 cm^{-1} [12].

For lower temperatures comparison with infra-red data can be made. No definite assignments were given before but it was suggested that the bands at 3310 , 2573 and 2080 cm^{-1} at -150°C reported in [12] may be the combinations of the bending or stretching modes of NH_4^+ ion with its librational mode usually designated by ν_6 . The values derived in this way for ν_6 are: 568 , 585 and 586 cm^{-1} and these are in fairly good agreement with the value ob-

tained in our case at -150°C (565 cm^{-1}). A smaller value in our case can be expected as in our measurements the momentum transfer is always considerable contrary to conditions in infra-red and Raman studies.

As can be easily seen there is an evident distortion of both peaks in Fig. 6a. The presence of some unresolved peaks can be suspected and this was one of the cases demanding the improved resolution. The measurements with the improved resolution are in progress.

Another remarkable feature of the NH_4F results is that the intensity of the librational peak is only slightly temperature dependent when compared with other ammonium halides. This may be again produced by the existence of very strong hydrogen bonds in this compound.

Temperature variations of the intensities of librational peaks

The temperature variations of the intensities of the librational peaks are shown in Fig. 8 for NH_4Br , NH_4I and NH_4NO_3 . The curve for NH_4Br seems to consist of two linear parts joining at the temperature of the λ -point transition. The curve for NH_4I becomes a straight line if intensity is plotted in logarithmic scale. These data are, however, preliminary.

On the other hand it is interesting to note that the intensity ratios at librational peak positions at -150°C and $+20^{\circ}\text{C}$ are: 1, 72; 2, 96; 4, 1; 4, 65

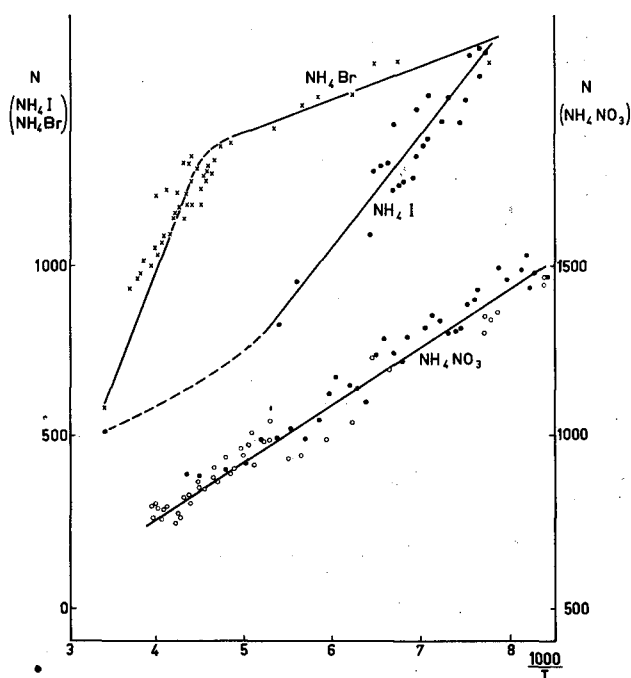


Fig. 8

Temperature variations of the peak intensities of the hindered rotation peak for ammonium halides (iodide and bromide) and of the highest peak for ammonium nitrate.

in order of increasing molecular volume of the halide. This trend is consistent with [1] where it is claimed that the only difference between ammonium halides is the magnitude of the molecular volume.

Ammonium nitrate

The measurements for this substance are not yet complete and further improvement of the statistics is desired. Nevertheless the data obtained so far seem to be of interest. The energy distributions at +20°C, -65°C and at -150°C are shown in Fig. 7. The distribution at +20°C shows no peaks at all and our first results at -65°C seemed to be similar to those obtained at +20°C. Later a badly-resolved peak was found at -65°C and at -150°C the peaks at 195, 335 and 420 cm^{-1} were well resolved. There is some slight indication of a band between 500-600 cm^{-1} and at ca. 780 cm^{-1} .

Ammonium nitrate is remarkable for rotation of both NH_4^+ and NO_3^- ions. The onset of free rotations of NO_3^- is assumed to be connected with the transition at +125°C. Below -18°C the hexagonal phase is stable and in addition the specific heat anomaly (λ -point) is known to appear at -60°C. GUTOVSKY and PAKE [13] observed the narrowing of the NMR absorption line at this temperature and they concluded that this means the onset of free rotation of the NH_4^+ ion. Our results are consistent with this view but more careful measurements are required in order to find at what temperature the peaks begin to appear. Ammonium nitrate was studied by Raman effect and infra-red spectroscopy but no Raman or infra-red bands coincide with the frequencies found in our experiment.

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Our thanks are due to Prof. B. Buras for the constant interest in the work and for stimulating discussions. We wish also to thank Mr. R. Kula and Mr. A. Hodyra for technical assistance.

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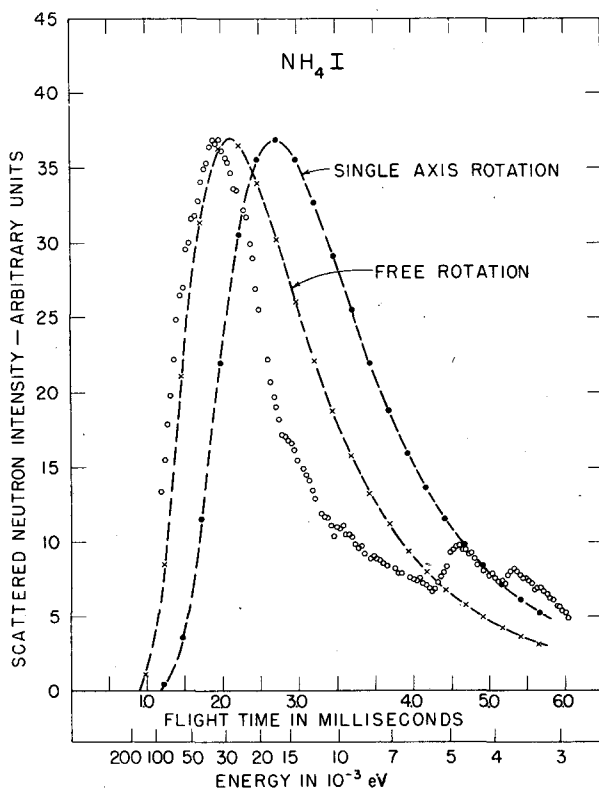
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DISCUSSION

H. STILLER: What were the energies of the hindered rotations?

K. MIKKE: They vary, for the different halides, from 30 to 70 meV. The exact values (in cm^{-1}) are summarized in Table II of the paper.

H. PALEVSKY: I would like at this point to report on an investigation along lines which we carried out at Brookhaven about two years ago. The figure below is a projection of some of the results of the study, which were



presented at the Kyoto Conference. They show very clearly that these cold neutrons constitute a powerful tool for observing rotational motions. The hachured curves are calculations of the Sachs-Teller mass-tensor type and clearly show that at room temperature NH_4I ion is undergoing large-amplitude torsional oscillations and making occasional torsional jumps. It should also be noted that the optical mode shows up weakly on the low-energy side of the distribution.

K. MIKKE: I might add that recent work on the infra-red technique by Hornig and Vedder also clearly indicates that none of these models, either the free rotational or the single-axis rotational, explains the results which were obtained in diluted compounds of this sort. This means that the ammonium ions were separated from each other in the lattice.

STUDY OF AMMONIUM HALIDES BY NEUTRON SPECTROMETRY

G. VENKATARAMAN, K. USHA, P.K. IYENGAR,
P.R. VIJAYARAGHAVAN AND A.P. ROY
ATOMIC ENERGY ESTABLISHMENT TROMBAY, BOMBAY,
INDIA

Abstract — Résumé — Аннотация — Resumen

STUDY OF AMMONIUM HALIDES BY NEUTRON SPECTROMETRY. The scattering of slow neutrons from the ammonium halides NH_4Cl , ND_4Cl , and NH_4Br has been studied at several temperatures with a view to elucidate the nature of the specific heat anomaly associated with these substances. According to Pauling the anomaly is due to the onset of free rotation of the ammonium ion, whereas according to Frenkel the anomaly is due to an order-disorder process. The present measurements rule out the possibility of free rotation thus confirming the Frenkel hypothesis. Values of the torsional frequencies and barrier heights for rotation have been derived and the relation of neutron scattering data to infra-red absorption, Raman scattering and NMR results are discussed.

ÉTUDE DES HALOGÉNURES D'AMMONIUM PAR SPECTROMÉTRIE DES NEUTRONS. Les auteurs ont étudié la diffusion des neutrons lents dans les halogénures d'ammonium NH_4Cl , ND_4Cl et NH_4Br à diverses températures, en vue d'élucider l'anomalie dans la chaleur spécifique qui caractérise ces substances. D'après Pauling, cette anomalie est due au fait que l'ion ammonium commence à tourner librement tandis que Frenkel l'explique par un processus d'ordre-désordre. Les mesures actuelles excluent toute possibilité de rotation libre, ce qui confirme l'hypothèse de Frenkel. Les auteurs déterminent les valeurs des fréquences de torsion et les hauteurs des barrières s'opposant à la rotation, ainsi que le rapport entre les données obtenues par diffusion des neutrons et l'absorption dans la zone infrarouge du spectre. Ils examinent également la diffusion de Raman et les résultats de la résonance magnétique nucléaire.

ИЗУЧЕНИЕ ГАЛЛОИДНЫХ СОЕДИНЕНИЙ АММОНИЯ С ПОМОЩЬЮ НЕЙТРОННОЙ СПЕКТРОМЕТРИИ. Рассеяние медленных нейтронов на галлоидных соединениях аммония: NH_4Cl , ND_4Cl и NH_4Br изучалось при нескольких температурах с целью объяснить природу аномалии удельной теплоемкости, связанной с этими веществами. По Паулингу, аномалия возникает в результате свободного вращения иона аммония, тогда как по Френкелю аномалия объясняется наличием процесса упорядочение-разупорядочение. Настоящие измерения исключают возможность свободного вращения, тем самым подтверждая гипотезу Френкеля. Вводятся значения частот вращательных колебаний и вращательного барьера, и устанавливается связь между данными по рассеянию нейтронов и поглощению инфракрасных лучей. Обсуждаются рамановское рассеяние и результаты по ядерному магнитному резонансу.

ESTUDIO DE LOS HALUROS DE AMONIO POR ESPECTROMETRÍA NEUTRÓNICA. Los autores han estudiado la dispersión de neutrones lentos por los haluros de amonio NH_4Cl , ND_4Cl y NH_4Br a diversas temperaturas con el fin de aclarar la naturaleza de la anomalía en el calor específico que presentan estas sustancias. Según Pauling, la anomalía se debe a que el ion amonio comienza a girar libremente mientras que, según Frenkel, se debe a un proceso de orden-desorden. Las mediciones efectuadas por los autores descartan la posibilidad de la rotación libre, confirmando con ello la hipótesis de Frenkel. Han podido derivar valores de las frecuencias de torsión y de las alturas de las barreras que se oponen a la rotación y han determinado la relación existente entre los datos obtenidos para la dispersión de neutrones y la absorción en la zona infrarroja del espectro. La memoria discute la dispersión de Raman y los resultados de la resonancia magnética nuclear.

I. INTRODUCTION

The problem of the ammonium halides is an old one in physics and goes back to the early twenties when SIMON [1] discovered a λ -type anomaly in

the specific heat. Since then the problem has received much attention both from the theoreticians and experimenters and as excellent summaries of these investigations are available in the literature [2] we shall not attempt any here. In brief there are two points of view concerning the nature of the anomaly. In one of these due to PAULING [3], the tetrahedral ammonium ion is held to be executing torsional oscillations at low temperatures in the potential well provided by the surrounding halogen ions. As the temperature is raised, the amplitude of these oscillations is supposed to increase until a stage is reached when the ions acquire sufficient energy to overcome the potential barrier and go into free rotation and it is this transition from the oscillating state to the freely-rotating state which causes the specific heat anomaly. According to FRENKEL [4] however, the ions do not break into free rotation but continue to execute torsional oscillations even above the λ point. What causes the anomaly is a transition from a state in which the

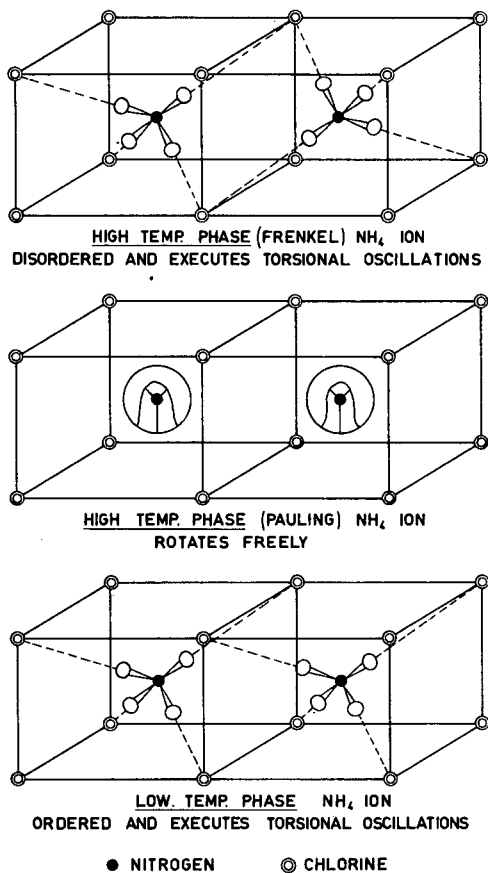


Fig.1

Schematic diagram illustrating the rotation and disorder theories.

ions are ordered, i. e. have the same orientation in all the unit cells*, to a state in which the ions are disordered, i. e. are randomly-distributed between the two positions available for the tetrahedral ion in the cubic lattice made up of the halogen ions. The two points of view are schematically shown in Fig. 1.

Various experiments, in particular neutron diffraction studies [2, 5] have established that the transition is indeed of the order-disorder type as envisaged by FRENKEL. While the order-disorder aspect of Frenkel's suggestion has been verified, it would be interesting to confirm the other half of the Frenkel model, namely the ammonium ions execute torsional oscillations and do this both above and below the λ point. Especially useful would be a knowledge of their frequencies and their lifetimes as these are connected with the height of the potential barrier. For such information one must resort to a dynamical experiment, i. e. an experiment which is sensitive to the dynamical changes in the system. In this category one usually includes infra-red absorption, Raman-scattering and nuclear magnetic relaxation experiments.

Several studies of infra-red absorption in the ammonium halides have been made, the most detailed of these being due to WAGNER and HORNING [6]. The torsional mode is not directly observed but its presence is indicated in some of the combination bands. Among Raman-scattering observations, the most extensive are those due to KRISHNAN [7]. Once again the torsional mode is not observed but indicated to the combination bands. Nuclear magnetic relaxation observations on the halides are principally due to COOKE and DRAIN [8] and GUTOWSKY *et al.* [9]; some recent work has also been reported by ITOH *et al.* [10]. While no direct knowledge of the torsional frequency is derived, valuable information concerning the lifetimes has been obtained. We report here an experiment using slow neutron scattering to obtain some of this information.

Inelastic scattering of slow neutrons by crystalline solids usually proceeds by exchange of energy by the neutrons with the normal modes associated with the translational degrees of freedom. In the case of molecular crystals there are additional degrees of freedom associated with the rotations and vibrations of the molecules. The energy distribution of neutrons scattered by such crystals contains therefore additional peaks arising from energy exchange with the rotations and vibrations. Knowing the energies of the incident and the scattered neutrons, the frequencies of the rotations and vibrations may be easily deduced. The neutron scattering experiments are thus the analogue of Raman scattering experiments in optics. Despite its comparatively low resolution, the neutron scattering method may be used to advantage in studying rotations and vibrations which are neither infra-red nor Raman-active as is the case with the torsional oscillations in the ammonium halides. The large n-p scattering cross-section makes the ammonium halides especially favourable for investigation by neutron spectrometry.

* The ordering in the case of the bromides is slightly different but the essential point is that the low temperature phase is an ordered phase.

II. EXPERIMENTAL DETAILS

Most of the results reported here have been obtained using the beryllium detector type of spectrometer introduced recently [11, 12]. In the spectrometer in operation at the Canada India Reactor, monochromatic neutrons are selected from the pile spectrum by Bragg reflection off the (111) planes of an aluminium crystal. These are then allowed to fall on the specimen and neutrons scattered at an angle of about 90° are viewed by a 2 in diam. 6 in long BF_3 counter placed with its axis vertical at a distance of 24 in from the sample. Interposed between the sample and the counter is a filter having overall dimensions of 2 in $\times$ 4 in $\times$ 4 in. The filter is assembled from blocks of smaller size suitably interleaved with cadmium to cut down in-scattering into the counter. The filter counter combination produces an energy analyser of constant window. We have used interchangeably both polycrystalline beryllium and beryllium oxide as filters in our experiments. With beryllium, the analyser window has a base width of 0.005 eV and a mean energy of ~ 0.003 eV while with beryllium oxide, the base width and mean energy are 0.0037 eV and ~ 0.0025 eV respectively. Both the counter and the filter are well shielded to minimize background. A thin BF_3 counter placed in the monochromatic beam serves as a monitor.

Spectra are taken by recording the scattered neutron intensity seen by the analyser as a function of incident energy. The scan over incident energies is performed by varying the Bragg angle of the monochromator in steps of 0.125° . A half-angling device ensures that the scatterer and the counter system are suitably moved to preserve the geometry of the scattering. For each setting of the monochromator, the analyser counts for a preset number of monitor counts are printed out. Next the monochromatic beam is cut off from the sample by introducing a cadmium foil and the background recorded. The spectrometer is then advanced to the next position and the process is repeated. The elapsed time of the monitor for each setting of the monochromator is also recorded. The operation of the spectrometer is completely automatic and the proper functioning of the spectrometer movements and the counting sequence is continuously monitored. The observed data are corrected for background and variation of the monitor counter efficiency with energy. No corrections are applied for second order contamination. This correction is expected to be small since a quartz filter is placed in the main beam, [13].

Some runs were also made by the time-of-flight method using a rotating crystal spectrometer. A collimated beam from the reactor is passed through a beryllium filter to produce a "cold" neutron beam. The beam is then allowed to fall on a crystal spinning at 8000 rpm to produce short monochromatic bursts. The crystal used is aluminium machined in the form of a sphere and oriented so as to produce two bursts per revolution by Bragg reflection from the (111) planes. The mean energy of the incident neutrons is 0.0045 eV. The sample is placed at a distance of 20 in from the monochromator and the time-of-flight spectrum observed at a distance of 160 cm. The detectors are two 2 in diam. 6 in long BF_3 counters. The reference pulse for starting the timing circuits is obtained by the usual lamp and photo cell arrangement and data is stored in a 100 channel time analyser. The measurements were made at a scattering angle of about 50° .

Using the spectrometers described above, runs were made with samples of NH_4Cl , NH_4Br and ND_4Cl at several temperatures. The samples were of different thicknesses, ranging from 10% scattering to about 40% scattering. The low temperature runs were made using a cryostat and the temperature was continuously monitored by two thermocouples attached to the sample. The temperature was constant to within $\pm 2^\circ\text{C}$. The high temperature run was done in an evacuated vessel. Once again the temperature was continuously monitored and held constant within $\pm 3^\circ\text{C}$. The results of these measurements may be seen in Figs. 2-5. All runs made on the beryllium detector spectrometer were checked for possible contamination by Bragg-scattered neutrons leaking through the filter.

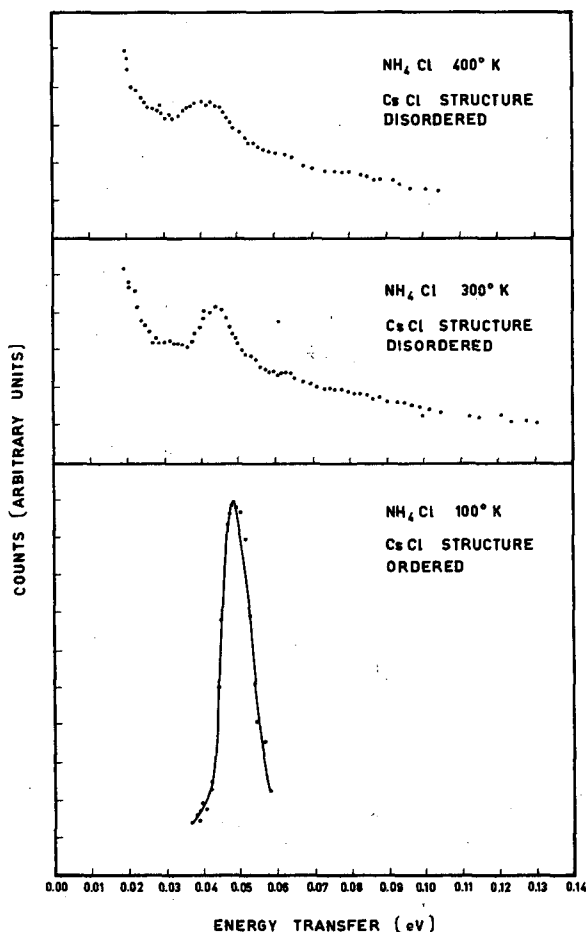


Fig. 2

Energy distribution for NH_4Cl at various temperatures obtained on the beryllium detector spectrometer.

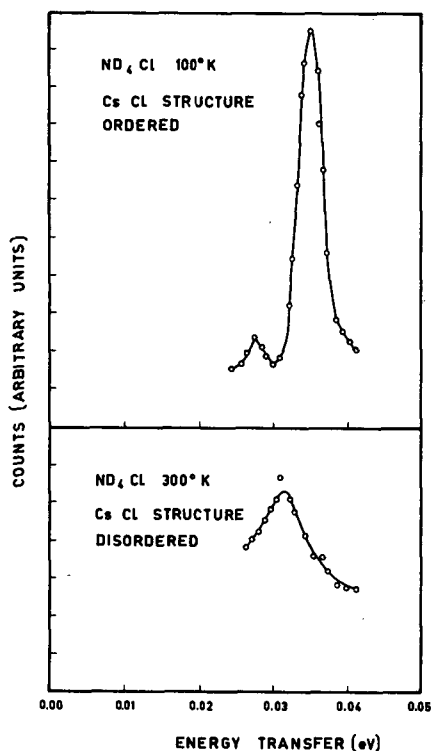


Fig.3

Energy distributions for ND_4Cl at 300°K and 100°K.

III. DISCUSSION

The ammonium chloride lattice consists of 6 atoms per unit cell. One of these is the chlorine ion and the remaining five go to form the rather well-bound NH_4 ion. The lattice therefore has 18°N of freedom associated with it on the whole, where N is the number of unit cells. Of these, 6°N are required to describe the translational modes (i.e. the acoustic and optical branches of the phonon spectrum) while the remaining 12°N describe the rotations and vibrations associated with the N ammonium ions, the distribution being 3°N for the rotations (or torsional oscillations) and 9°N for the vibrations respectively. Now the torsional oscillation of the ammonium ion in a CsCl type of lattice is known to be threefold degenerate [6]. If the different NH_4 ions did not interact with each other there would then be a 3N -fold degeneracy associated with the torsional frequency. On the other hand if the ions did interact the N-fold degeneracy would be removed and a band would be formed in much the same way as electron energy bands are formed when electrons from different atoms overlap in the solid state. The weaker the interaction the narrower would be the band. Like-

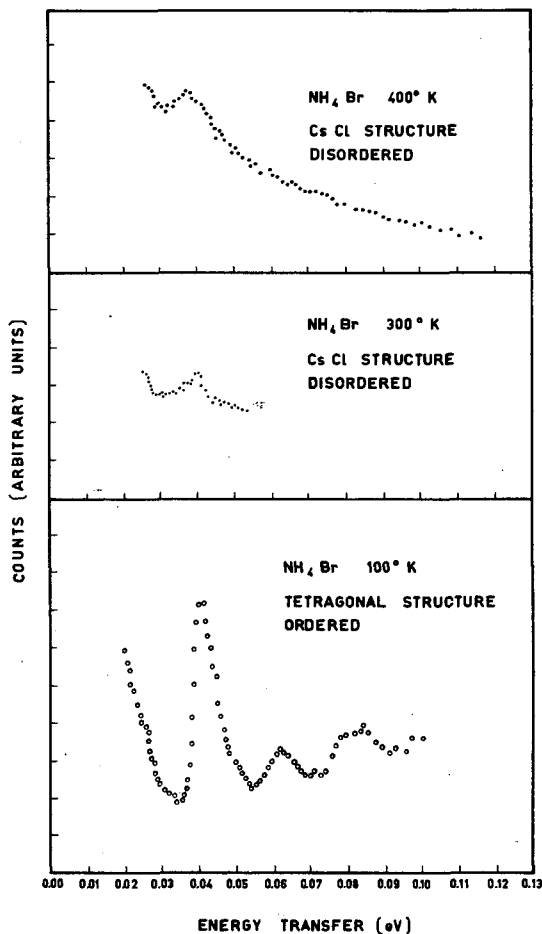


Fig. 4

Energy distribution for NH_4Br at various temperatures obtained on the beryllium detector spectrometer.

wise there would be four vibrational branches arising from the four vibrational frequencies of the free NH_4 ion [14]. The phonon spectrum of the ammonium halides lattice would therefore consist of one "torsional branch" and four "vibrational branches" in addition to the usual acoustic and optical branches, and the neutron spectrum should exhibit structure associated with the various branches.

Most of our data has been obtained in regions where the torsional modes are expected to contribute and the spectra of all the halides studied prominently exhibit peaks arising from energy exchange with the torsional oscillations. The occurrence of the torsional peak both above and below the λ point confirms Frenkel's predictions that the torsional oscillations do not

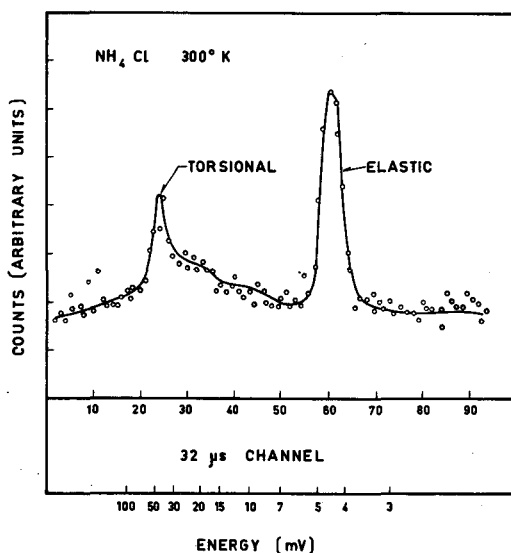


Fig. 5

Time-of-flight distribution for NH_4Cl at room temperature obtained on the rotating crystal spectrometer.

undergo major changes through the λ point. If the ion broke into free rotation above the λ point as is required by Pauling, the frequency would be very much reduced whereas what is observed is that the frequency remains practically the same apart from a small decrease which is probably due to "softening" of the oscillations. The frequencies of the torsional oscillations derived from the present measurements are indicated in Table I and are seen to agree quite well with estimates made earlier by Wagner and Horning on the basis of infra-red and Raman-scattering data. The ammonium chloride frequencies are also in agreement with previous neutron scattering measurements [10]. Using these frequencies, the barrier heights for rotation of the ammonium ion in the various halides have been calculated [9]. The results of the calculation are shown in Table II. The barrier heights thus obtained are in reasonable agreement with those estimated from electrostatic considerations.

The intensities for a given halide at the different temperatures are not directly comparable, as the sample thicknesses used in the different runs were often different, but it may be said that the intensity at the lower temperature is higher on account of increased population of the ground state.

The occurrence of the torsional mode in NH_4Cl and NH_4Br at 100°K which is below the temperature corresponding to the line width transition in the nuclear magnetic relaxation experiments confirms previous expectations that at these temperatures nothing drastic happens to the ions except for the reorientations being "frozen out".

A slight broadening of the line at higher temperatures is also perceptible but it is difficult to estimate the broadening on account of multiple scattering and complicated instrumental resolution. Preliminary measurements

TABLE I
FREQUENCIES OF TORSIONAL OSCILLATIONS

Halide	λ pt.	Temp.	Phase and structure	Torsional freq. this work		Estimates from infra-red measurements cm^{-1} (a)	Raman scattering cm^{-1} (b)	Neutron scattering (c)
				eV	cm^{-1}			
NH_4Cl	242.5°K	100°K	III CsCl (ordered)	0.0487	393	391	-	391
		300°K	II CsCl (disordered)	0.0434	350	359	-	-
		400°K	ibid.	0.0421	340	-	-	-
ND_4Cl	249.2°K	100°K	III CsCl (ordered)	0.0353	285	281	-	-
		300°K	II CsCl (disordered)	0.0327	264	269	-	-
NH_4Br	234.9	100°K	III Tetragonal (ordered)	0.041	331	319	335	-
		300°K	II CsCl (disordered)	0.0402	324	311	-	-
		400°K	ibid.	0.0369	298	-	-	-

(a) WAGNER, E.L. and HORNING, D.F., [6].

(b) KRISHNAN, R.D., [7].

(c) WOODS, A.D.B., et al., [11].

TABLE II

BARRIER HEIGHTS FOR ROTATION OF AMMONIUM ION

Halide	Barrier heights from obs. tors. freq. cal/mole	Barrier heights from electrostatic model cal/mole
NH_4Cl	5321	5400
ND_4Cl	5376	5400
NH_4Br	4472	3730

on the line shape made with a thin sample on a triple axis spectrometer indicate a line broadening several orders of magnitude higher than what one would expect from nuclear magnetic relaxation measurements on lifetimes. We believe therefore that the broadening is not due to an intrinsic lifetime

effect but to a change in the spectra of the torsional vibrations arising from the lower symmetry at the higher temperature. Similar effects have also been observed by WAGNER and HORNING [6].

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DISCUSSION

W. COCHRAN: If there are forces between adjacent ammonium ions, it is possibly not correct to describe a particular branch of the dispersion relation as "translational" or "librational". It may change its character as the wave vector varies, e. g. a branch may start by having purely translational properties at wave number zero and by the time you get to the zone boundary it may have changed its character and be a purely librational mode. So I don't think you can always simplify the situation as you did.

P. K. IYENGAR: I was only citing an analogy from electron band theory. The total number of branches, however, will be decided by the number of

atoms per unit cell. Their character may depend on the nature of interaction

K. E. LARSSON: What sort of energy shift did you observe when you did your deuteration experiments?

P. K. IYENGAR: I think it was roughly proportional to the square root of the mass ratios.

STUDIES OF PROTON VIBRATIONS IN γ -TITANIUM HYDRIDE

D. H. SAUNDERSON AND S. J. COCKING
NUCLEAR PHYSICS DIVISION, AERE, HARWELL, DIDCOT, BERKS.
UNITED KINGDOM

Abstract — Résumé — Аннотация — Resumen

STUDIES OF PROTON VIBRATIONS IN γ -TITANIUM HYDRIDE. The spectra of inelastically-scattered neutrons from a sample of titanium hydride (mixed α -titanium and f. c. c. γ -hydride phase) at room temperature were measured by cold neutron scattering and by the beryllium detector method.

The profile of the prominent peak at 0.140 eV due to the protons vibrating with respect to the lattice of metal atoms was studied in detail by the beryllium detector method. Scattering of slow incident neutrons provides additional information on the relative intensity and distribution of low frequency modes.

With these data the LEAP computer programme was used to show that the 0.140 eV peak profile could not result from an "Einstein" oscillator plus acoustic multiphonon scattering. A generalized frequency distribution, $p(\beta)$, fitting the data has been derived and shows that the majority of the normal modes of the proton vibrations are contained in a broad, asymmetric peak about 0.140 eV.

ÉTUDES DES VIBRATIONS PROTONIQUES DANS L'HYDRURE DE TITANE GAMMA. Les auteurs ont mesuré les spectres de neutrons diffusés inélastiquement dans un échantillon d'hydru de titane (mélange de titane- α et d'hydru- γ c. f. c.) à la température ambiante, par la méthode de diffusion des neutrons lents et par la méthode du détecteur au béryllium.

Ils ont étudié en détail, à l'aide d'un détecteur au béryllium, le profil du pic prédominant à 0,140 eV dû à la vibration des protons dans le réseau des atomes métalliques. La diffusion des neutrons lents incidents fournit des renseignements supplémentaires sur l'intensité relative et sur la distribution des modes de fréquences basses.

A l'aide de ces données, les auteurs ont utilisé le programme de calculatrice LEAP pour montrer que le profil du pic à 0,140 eV ne peut pas être dû à un oscillateur d'Einstein associé à la diffusion multiphonon acoustique. Ils ont déterminé une distribution de fréquences généralisée $p(\beta)$ s'adaptant aux données; cette distribution montre que la plupart des modes normaux de vibrations des protons sont contenus dans un pic asymétrique large à 0,140 eV.

ИССЛЕДОВАНИЕ КОЛЕБАНИЯ ПРОТОНОВ В ГИДРИДЕ γ -ТИТАНА. Спектры неупруго рассеянных нейтронов, полученные на образце гидрида титана (смесь α -титана и гранецентрированной кубической фазы γ -гидрида), были измерены в условиях комнатной температуры методом рассеяния холодных нейтронов с помощью бериллиевого детектора.

Профиль резкого пика при 0,140 эв, образованного колебаниями протонов в атомной решетке металла, был подробно изучен методом бериллиевого детектора. Рассеяние медленных бомбардирующих нейтронов дает дополнительную информацию об относительной интенсивности и распределении состояний малой частоты.

Исходя из этих данных, была использована программа LEAP для счетного устройства с тем, чтобы показать, что профиль пика при 0,140 эв не мог быть вызван "эйнштейновским" осциллятором совместно с акустическим мультифононовым рассеянием. Было выведено соответствующее этим данным обобщенное распределение частот $p(\beta)$; оно показывает, что большая часть нормальных состояний колебаний протонов содержится в широком асимметричном пике приблизительно при 0,140 эв.

ESTUDIO DE LA VIBRACIÓN DE PROTONES EN EL HIDRURO DE TITANIO- γ . Los autores han medido a la temperatura ambiente, por dispersión de neutrones fríos y por el método del detector de berilio, los espectros de los neutrones dispersados inelásticamente por una muestra de hidruro de titanio (mezcla de titanio α y de hidruro en fase γ , perteneciente al sistema cúbico centrado en las caras).

Han estudiado en detalle, por el método del detector de berilio, el perfil del pico prominente a 0,140 eV,

debido a la vibración de los protones respecto de la red de átomos metálicos. La dispersión de los neutrones lentos incidentes proporciona información complementaria sobre la intensidad y distribución relativas de los modos de baja frecuencia.

Con estos datos, han utilizado el programa de cálculo LEAP para demostrar que el perfil del pico correspondiente a 0,140 eV no puede ser resultado de un oscilador de "Einstein" más dispersión acústica de multifonones. Han deducido una distribución generalizada de frecuencias, $p(\delta)$, que se ajusta a los datos y muestra que la mayoría de los modos normales de las vibraciones protónicas están contenidas en un amplio pico asimétrico situado alrededor de los 0,140 eV.

INTRODUCTION

Recent interest in the lattice dynamics of transition metal hydrides has been stimulated by their value as reactor moderator materials. McREYNOLDS *et al.* [1] showed that the inelastic scattering of neutrons by $\text{ZrH}_{1.5}$ to 1.9 could be explained on the basis of an Einstein oscillator model in which the proton behaves as a three dimensional simple harmonic oscillator bound in a lattice of heavy metal atoms. BERGSMA and GOEDKOOP [2] have reported measurements on $\text{PdH}_{0.63}$ and AlTh_2H_n , including cold neutron-scattered spectra, and WOODS *et al.* [3] have reported measurements on $\text{ZrH}_{1.8}$ by the beryllium detector method. The principle feature of the spectra of these hydrides is a prominent peak at an energy of the order of 0,1 eV corresponding to the fundamental frequency of the Einstein oscillator. In each case the peak is broadened by more than the instrumental resolution. McREYNOLDS *et al.* [1] concluded that the width could be attributed to the Doppler broadening due to thermal motion of the metal lattice, whereas WOODS *et al.* [3] concluded from a measurement of the same level at 95°K that the width was due to a broad distribution of frequencies in the level.

Measurements are reported in this paper of the scattered neutron spectra from γ titanium hydride at room temperature by the complementary techniques of the beryllium detector method and cold neutron scattering. The former gives the observed peak profile in detail while the latter provides essential information on the low frequency acoustic spectrum. The results have been used to construct a frequency distribution function of the proton vibrations.

TITANIUM HYDRIDE

Titanium is a transition metal belonging to the same group, IVa, as zirconium and reacts with hydrogen in a similar way.

A sample of titanium hydride was formed by heating strips of titanium metal in an atmosphere of hydrogen, and allowing absorption to take place until an average composition of $\text{TiH}_{0.6}$ was obtained. This is the approximate composition of the high temperature β phase hydride at 320°C and subsequent experiments are intended to study the modification to the scattering behaviour on passing from the γ to the β phase. At room temperature a sample of this average composition separates into the face-centred cubic γ phase of composition $\text{TiH}_{1.6}$ [4] in equilibrium with the hexagonal close-packed α phase titanium metal.

LIBOWITZ [5] suggests that the transition metal hydrides form crystals of a definite structure but capable of existing with a large number of the hydrogen sites unoccupied. In the case of γ titanium hydride a fluorite structure is indicated with a stoichiometric composition TiH_2 . Bragg peaks were found in our measurements of the total scattered intensity as a function of momentum transfer (equivalent to an angular distribution measurement) confirming the presence of titanium atoms in both a hexagonal close-packed metallic lattice and a fluorite lattice with $a_0 = 4.4 \text{ \AA}$ in agreement with the X-ray measurements of HÄGG [6]. In the fluorite structure the protons occupy sites within a tetrahedron of metal atoms. The conditions for the Einstein model will apply if this highly symmetrical tetragonal environment approximates closely to spherical symmetry and there is negligible coupling between protons.

EXPERIMENTAL RESULTS

It is convenient in the presentation and analysis of the results to use the formalism of EGELSTAFF and SCHOFIELD [7] in which the measured differential cross-section $\partial^2\sigma/\partial\Omega\partial\epsilon$ is expressed in terms of the function $S(\alpha, \beta)$ where

$$S(\alpha, \beta) = \frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} \frac{k_0}{k_1} e^{\frac{\beta}{2}} \frac{4\pi}{\sigma_b} \quad (1)$$

$$\alpha = \frac{\hbar^2}{2Mk_B T} |\underline{K}|^2$$

$$\beta = \frac{\hbar\omega}{k_B T}.$$

$\hbar\mathbf{K} = \hbar(\mathbf{k}^1 - \mathbf{k}_0)$, the momentum transferred to neutron,

$\hbar\omega = \epsilon$, the energy transferred to neutron.

$\mathbf{k}_0$ and $\mathbf{k}^1$ are the incident and scattered wave vectors, T the sample temperature, M the mass of the scattering nucleus, and other symbols have their usual meaning.

$S(\alpha, \beta)$ can be separated into two components $S_s(\alpha, \beta)$ and $S_d(\alpha, \beta)$. $S_d(\alpha, \beta)$ governs the interference effects due to coherent scattering from pairs of nuclei. In the case of scattering from protons, which is predominantly incoherent, these effects are negligible and only the "self" part $S_s(\alpha, \beta)$ is important. For solids $S_s(\alpha, \beta)$ is related to the phonon frequency distribution.

Fig. 1 shows the results obtained by the beryllium detector method, similar to that described by WOODS et al. [3], using the Dido High Intensity Crystal Spectrometer. A beam of neutrons, energy E_0 , from the monochromator of the spectrometer are scattered by the sample and detected by B^{10}F_3 counters shielded by a polycrystalline beryllium filter. The intensity per count from a $1/v$ detector in the incident beam is proportional to:

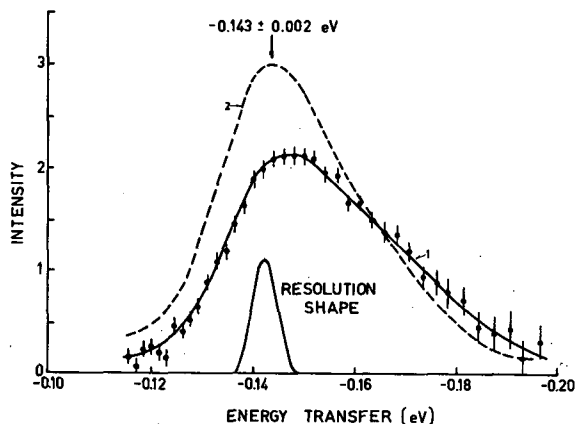


Fig. 1

Titanium hydride.

Observed peak of proton vibrating in the titanium lattice (by beryllium detector method).

Curve (1) Observed shape

Curve (2) Observed shape multiplied by the factor, $\exp \{hw/Ket\}$.

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \epsilon} \frac{k_0}{k^1} \frac{4\pi}{\sigma_b} = e^{-\beta/2} S(\alpha, \beta)$$

where $\beta = (\bar{E}^1 - E_0)/k_B T = (0.0034 - E_0)/0.0253$, for E_0 in eV.

Curve (1) shows the scattered intensity per monitor count; curve (2) shows the corresponding $S(\alpha, \beta)$ obtained by dividing through by $e^{-\beta/2}$. These results will be referred to as ELB for Energy Loss spectrum by beryllium detector method. The observed spectrum is seen to be a broad and asymmetrical peak about a most probable energy of 0.143 ± 0.002 eV.* This can be compared with the observation of McREYNOLDS and WHITEMORE [8] who quote 0.129 ± 0.007 eV for TiH_2 .

The approximate form of the resolution function of the apparatus is shown in Fig. 1 and is clearly narrower than the observed profile. Multi-phonon interactions involving the Einstein oscillator and acoustic modes in which the protons vibrate in phase with the metal atoms will also broaden the level. To obtain the necessary information about these acoustic vibrations of the proton, measurements were made using the Dido cold neutron scattering apparatus described in the accompanying paper entitled "A cold neutron monochromator and scattering apparatus" and referred to here as CN. The results showed the acoustic region in detail, but, because of poorer resolution and the effect of the Boltzmann factor, did not measure the Einstein level with the accuracy of the ELB method.

* Since this paper was submitted the spectrometer has been recalibrated, the correct figure now being 0.140 ± 0.0015 eV.

ANALYSIS

To calculate the effect of multiphonon broadening use was made of the LEAP programme which computes $S_s(\alpha, \beta)$ by a multiphonon expansion from an input function, $p(\beta)$, the generalized frequency distribution defined by EGELSTAFF and SCHOFIELD's Eq. (3.5) [7]. For a solid this is related to the usual phonon frequency distribution $\rho(\beta)$ by:

$$\rho(\beta) = \frac{2 \sinh(\beta/2) p(\beta)}{\beta} \quad (2)$$

In order to construct a feasible $p(\beta)$ it was necessary to know the shape of the acoustic part of the distribution and the relative areas contained by the acoustic and Einstein components. For this, the energy gain CN results were plotted in the form of $S\beta^2/\alpha$. Provided the observed S is largely due to single phonon processes the area under the components of the curve will give the ratio of areas under the components in $p(\beta)$ [7].

A comparison of the scattering cross-sections of titanium and hydrogen show that the effect of the former will be small. A check was made by performing the ELB measurements on a sample of pure titanium containing the same mass of metal in the sample and no effects were observed.

The area ratio was found to be 18:1 and the first $p(\beta)$ was constructed in the form of a Debye distribution with a cut-off at $\beta = 0.9$ (corresponding to $\Theta_D = 254^\circ\text{K}$), also derived from the CN results, and a δ -function containing 18/19ths of the total area at $\beta = 5.65$ ($\epsilon = 0.143$ eV). The computed $S_s(\alpha, \beta)$ is shown as curve 1 in Fig. 2 with the effect of the resolution included. The curve shows clearly that this model does not explain the shape of the observed distribution.

To test the possibility that the observed profile is due to the intrinsic frequency distribution of the level a second $p(\beta)$ was constructed. This used the CN data for the acoustic distribution with the above area ratio, and for the Einstein level used the shape of the ELB data (i.e. the solid line in Fig. 2).

The result of this second computation is shown as curve 2 in Fig. 2 compared to the solid line which represents both the observed data and the one-phonon term in this calculation. It can be seen that the multiphonon terms given by the difference in shape of the two curves have only a small effect. This leads to the conclusion that the observed breadth and asymmetry of the peak are intrinsic properties of the level.

Assuming this second $p(\beta)$ is reasonably accurate, the phonon frequency distribution, $Q(\beta)$, can be calculated through Eq. (2). The results are shown in Fig. 3. The ratio of areas under the two parts of this curve gives the relative number of normal modes of the proton vibration in the two components as 126:1, which may be compared to the ratio of masses of Ti and H of 48:1. A further test of the validity of this assumed $p(\beta)$ was made by calculating the scattered spectrum expected in a cold neutron measurement at 75° . The calculated spectrum gave a ratio of peak amplitudes of the Einstein to the acoustic distributions that agreed to within 10% of the measured value allowing for experimental errors.

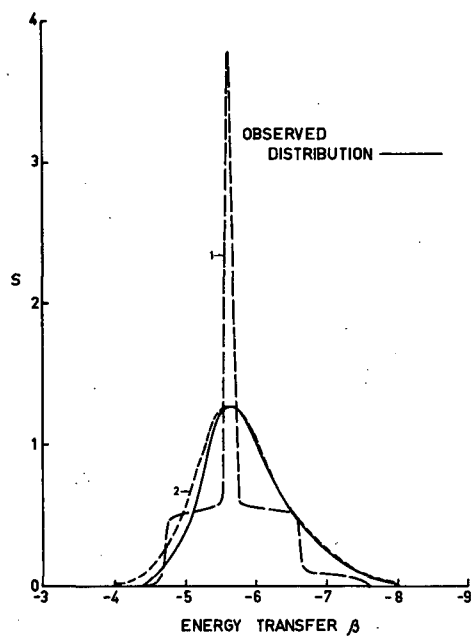


Fig. 2

Titanium hydride LEAP results.
Calculated shapes of level using:

- (1) δ -function optical level and Debye acoustic spectrum.
- (2) Observed shape of optical level and Debye acoustic spectrum.

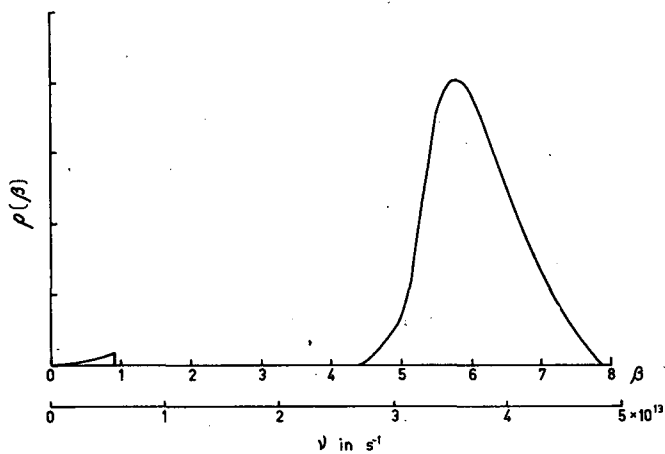


Fig. 3

Frequency distribution of proton vibrations in γ -titanium hydride derived from present results.

CONCLUSIONS

The evidence shows that the model based on an Einstein oscillator in a metal lattice for the proton dynamics in γ -titanium hydride is not valid, and this tends to support Woods' conclusion in the case of zirconium hydride. The finite breadth of the distribution may be due to the departure from perfect spherical symmetry of the tetragonal field or to coupling between protons. The latter effect would be sensitive to the density of hydrogen vacancies in the lattice which can be varied from 0 to about 40%. Unfortunately the lattice parameters also vary, tending to distort from cubic symmetry with increasing hydrogen concentration, so that the proton environment changes simultaneously.

An estimate of the amplitude of the proton vibrations can be obtained using the Einstein model with a frequency corresponding to the peak of the observed distribution. A root mean square displacement of $0.12 \pm 0.01 \text{ \AA}$ is obtained with a frequency $\nu = 3.46 \times 10^{13} \text{ s}^{-1}$. This is to be compared with a distance of 1.91 $\text{\AA}$ between the proton equilibrium position and the titanium atoms forming the tetrahedron.

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DISCUSSION

R. A. COWLEY: Is it possible that the width of your peak is due to the dispersion of the optical branches and also to the splitting of the longitudinal and transverse modes, similar to that show in alkali halides?

S. J. COCKING: I do not know, but it is very possible. So far we have only reached the stage of saying that the width is not due to multiphonon effects.

W. WHITTEMORE: In addition to the work on titanium hydride and zirconium hydride which I reported on at Vienna two years ago*, there was work of high statistical accuracy on zirconium hydride that we had published even earlier, when we were investigating the widths of the various levels, including the second vibrational level. Our findings were obtained by energy-gain measurements. Those results agreed rather well with others, obtained by energy-loss measurements, which were reported by Brockhouse and Woods at the same meeting.** Both sets of results showed that the second level is about 2 times the width of the first level, not $\sqrt{2}$ times, as might be expected. Do you observe a similar result for the second excited level in the case of titanium hydride?

S. COCKING: We have not yet studied the second level, although we could do so.

B. N. BROCKHOUSE: I think we would be rather reluctant to have that upper level width assigned on the basis of your curve. The peak, while clearly discernible, is a broad and low-lying one and is rather weak.

H. PALEVSKY: Can't you already say from your results that the interpretation based on nuclear magnetic resonance is wrong? In other words, if hydrogen was really diffusing the way you said it was, you wouldn't get your sharp peak. You could at least give some limits from the width of the peak if hydrogen was really diffusing the way you said it was, you wouldn't get your sharp peak. You could at least give some limits from the width of the peak that you already have, indicating how much diffusive motion there is.

S. COCKING: One could do this, although we haven't done anything along those lines yet.

N. A. TCHERNOPOLEKOV: Did you make any attempt to explain the observed width and form of the lines of the optical oscillations on the basis of the superposition of two optical levels, corresponding to two possible positions of the hydrogen atom in the lattice, namely, in the octahedral and the tetrahedral vacancies? This would seem to be acceptable for a complete explanation of both the width and the asymmetry of the optical level.

S. COCKING: We have not made such an analysis. However, Gatowsky and Stalinsky, who publish data in J. chem. Phys. on the hydrogen motion in titanium hydride, show that the occupation of the octahedral site is 10^{-4} of that of the tetrahedral site. The line of our subsequent work will be to examine the optical mode in the high-temperature phase of the hydride, in which the structure changes and the proton possibly occupies an octahedral site in the body-centred lattice.

* "Inelastic Scattering of Neutrons in Solids and Liquids", Vienna, IAEA, (1961) 511.

** Op. cit., p. 487.

LOW FREQUENCY HYDROGEN VIBRATIONS IN POTASSIUM DIHYDROGEN PHOSPHATE*

H. PALEVSKY, K. OTNES AND Y. WAKUTA**

BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK
UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

LOW FREQUENCY HYDROGEN VIBRATIONS IN POTASSIUM DIHYDROGEN PHOSPHATE. The BNL cold neutron facility was used to investigate the low energy states in KH_2PO_4 and KD_2PO_4 at room temperature and below the transition temperature. The energy interval covered ($8-170 \times 10^{-3}$ eV) corresponds to wave numbers of $25-1300 \text{ cm}^{-1}$, a region which is difficult to investigate by infrared absorption techniques. At very low energies broad peaks corresponding to the acoustic modes of the crystal are observed; at the high energy end the vibrations characteristic of the PO_4 molecule are found. The excitation modes associated with hydrogen are identified by the change in scattering intensity with deuteration. By this means, it is shown that a band of frequencies centered around 180 cm^{-1} is associated with hydrogen vibrations. The spectra for both KH_2PO_4 and KD_2PO_4 below their ferro-electric transition temperatures was found to have the same general shape as their corresponding room temperature data, the major changes in shape being accounted for by the Boltzman population factor. A comparison of these inelastic neutron scattering results with those obtained from neutron diffraction and infrared measurements will be discussed.

VIBRATIONS DE L'HYDROGÈNE A BASSE FRÉQUENCE DANS LE PHOSPHATE MONOPOTASSIQUE. Les auteurs ont utilisé le dispositif à neutrons lents du BNL pour étudier les états de basse énergie dans KH_2PO_4 et KD_2PO_4 à la température ambiante et à des températures inférieures à celles de transition. L'intervalle d'énergie considéré ($8-170 \cdot 10^{-3}$ eV) correspond au nombre d'ondes de 25 à 1300 cm^{-1} ; c'est une région qu'il est difficile d'étudier par la méthode d'absorption des rayons infrarouges. Aux énergies très basses, les auteurs ont observé des pics larges correspondant aux modes acoustiques du cristal; à l'extrémité correspondant aux énergies élevées, ils ont trouvé les vibrations caractéristiques de la molécule de PO_4 . Les modes d'excitation associés à l'hydrogène sont identifiés grâce à la variation de l'intensité de diffusion due à la deutération. Par ce moyen, on montre qu'une bande de fréquences centrée autour de 180 cm^{-1} est associée aux vibrations de l'hydrogène. Les auteurs ont trouvé que pour des températures inférieures aux températures de la transition ferroélectrique, les spectres de KH_2PO_4 et KD_2PO_4 ont la même forme générale que les données correspondantes relatives à la température ambiante, les changements de forme les plus importants s'expliquant par le facteur de population de Boltzman. Les auteurs comparent les résultats relatifs à la diffusion inélastique des neutrons et ceux que l'on obtient par la diffraction neutronique et par des mesures avec les rayons infrarouges.

НИЗКОЧАСТОТНЫЕ КОЛЕБАНИЯ АТОМОВ ВОДОРОДА В ПЕРВИЧНОМ КИСЛОМ ФОСФАТЕ КАЛИЯ. Установка для получения холодных нейтронов в Брукхейвенской национальной лаборатории была использована для изучения состояний низкой энергии в KH_2PO_4 и KD_2PO_4 при комнатной температуре и ниже температур перехода. Интервал энергии ($8-170 \cdot 10^{-3}$ эв) соответствует волновым числам $25-1300 \text{ см}^{-1}$, т.е. области, в которой трудно проводить исследования методами поглощения инфракрасных лучей. При очень низких энергиях наблюдаются широкие максимумы, соответствующие акустическим колебаниям кристалла. На границе области высокой энергии обнаружены колебания, характерные для молекул PO_4 . Виды возбуждения, связанные с водородом, определяются по изменению интенсивности рассеяния при дейтеризации. Таким образом показано, что полоса частот вблизи 180 см^{-1} связана с колебаниями атомов водорода. Было обнаружено, что спектры как для KH_2PO_4 и KD_2PO_4 ниже их сегнетоэлектрических температур перехода имеют тот же общий вид, как и соответствующие им спектры при комнатных температурах. При этом основные изменения формы обусловлены коэффициентом заполнения Больцмана.

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** IAEA Fellow. Present address: Faculty of Engineering, Kyushu University, Fukuoka, Japan.

Будут обсуждены результаты сравнения этих данных по неупругому рассеянию нейтронов с данными, полученными изучением дифракции нейтронов и измерением инфракрасного излучения.

VIBRACIONES DE BAJA FRECUENCIA DEL HIDRÓGENO EN EL FOSFATO DIACIDO DE POTASIO. Los autores han utilizado el aparato de neutrones fríos del Laboratorio Nacional de Brookhaven para investigar los estados de baja energía del KH_2PO_4 y del KD_2PO_4 a temperatura ambiente y por debajo de las temperaturas de transición. El intervalo de energía abarcado (8 a $170 \cdot 10^{-3}$ eV) corresponde a números de onda de 25 a 1300 cm^{-1} , esto es, a una región que es difícil de investigar por procedimientos de absorción infrarroja. A energías muy bajas, se observan picos aplanados correspondientes a los modos acústicos del cristal; en el extremo correspondiente a las energías elevadas, aparecen las vibraciones características de la molécula de PO_4 . Los modos de excitación asociados al hidrógeno se identifican por la variación de la intensidad de dispersión con el contenido de deuterio. Por este medio, se demuestra que hay una banda de frecuencia centrada en torno a 180 cm^{-1} , asociada a las vibraciones del hidrógeno. Se ha observado que por debajo de sus temperaturas de transición ferroeléctrica los espectros del KH_2PO_4 y del KD_2PO_4 presentan la misma forma general que los datos respectivos correspondientes a la temperatura ambiente, debiéndose al factor de población de Boltzman los cambios de forma más importantes. El autor compara los resultados de esta dispersión inelástica con los obtenidos por difracción neutrónica y espectroscopia infrarroja.

1. INTRODUCTION

From the neutron diffraction work of BACON and PEASE [1], it is known that below the ferroelectric Curie point ($T = 122^\circ\text{K}$) the protons in a single crystal of KH_2PO_4 are ordered, and asymmetrically arranged between oxygen atoms of adjacent PO_4 ions. Above the Curie point, the diffraction patterns show that the protons are symmetrically situated between oxygen atoms. In general, these results can be explained in two ways. First, the proton at each site is indeed located symmetrically between oxygen atoms; and second, the proton is located in a symmetric two-minima potential, centred between oxygen sites, and, therefore, is randomly distributed among the two minima at different sites. Bacon and Pease estimate that the zero point vibrational energy of the hydrogen is 0.079 eV ($\sim 900^\circ\text{K}$) and, therefore, it is clear that the disordering that occurs above the Curie point is not the result of the excitation of a vibrational level above the maximum of a two-minima potential. Nevertheless, the two-minima potential model can still explain the neutron diffraction results by invoking the quantum mechanical tunnelling process. This model also predicts that below the transition temperature, the two-minima symmetric well becomes asymmetrical, with the result that the protons populate the lower minima.

Infra-red and Raman measurements [2, 3], investigating the vibrational states of the protons in KH_2PO_4 have failed to show the splitting that would be expected from tunnelling or the change in spectra as might be expected as the sample temperature is changed from above the transition point to below. These results have been quoted as substantiating the existence of a double minima potential by one group of experimenters [2], and as proof against this model by another group [3]. REID [4] has proposed a model where the order and disorder comes about from correlated low frequency motions of a group of KH_2PO_4 molecules. This model would not necessarily give rise to a splitting in the vibrational states of an excited proton. PELAH et al. [5] have compared the scattered neutron spectra obtained with KH_2PO_4 with those obtained with K_2HPO_4 and K_3PO_4 . All three compounds exhibit broad hydrogen bands in the region of 10 - 1000 wave numbers.

We have used the cold neutron facility at Brookhaven to carry out measurements on KH_2PO_4 and KD_2PO_4 . Beryllium-filtered pile neutrons are incident on the samples and the scattered neutrons are energy analysed by the time-of-flight method. A photograph of the scattering apparatus is shown in Fig. 1.

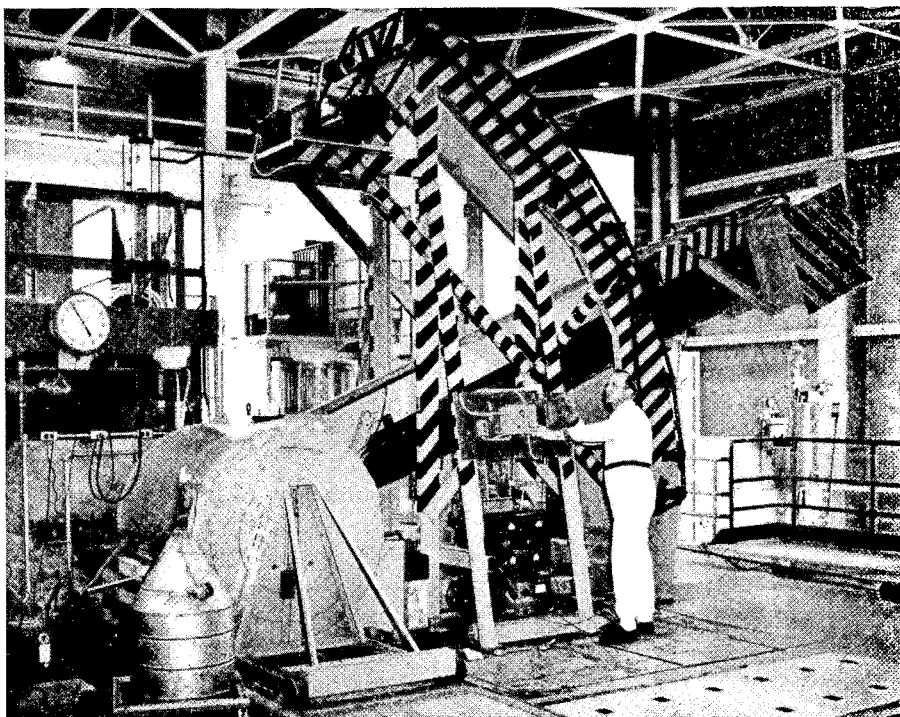


Fig. 1

The cold neutron scattering facility on the top of the Brookhaven Graphite Reactor. The direction of the incident neutrons is vertical. The sample is located at the centre of the cylindrical shield. A 5-m arm carrying the detector at the far end is connected to the shield, and the scattering angle is varied by means of the frame shown in the photograph.

2. RESULTS

Fig. 2 shows the spectra obtained with a thin sample ($0.6 \text{ cm} \times 5 \times 10 \text{ cm}$) of KH_2PO_4 at room temperature and at $T = 118^\circ\text{K}$. The incident beryllium-filtered spectrum is seen at 0.005 eV . The spectrum at energies greater than 0.007 eV arise from hydrogen motions of the sample. The details of the shape of the spectrum obtained at $T = 118^\circ\text{K}$ is what one would expect from the room temperature spectra, and the difference in the population of states as calculated from the Boltzmann factor. Therefore, we do not find any evidence for a change in these low frequency modes in going from the paraelectric to ferroelectric phase.

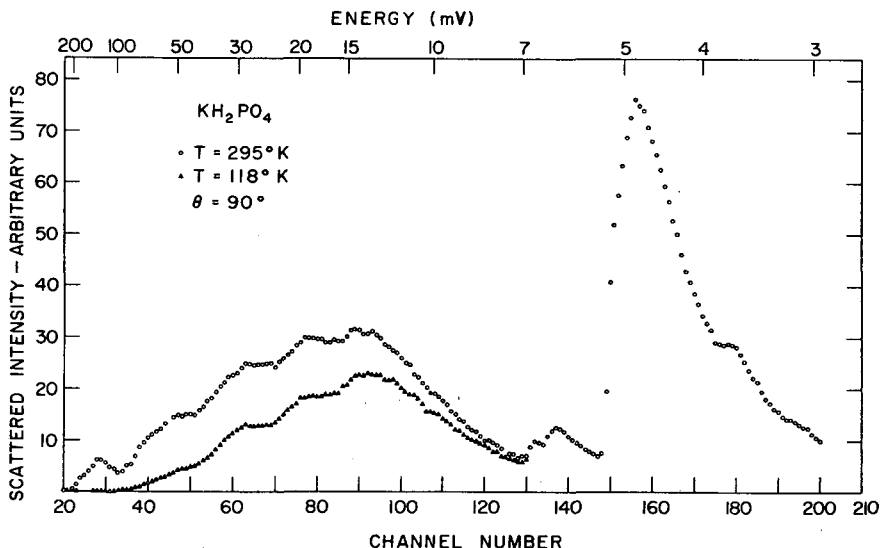


Fig. 2

Scattered neutron intensity at 90° from the incident beam for a sample of KH_2PO_4 at $T = 295$ and 118°K . The spectrum shape at 5 mV is characteristic of the incident beryllium-filtered pile spectrum.

Fig. 3 is a comparison of KH_2PO_4 and KD_2PO_4 data taken at room temperature, and is shown on an expanded energy scale. The observed intensity of the KD_2PO_4 spectrum at the low energy end ($9\text{--}15 \times 10^{-3}\text{ eV}$) was actually a factor of 4 less (per molecule) in KD_2PO_4 as compared to KH_2PO_4 . This factor corresponds to the ratio of the average scattering cross-sections of the KH_2PO_4 to KD_2PO_4 molecules. We, therefore, conclude that the

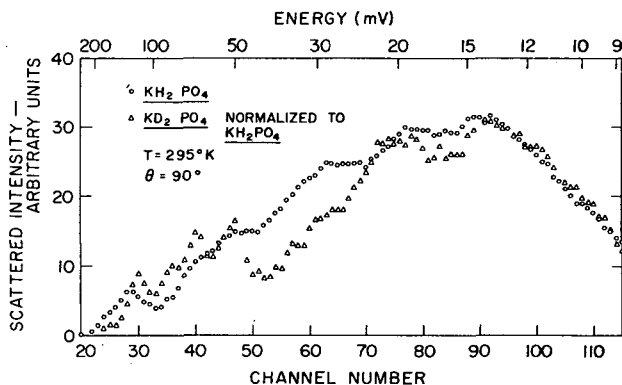


Fig. 3

Comparison of the scattered neutron intensity from samples of KH_2PO_4 and KD_2PO_4 . The KD_2PO_4 observed intensity has been multiplied by a factor of four for comparison purposes with KH_2PO_4 .

spectrum from 9 to approximately $25 \times 10^{-3} \text{ eV}$ arises mainly from low frequency motions of the entire molecule. In a band-centred $\sim 30 \times 10^{-3} \text{ eV}$, we note that the relative neutron intensity from KD_2PO_4 is far below that of KH_2PO_4 . Because the neutron cross-section for deuterium is an order of magnitude less than that of hydrogen, this band must be associated with some localized motion of hydrogen in the KDP molecule. The small differences in spectra at higher energies can probably be explained by coherent effects present in KD_2PO_4 .

3. DISCUSSION

The band of low frequency hydrogen vibrations found in KH_2PO_4 is centred around a transition energy of 0.028 eV (220 cm^{-1}). This is, at first, puzzling because Bacon and Pease conclude, "...the thermal motion of the hydrogen atoms at 77, 132 and 293°K is practically independent of temperature and is due to zero point energy."

Fig. 4, taken from the above reference, shows the measured mean square displacement of the hydrogen atom as a function of temperature, as

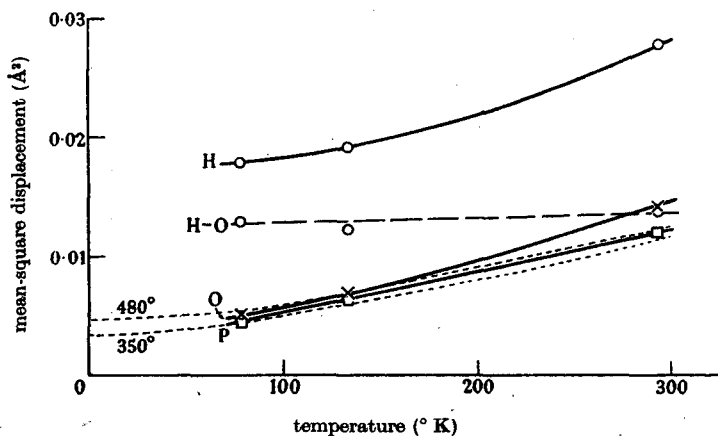


Fig. 4

Mean Square displacements of atoms in KH_2PO_4 , as measured by neutron diffraction techniques.

the points on the uppermost curve. From this is subtracted the motion of the KPO framework determined by observing the mean square displacements of the oxygen atoms and assuming that these motions are independent of each other. This results in the curve marked H-O in Fig. 4.

We interpret the low frequency hydrogen motion observed with cold neutrons as a correlated motion of the proton with respect to the oxygen atoms. The simplest model, and the first that comes to mind, is a motion of the hydrogen correlated with the O—O stretching motions. Fig. 5 shows a plan view of KDP crystal structure. The squares represent the PO_4 tetrahedrons as seen from above, with the oxygens at the corners. The black dots

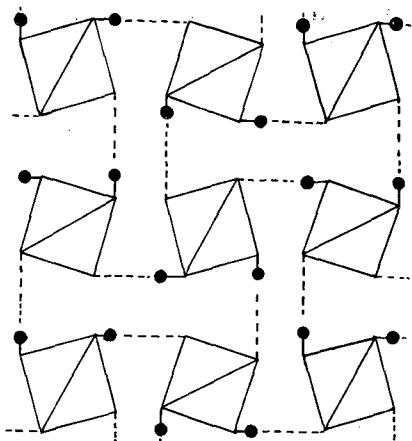


Fig. 5

The H-bonding arrangement between phosphate tetrahedra. Each phosphate group is bonded to neighbours in the planes above and below it, so that the 4H bonds forming a loop are not all in the same plane.

are the hydrogen atoms. An estimate made by Reid of the O—O stretching frequency based on a pair of freely-vibrating PO_4 groups gives a wave number of 237 cm^{-1} , and this is in very good agreement with our measured value of a band centred at 220 cm^{-1} . Our picture of the motion of the hydrogen atom is first a large zero point motion resulting from the motion of the proton in some spatially fixed potential. Then, as the oxygen atoms stretch, this potential moves in space and gives rise to a correlated motion of the hydrogen relative to the oxygen. Because the zero point motion is so large, the correlation has only meaning with respect to the average position of the zero point motion.

Our results indicate that the motions of the protons in KH_2PO_4 are close to the model proposed by Reid. This fact, together with the unobserved splitting in the vibrational spectrum of the protons makes it appear plausible that the ferroelectric transition is associated with low frequency modes of vibration of the KDP system. Reid's semi-empirical theory for KH_2PO_4 , therefore, would seem to us a good starting point for a more refined theory of KH_2PO_4 .

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DISCUSSION

W. COCHRAN: The fact that you did not see any significant difference in the results above and below the transition temperature, is, I think, something which must be expected when this technique is used. For one thing, you are averaging over all the reciprocal space in the experiment; for another, a ferroelectric mode has a wave-vector zero and modes near this value of q make very little contribution to the frequency distribution. I think this is borne out by an experiment reported at the Vienna meeting by Lefkowitz and Pelah on barium titanate*. We know from Cowley's work that there must be a big change in the frequency of the modal wave number zero in barium titanate as it goes through the transition. Yet in their experiment, which was essentially the same one as you are describing, they did not see any difference between barium titanate above the transition and barium titanate below the transition.

H. PALEVSKY: The situation may be even worse in the case I am describing because this is really all incoherent scattering, whereas there is some chance in the barium titanate that you could see coherence, or $q = 0$, if you looked in the right direction.

W. COCHRAN: One must ask what might be the order of magnitude of the frequency of the ferroelectric mode in KH_2PO_4 . This is a more difficult question in the case of KH_2PO_4 than in that of barium titanate or strontium titanate because you have to make very great assumptions in applying any kind of pseudo-harmonic theory to a situation like this where you have disorder in the hydrogen positions. I have made an attempt at estimating the frequency and reached a figure of about 85 cm^{-1} , which is considerably lower than the one that you mention. Moreover, recent infra-red measurements by Barker show that the mode associated with the anomalous dielectric properties is very strongly damped (overdamped). If it is meaningful to associate a frequency with it, then that frequency is considerably lower than the one you have detected.

H. PALEVSKY: I think that such a picture would be reasonable if the mode was at lower frequency than this zero-zero stretching frequency, because as you get up to the transition point it might be just the zero-zero motions which cause the disordering at the transition temperature.

P. EGELSTAFF: I can see very little reason, from the experimental point of view, for comparing the two spectra as the authors have done. In the case of the deuterated compound, about half of the scattering comes from the other atoms, whereas in that of the hydrated compound, nearly all of it comes from hydrogen. You therefore have to make an enormous allowance for both effects. Moreover, in the deuterated case, the coherent factors will be very much larger than in the other case. These matters are extremely complicated and their effect may be to falsify your interpretation.

H. PALEVSKY: I disagree. The fact is that this is not a very quantitative experiment. One question that we might ask is this: is the zero-zero stretching frequency shifted when deuterium is put in instead of hydrogen? It would be difficult to answer that, using your approach, but the fact is that the average scattering amplitude for hydrogen, say compared to deu-

* *Op. cit.*, p. 601.

terium, is less by a factor of nearly 10. If you add oxygen, i.e. hydrogen plus oxygen, it still is less by a factor of about 7. I think it is just the difference in the scattering amplitude that gives the effect. It may be that the deuterium is there and moving but it is way down.

P. EGELSTAFF: I do not think this is correct. It seems to me that in comparing data on hydrogenated and deuterated compounds three important correction factors have to be considered: (i) coherent scattering factors; (ii) the change in the relative importance of the scattering by the other atoms; (iii) the difference in the frequency spectrum or amplitude of vibration of deuterium and hydrogen. In the case of H_2O and D_2O , we have shown that all these effects are quite important (see the paper by Egelstaff, Haywood and Thorson entitled "The Motion of Hydrogen in Water" *). As I understand your work, you do not seem to have corrected for these factors, and consequently I cannot agree that your interpretation is valid.

H. PALEVSKY: Again I disagree. In the second case, the hydrogen has gone and the scattering amplitude from the deuterium is small.

P. EGELSTAFF: I think we agree on that. Where we differ is on how you go on from there.

B. JACROT: My question is more for Dr. Cochran. As far as I remember, there is a huge difference between the transition temperature of the hydrogenated substance and the deuterated substance. If different processes enter into the explanation of their respective ferroelectric characteristics, a comparison of the two substances becomes even more difficult.

W. COCHRAN: Yes, I agree. There is a considerable difference between the Curie temperatures of KH_2PO_4 and KD_2PO_4 . I believe it can be explained qualitatively in terms of lattice dynamics; without invoking any particular model, such as that of Pirene.

W. KLEY: In the light of the two measured frequency distributions of light and heavy water reported at yesterday afternoon's session, I must disagree somewhat with Dr. Egelstaff's remarks. As we saw, there was fairly similar behaviour on the part of the two different frequency distributions.

B. N. BROCKHOUSE: I think Dr. Egelstaff would say that he is using a procedure to get rid of the coherent effects, something which has not been done in the present case. However, the experiments that seem to me to give some hope that Dr. Palevsky's procedure is all right are those in which a comparison is made of the isotopic and natural nickel frequency distributions. From the evidence presented, these seem to be fairly close together. In the natural nickel there are large coherent effects and they occur in the same frequency range and were obtained with the same kind of apparatus as those of the later experiments.

* See these proceedings.

ENERGY DISTRIBUTION OF NEUTRONS SCATTERED FROM SOLID METHANE

H. STILLER

INSTITUT FÜR REAKTORWERKSTOFFE DER KERNFORSCHUNGSANLAGE JÜLICH
FEDERAL REPUBLIC OF GERMANY

AND

S. HAUTECLER

DÉPARTEMENT PHYSIQUE NEUTRON
CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE, MOL
BELGIUM

Abstract — Résumé — Аннотация — Resumen

ENERGY DISTRIBUTION OF NEUTRONS SCATTERED FROM SOLID METHANE. The energy distributions of neutrons scattered from solid methane at 84°K and 18°K are measured with the beryllium filter technique for incident neutron energies between 23 and 5.2 meV. The observed spectrum is interpreted as due to excitation of lattice vibrations and of rotational motions. The spectrum of lattice vibrations at 18°K can be best explained under assumption of attractive Van der Waals forces and repulsive octopole-octopole interaction. The rotational motions are found to be completely hindered at 18°K, giving rise to two bands of frequencies of "torsional waves". This distribution is compared to two models for the equilibrium orientation of the molecules. At 84°K lattice vibrations and rotational motions appear less well separated.

DISTRIBUTION DE L'ÉNERGIE DES NEUTRONS DIFFUSÉS PAR DU MÉTHANE SOLIDE. La distribution de l'énergie des neutrons diffusés par du méthane solide à 84°K et 18°K a été mesurée à l'aide d'un filtre de béryllium, l'énergie du faisceau de neutrons incidents étant comprise entre 23 et 5,2 meV. On pense que le spectre observé est dû à l'excitation des vibrations de réseau et des mouvements rotatoires. Pour expliquer la forme du spectre des vibrations de réseau à 18°K, la meilleure hypothèse consiste à admettre l'existence de forces d'attraction de Van-der-Waals et d'une interaction de répulsion octopole-octopole. On constate que les mouvements rotatoires sont totalement inhibés à 18°K, ce qui provoque l'apparition d'ondes de torsion appartenant à deux bandes de fréquences différentes. Cette distribution est comparée à celle de deux modèles pour l'orientation des molécules à l'état d'équilibre. Il semble qu'à 84°K la séparation des vibrations de réseau et des mouvements rotatoires soit moins nette.

РАСПРЕДЕЛЕНИЕ ЭНЕРГИИ НЕЙТРОНОВ, РАССЕЯННЫХ НА ТВЕРДОМ МЕТАНЕ. Распределение энергии нейтронов, рассеянных на твердом метане при температурах 84 K и 18°K, измерено с помощью метода с Ве-фильтром для энергии случайных нейтронов в диапазоне между 23 и 5,2 мэв. Наблюдаемый спектр объясняется возбуждением колебаний решетки и вращательными движениями. Спектр колебаний решетки при 18°K может быть лучше всего объяснен наличием сил притяжения Ван-дер-Ваальса и отталкивающего внутреннего взаимодействия "октуполь-октуполь". Установлено, что вращательные движения полностью устраняются при 18°K, вместо них появляются две полосы частот "крутильных волн". Это распределение сравнивается с двумя моделями ориентации равновесия молекул. При температуре 84°K колебания решетки и вращательные движения разделяются менее отчетливо.

DISTRIBUCIÓN ENERGÉTICA DE LOS NEUTRONES DISPERSADOS POR METANO SÓLIDO. Mediante la técnica del filtro de berilio se midió la distribución energética de neutrones dispersados por metano sólido a 84°K y 18°K, para energías de incidencia comprendidas entre 23 y 5,2 meV. El espectro observado puede atribuirse a la excitación de vibraciones reticulares y a movimientos de rotación. La mejor manera de explicar el espectro de vibraciones reticulares a 18°K es suponer la existencia de fuerzas de atracción de Van der Waals y de fuerzas de repulsión octopolo-octopolo. Los movimientos de rotación cesan a 18°K, originando dos bandas de frecuencias de "ondas de torsión". Se compara esta distribución con dos modelos para la orientación molecular en equilibrio. A 84°K, las vibraciones reticulares y los movimientos de rotación aparecen menos separados.

In a crystal composed of individual atoms only two kinds of motions are possible; vibrations around equilibrium positions and translations between these positions. In a molecular crystal the same two motions are possible for the molecular centres of masses; in addition, however, there are three further possibilities: vibrations of the atoms within the molecules, migration of atoms in the lattice, rotations of the molecules or of atomic groups. The following study of the internal dynamics of solid CH_4 shall be concerned with (i) the vibrations of the molecular centres of masses and (ii) the molecular rotations. The energies of these two motions are of comparable order of magnitude, whereas the vibrations of the atoms in the molecules have higher energies, outside the energy range investigated. The occurrence of classical translations is so improbable that it will not influence the observations.

The two named motions of CH_4 molecules in the crystalline state are observed by an analysis of the energies of scattered neutrons. Since the neutrons are scattered almost entirely by the protons and since this scattering is mostly incoherent, the quasi-continuous spectrum of lattice vibrations can be directly measured. As to the rotations a similarly continuous spectrum is to be expected, if in this motion the molecules are hindering each other such that these motions are proceeding through the crystal-like waves. As the motion of the particle then will be a torsional oscillation rather than a rotation, these waves may be called "torsional waves"; to distinguish them from the familiar vibrational waves. If, on the other hand, there is no hindrance between the molecules, the energies of individual transitions between free rotational states will appear in the energy distribution of the scattered neutrons, as observed in liquid CH_4 [1]. Between these two limiting cases, i. e. with weak hindering, one may expect with decreasing temperature a transition from quasi-free rotations, with still definite angular momenta and spin states, to damped torsional waves, that is: waves extending only over limited crystal regions, the mean size of these regions depending on the probability for a molecule to break loose from its state of torsional oscillation and to perform a rotation.

EXPERIMENTAL METHOD AND RESULTS

The measurements were carried out with the same experimental technique as for liquid CH_4 [1]; the beryllium filter method. With this method the number of detected neutrons is

$$N(E_0) \propto \int_{-\infty}^{\infty} R(E_0 - \epsilon) d\epsilon' \int_0^{E_f} S(\epsilon - E) dE,$$

where E_0 is the energy of the neutrons incident on the sample, $R(E_0 - E)$ the resolution function of the apparatus, $S(\epsilon - E)$ the energy distribution of the scattered neutrons, E_f the cut-off energy of the beryllium filter. Peaks in the energy distribution $S(\epsilon - E)$ appear as increases of $N(E_0)$.

The measurements were performed at two sample temperatures; at $84(\pm 1)^\circ\text{K}$ and at $18(\pm 2)^\circ\text{K}$. The latter temperature was reached by pumping on liquid hydrogen. For each temperature the observations were made at two scattering angles ϕ , for 84°K at $\phi = 65^\circ$ and 90° , for 18°K at $\phi = 70^\circ$ and 90° . Among the observed increases of $N(E_0)$ only those, which appeared for both scattering angles at the same energy positions, were interpreted as due to energy transfers between the neutrons and the molecules. A few increases, the positions of which varied with ϕ , proved to be due to coherence effects. They are not shown in the figures.* As in the study of liquid CH_4 the (001) reflection from sheets of Thermica was used for monochromizing the incident neutron beam.

Figs. 1 and 2 show the experimental results, normalized to constant incident flux (for details on the normalization see [1, 2]). The open circles

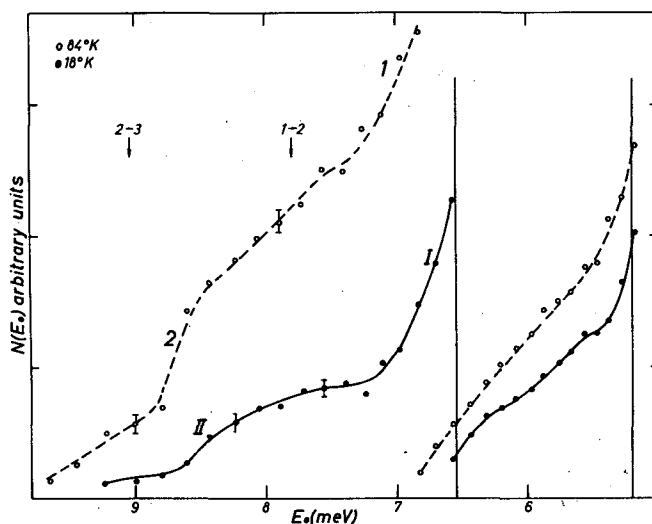


Fig. 1

Experimental results, normalized to constant incident flux.

represent the results at 84°K , the solid points represent the results at 18°K . The increases of $N(E_0)$ observed at 84°K are labelled by Arabic, the increases observed at 18°K by Roman numbers. The two vertical lines in Fig. 1 indicate the two filter cut-offs, namely $E_{f1} = 5.20 \text{ meV}$ and $E_{f2} = 6.55 \text{ meV}$

* In the measurements at 84°K there seemed to be a coherence effect between $E_0 = 11.2$ and $E_0 = 10.7 \text{ meV}$. At the other scattering angle a Bragg reflection from the sample container appeared in the same region. At this temperature the energy distribution, therefore, is still uncertain between these energies.

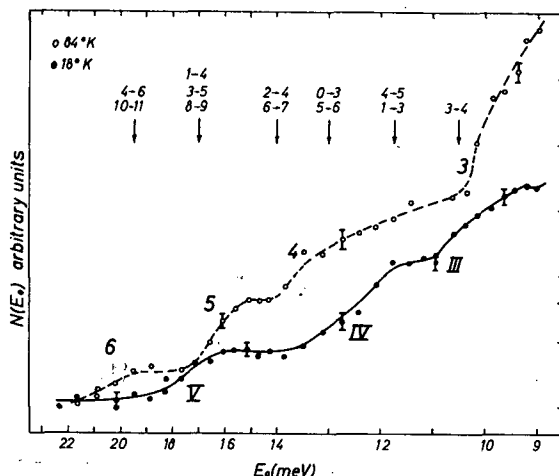


Fig. 2

Experimental results, normalized to constant incident flux.

(for more details compare [1]). One sees that both the increase at the lowest energies shown and the increases labelled I and 1, represent the elastic peaks, once at E_{f1} and once at E_{f2} . For both temperatures there is considerable increase of $N(E_0)$ also between the two cut-offs. This indicates, that the first inelastic increases (II and 2) actually extend down to E_{f1} ; i. e. they represent spectra with rather long tails reaching to zero energy transfer.

The arrows in Figs. 1 and 2 indicate energies E_0 , for which increases of $N(E_0)$ were observed in liquid methane, and which correspond to transitions between free rotational states $B L(L+1)$ with $B = 0.647$ meV. The numbers at the arrows give the angular momenta L involved in these transitions. One sees, that the increases observed here no longer correspond to transitions between levels of free rotations.

In Table I the energies E_0^1 , for which the curvatures of the increases change their sign, are listed. The last columns of the table give the corresponding energy transfers $E_0^1 - E_f$. Since for $E_0 \geq 11$ meV the resolution of the apparatus cannot distinguish between the two filter cut-offs, a mean value, 5.8 meV, was taken for E_f in this region.

DISCUSSION

X-ray measurements [3] have shown that methane crystallizes in face-centred cubic lattice structure and that this structure does not change with temperature down to 13.9°K. The equilibrium orientation of the molecules within this lattice is not known. For the case that this orientation is determined by attractive forces NAGAMIYA [4] has shown that there are only two possibilities for a regular arrangement with equal minimum distances between neighbouring protons. The CH_4 tetrahedra can be oriented either in

TABLE I

OBSERVED ENERGY TRANSFERS
(All energies in meV)

	Incr.	E_0^*	$E_0^* - E_{f1}$	$E_0^* - E_{f2}$
84°K	1	6.5		0
	2	8.75	3.55	
	3	10.1		3.6
	4	13.7	7.9	
	5	16.4	10.6	
18°K	I	6.5		0
	II	8.5	3.30	
	III	10.75	5.55	4.25
	IV	13.0	7.2	
	V	17.6	11.8	

such a way that each corner points into the direction of a cubic diagonal (model 1) or such that only one corner points into one of these directions, while the other three C-H arms tend to stay as close as possible to the cubic axes (model 2). For the other case, repulsive forces, JAMES and KEENAN [5] have found from thermodynamic considerations, under assumption of pure octopol-octopol interaction, that at low temperatures the most probable orientation would be one with proton coordinates of the form $x=0$, $\gamma = \sqrt{2/3}$, τ_{CH} , $z = l_{CH}/\sqrt{3}$, if τ_{CH} is the C-H distance in the molecule. That is: all C-H arms would lie in the planes of cubic faces (model 3). With models 1 and 3 there is one, with model 2 there are four molecules in the unit cell of the lattice.

1. LATTICE VIBRATIONS

The torsional waves cannot have an acoustical band of frequencies. In consequence, increase II, which extends to $E_0 - E_{f1} = 0$, must be due to excitation of lattice vibrations. As one can see from Table I, increase III obviously represents the same excitation as increase II, only relative to E_{f2} , with some eventual superposition of energy transfers relative to E_{f1} . This superposition may be the reason for the distance of the two increases not being exactly $E_{f2} - E_{f1}$. Increase III also extends to zero energy transfer.

In case of an orientation as proposed in model 2 (four molecules in the unit cell) one would expect optical bands of the lattice vibrations. However, since the particles all have equal masses there should be considerable overlapping of all bands. Unfortunately it is not quite certain from the experimental data whether or not increases IV and III overlap (see Fig. 2). Only increase V certainly does not overlap anywhere; increase V, therefore, can only be due to excitation of rotational motions.

If only increases II and III are due to excitation of lattice vibrations, the vibrational force constant

$$f = 1/8 M \omega_{\max}^2$$

is found to be 260 g sec^{-2} ($\hbar \omega_{\max} = 5.5 \text{ meV}$). If also increase IV is caused by or contains contributions from the lattice vibrations, f is found to be 470 g sec^{-2} ($\hbar \omega_{\max} = 7.8 \text{ meV}$).

Both these values are smaller than what one would expect from a Lennard-Jones 6-12 interaction:

$$V = 4\epsilon \left[\left(\frac{b}{r} \right)^{12} - \left(\frac{b}{r} \right)^6 \right]. \quad (1)$$

A calculation of

$$f = \left(\frac{d^2 V}{dr^2} \right)_{r=R_0}$$

with the potential (1) gives $f = 710 \text{ g sec}^{-2}$, with $b^6 = 1/2 R_0^6$, with the equilibrium distance of nearest neighbours $R_0 = 4.12 \text{ \AA}$ [3] and with $\epsilon = 7.8 \text{ meV}$, calculated from the heat of evaporation and the heat of melting $Q = 2.154 \text{ kcal/mol}$ [6]; $-\epsilon = Q/12$.

This comparison suggests, that actually the repulsive part of the potential does not obey a r^{-12} law. In view of the C-H distance being small compared to the lattice constant this law, which phenomenologically describes the mutual penetration of electron clouds, also may not be expected to hold in the crystal of CH_4 molecules. We will assume, therefore, that the repulsive potential is rather due to an octopol-octopol interaction:

$$V = \eta \left[\left(\frac{b}{r} \right)^7 - \left(\frac{b}{r} \right)^6 \right]. \quad (2)$$

In this case, with $b = 6/7 R_0$ and $\eta = (7/6)^6 a/12(1 - 6/7)^{-1}$, one finds $f = 270 \text{ g sec}^{-2}$, in very good agreement with the value calculated from $\hbar \omega_{\max} = 5.5 \text{ meV}$ (increase III).

Increases 2 and 3, observed at 84°K , also extend to $E_0 - E_f = 0$ and have maximum frequencies nearly equal to the ones observed with increases II and III at 18°K (see Table I). However, the shapes of the increases are very different at the two temperatures. Moreover, the distance between increases 2 and 3 is exactly $E_{f2} - E_{f1}$. Fig. 3 shows increases 2 and II differentiated and multiplied by

$$K(E_0) = \frac{K_f}{K_0} \frac{E_0 - E_f}{(K_0 - K_f)^2} \left(1 - \exp \left[- \frac{E_0 - E_f}{k_B} \right] \right). \quad (3)$$

One sees, that the difference is not only due to the difference in thermal

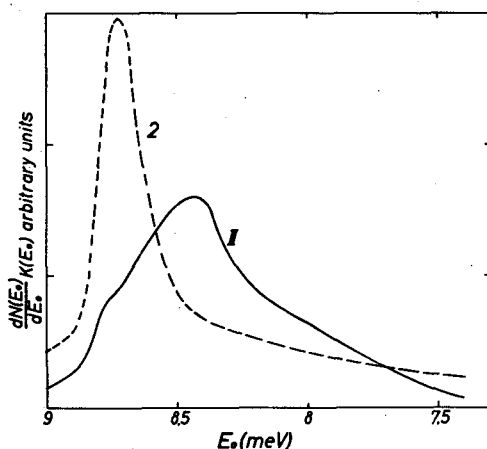


Fig. 3

occupation. However, the measurements do not allow to decide whether the difference is caused by a superposition of other motions on the lattice vibrations at 84°K or by an independent change in the lattice vibrations.

2. ROTATIONAL MOTIONS

If the increases due to excitation of lattice vibrations are identified as above, then increases V and IV, observed at 18°K, both must be due to excitation of rotational motions. The broadness of both increases indicates that these motions take place with many frequencies, presumably with a quasi-continuous spectrum as one would expect for complete hindrance. This means that the potential for the motions should be written

$$V = V_0 + \sum_i V_i^m \varphi_i^m + 1/2 \sum_{mn} \sum_{ij} V_{ij}^{mn} \varphi_i^m \varphi_j^n + \dots \quad (4)$$

where the φ_i are the components of the torsional amplitudes. In harmonic approximation only the second order term would be retained.

However, we have not yet attempted any direct calculation of the spectrum of torsional waves. Rather we want to compare the experimental results with some characteristics to be expected from two of the proposed models for the molecular equilibrium orientation. To this purpose we approximate the observed spectrum by an Einstein model for torsional waves in defining Einstein frequencies ω_E as

$$\omega_E^2 = \frac{\int \omega^2 Z(\omega) d\omega}{\int Z(\omega) d\omega} \quad (5)$$

where $Z(\omega)$ is the observed spectrum. In the spectrum of frequencies given, by Eq. (4) the Einstein frequency corresponds to

$$\bar{\omega}^2 = \frac{1}{NJ} \sum_{m,i} V_{ii}^{mm},$$

if N is the number of torsional oscillators and J the moment of inertia of the molecule, Eq. (5) follows, if the sum is replaced by

$$J \int \omega^2 Z(\omega) d\omega.$$

Fig. 4 shows increases IV and V differentiated and multiplied again by the factor (3). The curve of Fig. 4 thus represents $Z(\omega)$ without correction for

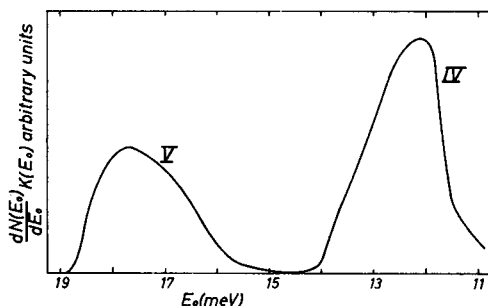


Fig. 4

the resolution of the apparatus and for eventual convolutions with other motions. With the help of this curve one finds $\hbar\omega_{EIV} = 6.7$ meV for increases IV and $\hbar\omega_{EV} = 11.6$ meV for increase V.

We will assume that the torsional amplitudes are sufficiently small, so that the potential may be approximated by an oscillator potential of the form

$$V_{\text{osc}} = -C + 1/2 f (\varphi_x^2 + \varphi_y^2 + \varphi_z^2),$$

where φ_x , φ_y , φ_z are the components of the amplitudes relative to the cubic axes. The energies of the oscillator are then

$$E_n = C + \hbar\omega_E (n + 1/2)$$

with

$$\omega_E = \sqrt{f/J}. \quad (6)$$

James and Keenan have given in explicit form the potential, which under

their assumption of mere octopol-octopol interaction would hold the molecules in the orientation of model 3*. In their notation it is

$$V = A \left(\frac{9\pi}{140} \right)^{1/2} \sum_{\nu} T_Z \left(\underline{\Omega}_{\nu}(\underline{\theta}) \right), \quad (7)$$

where $\underline{\Omega}_{\nu}$ is the position of proton ν (in polar coordinates) for the equilibrium orientation $\underline{\theta}$ (in Eulerian angles) of the molecule. In Cartesian coordinates

$$T_Z = \left(\frac{105}{6\pi} \right)^{1/2} \frac{Z(x^2 - y^2)}{r^3}.$$

In oscillator approximation this potential has been shown by HAHN and STOCKMEYER [7] to become

$$V_{\text{osc}} = A \left(-1 + \frac{5}{4} \varphi_x^2 + \frac{5}{4} \varphi_y^2 + 2\varphi_z^2 \right).$$

In consequence, two frequencies are to be expected in this model, namely

$$\omega_x = \omega_y = \left(\frac{5A}{2J} \right)^{1/2} \quad \text{and} \quad \omega_z = \left(\frac{4A}{J} \right), \quad (8)$$

so that $\omega_z/\omega_x = \omega_z/\omega_y = 1.26$. Experimentally we find $\omega_{\text{EV}}/\omega_{\text{NV}} = 1.73$. The excitation should be $I_{x,y} = 2I_z$; the present experimental data give $I_{\text{IV}} = 1.7I_{\text{V}}$. A comparison with the models proposed by Nagamiya is less straightforward, because here additional assumptions have to be made with regard to the nature of the interaction. As already mentioned the orientations of models 1 and 2 are possible only if the arrangement is determined by attractive forces. Hence Van der Waal's interaction must be taken into account.

The simplest potential holding the molecules in the orientation of model 1 would be

$$W = -g \sum_{\nu} x_1^{\nu} x_2^{\nu} x_3^{\nu}, \quad (9)$$

if $\underline{r}^{\nu} = (x_1^{\nu}, x_2^{\nu}, x_3^{\nu})$ is the position of proton ν relative to the centre of its molecule and if x_1, x_2, x_3 are cubic coordinates. In general, under assumption of central forces only, the potential could be written

$$W = \sum_{\alpha \neq 0} \sum_{\mu, \nu} \phi(|\underline{R}^{\alpha} + \underline{r}^{\mu} - \underline{r}^{\nu}|), \quad (10)$$

if $\underline{R}^{\alpha}$ is the distance of the centre of molecule α (with protons μ) from the centre of the molecule with protons ν . It has been shown by HAHN and STOCKMEYER [7] that the potential (9) is the sixth order term of an ex-

* The arguments, given in [5], are strictly valid for CD_4 only. However, this should not restrict their applicability to CH_4 as far as symmetry considerations are concerned.

pansion of (10) in orders of r^ν/R^α and r^μ/R^α , and that then, if only nearest neighbour interaction is considered,

$$\tilde{g} \equiv g \left(\frac{r_{CH}}{\sqrt{3}} \right)^3 = P \phi(R_0) \quad (11)$$

with

$$P = 12 \left(\frac{r_{CH}}{\sqrt{3}} \right)^6 (0_3^3 + 4R_0^2 0^4 + 4R_0^4 0^5). \quad (10)$$

Here R_0 is the equilibrium distance of nearest C-atoms and 0 is the operator $r^{-4} \partial/\partial r$. In oscillator approximation the potential (9) becomes [7]

$$W_{osc} = -4 \tilde{g} + 6 \tilde{g} (\varphi_x^2 + \varphi_y^2 + \varphi_z^2),$$

so that in Eq. (6)

$$f = 12 \tilde{g}. \quad (13)$$

We will now assume that the interaction is composed of two terms, a repulsive interaction W_r and an attractive Van der Waal's term W_w ;

$$W = W_r + W_w \quad (14)$$

$$W_r = g_r \sum_{\nu} x_1^{\nu} x_2^{\nu} x_3^{\nu} \quad (15)$$

$$W_w = g_w^i + g_w \sum_{\nu} x_1^{\nu} x_2^{\nu} x_3^{\nu}.$$

The constant g_w^i represents the angular independent part of the Van der Waal's interaction. From Eq. (11)

$$\tilde{g} = P \phi(R_0), \quad \tilde{g} = P \phi(R_0). \quad (16)$$

$$\phi_w = -\frac{c}{r^6}. \quad (17)$$

In order to avoid any particular assumptions with regard to the nature of the repulsive forces we will determine their value at the equilibrium orientation from the total force acting between the molecules. For this force the best agreement with the observed spectrum of lattice vibrations was found with the potential (2), which we will now write in the form

$$V = \frac{a}{r^7} - \frac{b}{r^6}; \quad V_{min} = \frac{a}{R_0^7} - \frac{b}{R_0^6}. \quad (18)$$

The minimum value W_{min} of W must be $W_{min} = 12 V_{min}$, if only nearest neighbours are considered. By comparison of Eq. (15) and (18) one thus obtains

$$W_{r\min} = 4 \tilde{g}_r = 12 a R_0^{-7}; \quad \tilde{g}_r = 2.57 \text{ meV.} \quad (19)$$

For the Van der Waal's constant c in Eq. (17) we assume, that the attractive force between two molecules is the sum of Van der Waal's attractions between protons, so that $c = b/16$. This assumption leads to the largest possible value for $\tilde{g}_w$. One then finds from (16) with (12)

$$\tilde{g}_w = -3.6 \times 10^6 \left(\frac{r_{CH}}{\sqrt{3} R_0} \right)^6 \frac{b}{16 R_0^8} = -2.52 \text{ meV.} \quad (20)$$

Both values are calculated with a and b expressed again by ϵ and R_0 and with the same values for these constants as before. With $|\tilde{g}| = |\tilde{g}_r + \tilde{g}_w|$ and with Eq. (13) the Einstein frequency becomes

$$\hbar\omega_E = \left(\frac{12 \hbar^2}{J} |\tilde{g}| \right)^{1/2} = 0.6 \text{ meV.} \quad (21)$$

This is in poor agreement with the experimental results*. The agreement would be improved, if no repulsive forces were taken into account. But it seems difficult to visualize a complete absence of repulsive forces acting on the molecular orientation.

The results obtained at 84°K are much more difficult to discuss. In the region $E_0 > 14$ meV (Fig. 2) the measured energy distribution has a more distinct structure, in the region $14 \text{ meV} \geq E_0 \geq 11$ meV it has a less distinct structure than at 18°K. Qualitatively this behaviour suggests quasi-free rotations rather than damped torsional waves. On the other hand, if the decomposition of the rotational levels $L=1$ and $L=2$ is calculated in first order perturbation with a potential of the form (9);

$$W = 4\tilde{g} \cdot [1/2 \sin 2\psi \sin 2\varphi (3 \cos^2 \theta - 1) - \cos 2\psi \cos 2\varphi \cos 2\theta],$$

where ψ , φ and θ are the Eulerian angles, one finds that the transitions between the different sub-levels should have an intensity distribution as shown in Fig. 5. The distribution is calculated without taking into account degeneracies due to the three different molecular spin states. Even so, of the three peaks the lower ones are found to have a full width at half maximum of approximately $\tilde{g}$, and the main peak in the centre shows a width of about $2\tilde{g}$. If $\tilde{g}$ is calculated from Eq. (21) with the experimental value $\hbar\omega_E = 11.6$ meV, one finds $\tilde{g}_{\text{exp}} = 8.7$ meV. From Fig. 1 one sees, that in view of its energy position increase 2 might contain contributions from transitions between sub-levels around $L=1$ and 2; but if so, then only in form of a base, because increase 2 is much narrower than $\tilde{g}_{\text{exp}}$.

However, this discrepancy can have two different reasons. Either the molecules are not in a state of quasi-free rotations, to which a perturbation calculation can be applied. Or the calculation is quantitatively wrong,

* With the values (19) and (20) $\tilde{g} = \tilde{g}_r + \tilde{g}_w$ even turns out positive, which is inconsistent with model 1. It also should be noted that, if instead of the potential (18) a Lennard-Jones 6-12 potential had been used, $\tilde{g}$ definitely would be positive.

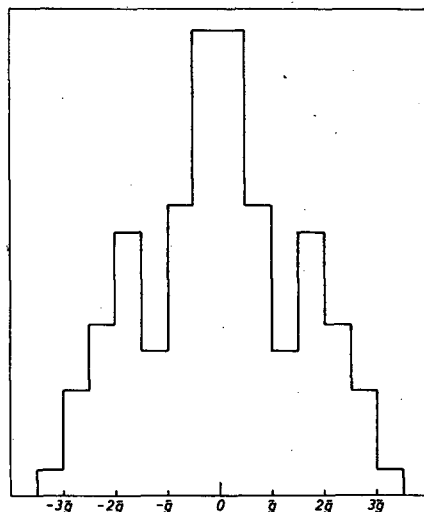


Fig. 5

Intensity distribution of transitions between levels decomposed from rotational levels
 $L = 1$ and $L = 2$, calculated in first order perturbation.

because (i) the potential (9) is not the actual one, that is: the equilibrium orientation is different from model 1 also for 84°K, or (ii) the potential is weaker at 84°K than at 18°K, i. e. the above value for $\tilde{g}$, taken from the experimental data at 18°K, should not be used here. A decision between the two possibilities is not yet possible.

Table II summarizes our interpretation of the observed neutron energy distribution.

TABLE II

INTERPRETATION OF EXPERIMENTAL RESULTS

	Incr.	Range of frequencies (in meV)	Interpretation
18°K	II	5.5 to 0	Lattice vibrations ($\theta_D = 63^\circ\text{K}$)
	III		
	IV	8.5 to 5.8	Torsional oscillations
	V	15 to 10.2	Torsional oscillations
84°K	2	3.6 to 0	Lattice vibrations perhaps rotational motions
	3		
	4	9 to 5.3	Rotational motions perhaps lattice vibrations
	5	13 to 10	Rotational motions

3. THE λ -POINT

At 20.4°K a λ -transition appears in the specific heat of solid CH₄ [8, 9]. Very recently a second irregularity in the specific heat has been found at 8°K [10]. In solid CD₄ two λ -points can be observed very clearly [11], separated by only a few degrees, namely at 22.2°K and at 27.1°K. The fact that none of these transitions are associated with a change in the crystalline structure, of course, leads to the assumption that the transitions are due to changes in the molecular orientations, i. e. to changes in the rotational motions [12]. The results of the present experiments show, however, that the change cannot be simply a transition from a state of free to a state of hindered rotations, because already at 84°K considerable hindrance is observed. In a more indirect way it could be concluded already earlier from nuclear magnetic resonance [13, 14] and from infra-red measurements [15] that the nature of the transitions must be more complicated.

One is thus led to the assumption that the transitions represent changes in the hindrance of the rotations. From the mentioned three models for the orientational arrangement of the molecules different models also for the change of the hindrance can be derived. In agreement with conclusions drawn by SAVITSKY and HORNIG [15] from their infra-red measurements the present experimental results suggest that the arrangement proposed in model 1 is not the stable one below the λ -point. A decision between the other models is not yet possible. Further neutron experiments and more detailed calculations on the torsional waves are in progress. It is hoped that they will serve to solve the problem more completely.

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V

MAGNETIC SCATTERING

SPIN WAVES IN MAGNETITE FROM NEUTRON SCATTERING

B. N. BROCKHOUSE* AND H. WATANABE**
ATOMIC ENERGY OF CANADA LTD., CHALK RIVER, ONTARIO
CANADA

Abstract — Résumé — Аннотация — Resumen

SPIN WAVES IN MAGNETITE FROM NEUTRON SCATTERING. This paper reports measurements of the acoustical and optical spin waves in magnetite by means of neutron spectrometry. The complete acoustical branch, and part of an optical branch, were determined for the [100] direction of the reduced zone, principally using the "constant Q ," and constant energy transfer methods. The optical frequency at which the A and B sub-lattices precess as units is 0,058 eV. The measurements largely conform the existing theory of T. A. Kaplan and others. The results indicate a value of J_{AB} of 2.3×10^{-3} eV, with a much smaller (and probably ferromagnetic) B-B interaction. The results so far are not very sensitive to the A-A interaction. The difficulties in the experiments largely arise from the irreconcilable requirements: (a) that the energy transfers be large because the quantum energies are large, and (b) that the momentum transfers be small in order that the magnetic form factor be of acceptable size. These and other aspects of the experiments will be discussed.

ONDES DE SPIN DANS LA MAGNÉTITE PAR SUITE DE DIFFUSION NEUTRONIQUE. Dans ce mémoire, les auteurs donnent les résultats de mesures des ondes de spin optiques et acoustiques dans la magnétite, par la spectrométrie neutronique. Ils ont déterminé la branche acoustique complète ainsi qu'une partie de la branche optique le long de la direction [100] de la zone réduite, en utilisant principalement la méthode du Q constant et la méthode du transfert d'énergie constante. La fréquence optique pour laquelle les sous-réseaux A et B subissent la précession est de 0,058 eV. Les mesures concordent dans l'ensemble avec la théorie de T. A. Kaplan et al. Les résultats indiquent une valeur de $2,3 \cdot 10^{-3}$ eV pour J_{AB} , avec une interaction B-B beaucoup plus faible (probablement ferromagnétique). Jusqu'ici les résultats ne sont pas très sensibles à l'interaction A-A. Les difficultés de l'expérience proviennent surtout de ce qu'elle est sujette aux conditions suivantes qui sont incompatibles : a) les transferts d'énergie doivent être grands vu que les énergies quantiques sont grandes et b) les transferts d'impulsions doivent être petits de manière que le facteur de forme magnétique ait une valeur acceptable. Les auteurs discutent ces aspects de l'expérience ainsi que d'autres.

СПИНОВЫЕ ВОЛНЫ В МАГНЕТИТЕ ПРИ НЕЙТРОННОМ РАССЕЯНИИ. В этом докладе приводятся данные об измерении звуковых и оптических спиновых волн в магнетите, проведенных посредством нейтронной спектрометрии. Акустическая кривая в целом и часть оптической кривой определены для [100] направления сокращенной зоны, используя при этом "константу Q " и методы передачи постоянной энергии. Оптическая частота, при которой подрешетки A и B прецессируют, равняется 0,058 эв. Измерения в большинстве случаев совпадают с существующей теорией Т.А. Каплана и других. Эти результаты достигают величин для J_{AB} $2,3 \cdot 10^{-3}$ эв и значительно меньше (повидимому, в случае ферромагнитного) B-B взаимодействия. Результаты пока что не очень соответствуют взаимодействию A-A. Трудности при проведении опытов в основном возникают из-за несовместимых требований: а) чтобы передача энергии была большей, ввиду значительной энергии кванта; б) чтобы момент передачи был меньше, для того чтобы фактор магнитической формы был приемлемого размера.

ONDAS DE ESPÍN PRODUCIDAS EN LA MAGNETITA POR DISPERSIÓN NEUTRÓNICA. La memoria trata de la medición de ondas de espín acústicas y ópticas en la magnetita por espectrometría neutrónica. En la dirección [100] de la zona reducida, se ha determinado la rama acústica completa y parte de la rama

** Now at Physics Department, McMaster University, Hamilton, Ontario, Canada.

* IAEA Fellow from Research Institute for Iron, Steel and other Metals, Tohoku University, Sendai, Japan. Now returned.

óptica, aplicando principalmente el método de Q constante y el de la transferencia de energía a constante. La frecuencia óptica a la que las subredes A y B describen unitariamente un movimiento de precesión es 0,058 eV. Los valores medidos concuerdan en grado considerable con las predicciones teóricas de T. A. Kaplan y otros autores. Los resultados indican un valor de J_{AB} igual a $2,3 \cdot 10^{-3}$ eV, con una interacción B-B mucho menor (probablemente ferromagnética); hasta ahora no parecen ser muy sensibles a la interacción A-A. Las dificultades experimentales se deben en gran parte a dos requisitos incompatibles: a) que las transmisiones de energía sean elevadas, pues también lo son las energías cuánticas, y b) que las transmisiones de cantidad de movimiento sean reducidas para que el factor de forma magnética sea de magnitud aceptable. Los autores examinan estos y otros aspectos de los experimentos.

I. INTRODUCTION AND THEORY

Magnetite (Fe_3O_4) is one of the ferrite group of metal oxides having the spinel crystal structure with the ferrimagnetic structure originally proposed by NÉEL [1, 2]. The iron atoms lie on two interpenetrating sublattices A and B. The structure is face-centred cubic with two A-type iron atoms, four B-type iron atoms and eight oxygens in the primitive unit cell (with four times these numbers in the cubic unit cell). Magnetite has the so-called "inverted" spinel structure with two Fe^{3+} ions on the A-sites, and two Fe^{3+} and two Fe^{2+} ions on the B-sites. In the Néel structure, confirmed by neutron diffraction [3, 4], the moments on the A-sites are aligned together and are directed antiparallel to the also aligned moments on the B-sites. According to Néel the exchange interaction between nearest neighbour atoms on the A and B sites is large and antiferromagnetic, dominating the also antiferromagnetic, but weaker, interactions among the atoms on the A-sites. The mutual interactions of the atoms on B-sites are weak; most of the evidence suggests that the B-B interaction is antiferromagnetic, although the magnetic short-range order developed in zinc ferrite indicates that it is ferromagnetic [5].

From measured dispersion curves for the spin waves in ferrites, it should be possible to actually determine the exchange interactions between the various atoms in the crystal. Earlier experiments [6-8] demonstrated the existence in magnetite of acoustic spin waves with the expected properties. In this paper a more nearly complete set of experiments is presented [9], which demonstrate the existence of "optical" spin waves, and from which some quantitative information about the spin waves can be deduced. These experimental results, to be discussed in the following sections, are summarized in Fig. 1.

1. SPIN WAVE THEORY

The theory of the spin waves in ferrites has been successively developed by H. KAPLAN [10], J. S. KOUVEL [11], and T. A. KAPLAN [12]. There are six branches to the spin wave spectrum, corresponding to the six atoms in the primitive unit cell. One of the branches is "acoustical"; at small wave vector (q) its quantum energy ($\hbar\omega$) is proportional to $[q]^2$. The other five branches are "optical" and have finite energies at $q = 0$. According to KOUVEL [11], the branches have the following properties at $q = 0$: The acoustical branch (following T. A. Kaplan, designated here

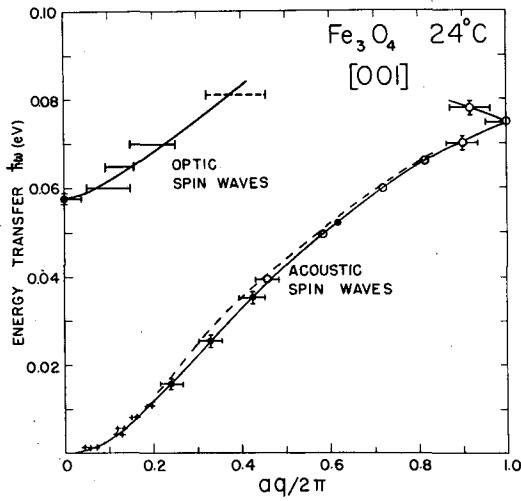


Fig. 1

Experimental dispersion curve for spin waves in Fe_3O_4 at room temperature.
(For symbols, see text.)

The dashed curve gives the results before correction for resolution.

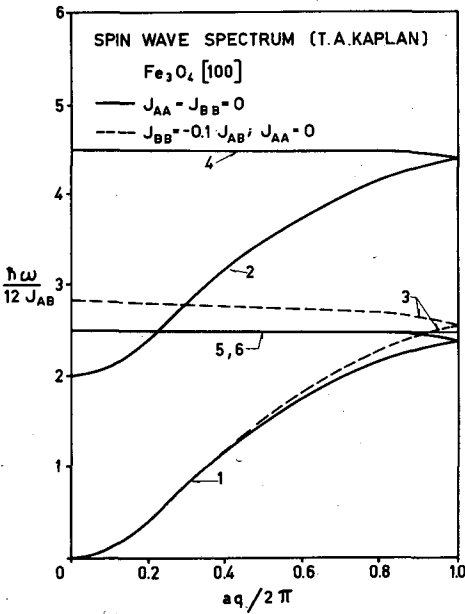


Fig. 2

Theoretical dispersion curves according to T. A. Kaplan for models described
in the insert and the text.

as 1) and one of the optical branches (designated 2) cause the still fully-aligned A and B sub-lattices to precess about each other (with different phases for the two branches). Another optical branch (designated 4) disorganizes the A-sites, the B-sites remaining fully aligned in the motion. A triply degenerate optical branch (designated 3, 5, 6) disorganizes the B-sites, the A-sites remaining aligned. (T.A. Kaplan has shown that the three-fold degeneracy lifts for $q \neq 0$, but that, at least under the usual assumptions of forces, branches 5 and 6 remain degenerate). Dispersion curves calculated by T.A. KAPLAN [12] for the [100] directions of the reduced zone are shown in Fig. 2. In these directions degeneracies occur at the zone boundary by reason of symmetry; branch 3 is continuous with branch 1, and branch 4 with branch 2. For interactions between nearest neighbours only on the B-sites, the degenerate branch 5, 6 is flat; this would not be the case, however, for more complicated B-B interactions.

The solid lines of Fig. 2 show the dispersion curves calculated on the assumption of nearest neighbour A-B interactions only. The resemblance of the lower branches to the measured curves of Fig. 1 is striking, and indicates the general correctness of the theoretical ideas. The dashed lines show the effect on branches 1 and 3 of including a small ferromagnetic B-B interaction. (Branches 2 and 4 are not much affected by the B-B interaction, and conversely, branches 1 and 3 are insensitive to A-A interactions.) The agreement with experiment is probably improved, suggesting again that, while the B-B interactions are certainly weak, they may be ferromagnetic.

2. THEORY OF THE EXPERIMENTS

As is now well known neutrons are scattered by spin waves in processes which cause the creation or annihilation of a single spin wave quantum (a magnon), energy and quasi-momentum being conserved between the neutron and magnon. The incoming and outgoing neutron energies (E_0 , E') and wave vectors ($\underline{k}_0$, $\underline{k}'$) are related to the energy ($\hbar\omega$) and wave vector ($\underline{q}$) of the magnon by equations

$$E_0 - E' = \pm \hbar\omega \quad (1a)$$

$$\underline{Q} = \underline{k}_0 - \underline{k}' = 2\pi \underline{\tau} - \underline{q}, \quad (1b)$$

where τ is a vector of the reciprocal lattice. The reciprocal lattice for the (1, $\bar{1}$, 0) plane of magnetite is shown in Fig. 3. Because of Eqs. (1) and the existence of a dispersion relation $\omega = \omega(\underline{q})$ for the spin waves, the scattered neutrons occur in groups in the angular and energy distribution.

The theory of neutron scattering by spin waves has been discussed by ELLIOTT and LOWDE [13] and others for general materials, and by T.A. KAPLAN [14] for ferrites. Aside from trivial factors, the intensities of the neutron groups are given [13, 6] by the product of a population factor, a geometrical factor (the Waller-Froman factor $[J]^{-1}$ which sums over the number of spin waves which contribute to a group), and magnetic inelastic structure factor $|G|^2$ which includes the atomic form factors of the magnetic atoms.

The intensity as a function of the position in reciprocal space is largely determined by the structure factor. If the magnetic atoms are substantially identical and at special positions in the unit cell, then (except for the common form factor) the structure factor repeats itself over reciprocal space, the unit of repetition being larger than the reduced zone. For magnetite this "large zone" is indicated by the dashed lines in Fig. 3.

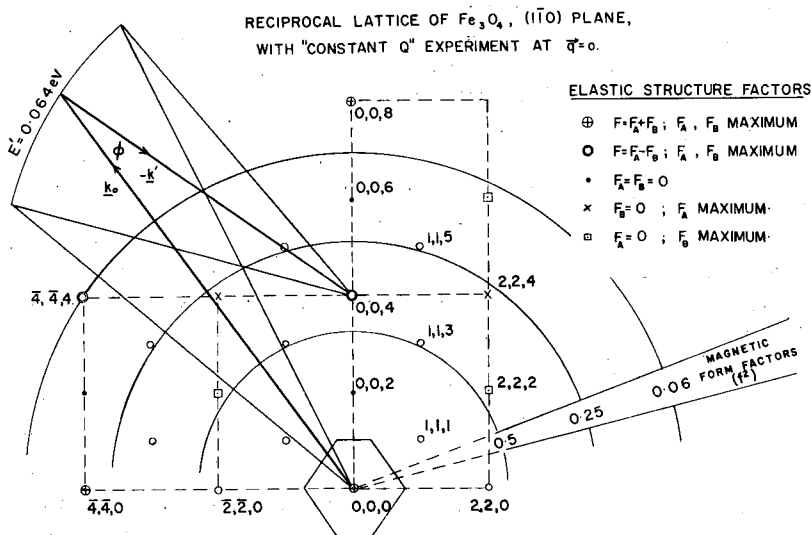


Fig. 3

Reciprocal lattice of Fe_3O_4 , showing the reduced zone about the origin, and the large zones indicated by dashed lines. The initial and final positions of a "Constant Q" experiment are given together with the diagram for the measured group g in Fig. 4.

The design of the experiments is considerably aided by consideration of the elastic magnetic structure factors F . For branches 1 and 2 near $q = 0$, the moments on the two sub-lattices are completely aligned; only the orientations of the individual sub-lattices vary in the motion. Thus for these branches, measurements should be made at positions in Q -space for which the individual structure factors, approximately equal to F_A and F_B , have near maximum values. (At the points $[0, 0, 2]$ or the equivalent $[0, 0, 6]$, for example, branches 1 and 2 both have zero intensity since for these points $F_A = F_B = 0$. On the other hand, these are probably good points to study other branches, which disorganize the sub-lattices.) The point $[0, 0, 4]$ is particularly good for the acoustic branch 1, since, because of the ferromagnetic structure, F_A and F_B are of opposite sign but yet have their maximum possible absolute values, and hence the overall structure factor $|F_A - F_B|$ is a maximum. Point $[0, 0, 4]$ turns out also to be almost as good for branch 2, although this is more difficult to see intuitively. For the other branches the expected intensities at $[0, 0, 4]$ turn out to be zero, as might be expected since $|F_A|$ and $|F_B|$ are maxima and the disorganized sub-lattices must have much smaller scattering power.

In carrying out the experiments we have been guided by a variety of considerations such as the above, and by some detailed calculations of structure factors made (for the simple model of first neighbour A-B interaction only) by T. A. KAPLAN [14 and private communication] .

The experiments are made difficult by the high energies of the magnons. It turns out that branch 2 starts at $q = 0$ with an energy of 0.058 eV and then rises. It is expected that branch 4 has energies in excess of 0.1 eV. These energies are already somewhat difficult to measure because of the limited spectrum of neutron energies available from a reactor. However, the difficulties are compounded many times by the fact that it is necessary to keep the wave vector transfer Q small, in order that the magnetic atomic form factor f should have a reasonable value. Values of the form factor for iron atoms in ferrites [4] are indicated in Fig. 3 as part circles. It is clear that this effect drastically limits the region of Q -space available for the experiments, and also the neutron energy ranges which can be used. (For example, it would not be possible to measure branch 4 with either E_0 or E' in the "cold neutron" range even with considerably higher neutron fluxes than are now available.) In order to stay within the acceptable region of Q -space both energies must be rather high and this again compounds the effect of the limited reactor energy spectrum.

II. EXPERIMENTS

Experiments were carried out on both [15] the triple axis crystal spectrometer and the rotating crystal time-of-flight spectrometer at the NRU reactor. The specimens were cut from a natural magnetite crystal [6] and have been described elsewhere [9] . The triple axis spectrometer was used to study the higher energy part of the acoustic branch and the optical branch. The rotating crystal spectrometer was used to study the low energy part of the acoustic branch under the especially high resolution available with this instrument.

1. CRYSTAL SPECTROMETER EXPERIMENTS

The crystal spectrometer was used in two modes of operation [15] :
(a) "Constant Q " mode

The angle of scattering ϕ and the crystal orientation ψ are varied step by step with the incoming energy E_0 (and wave vector k_0) in such a way as to keep the wave vector transfer Q fixed, the analysing spectrometer being meanwhile held constant at some fixed energy E' . The results for two typical experiments of this type are shown in Fig. 4. In the experiments E' was always smaller than E_0 ; consequently the (111) plane of an aluminium crystal was used in the analysing spectrometer, while higher order planes (usually (220)) were used in the monochromator for the incident beam, in order to match resolutions. The vector diagram for an experiment to determine the optical mode 2 at $q = 0$ is shown in Fig. 3. This experiment gave the result shown in Fig. 4(a).

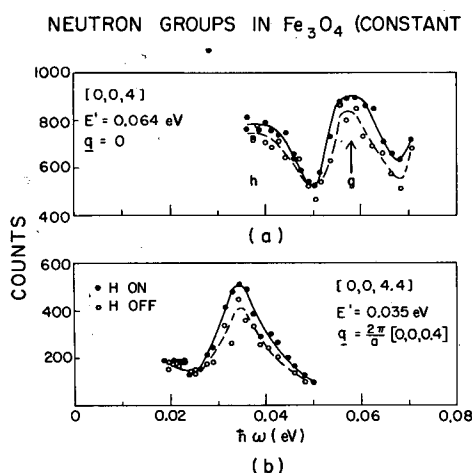


Fig. 4

Two "Constant $\vec{Q}$ " experiments.

(b) Constant energy transfer mode

With E_0 and E' fixed to give the desired energy transfer $\hbar\omega$, the angles ϕ and ψ are varied in step in such a way as to cause the end point of the vector $\vec{Q}$ to traverse a desired straight line in reciprocal space. If the frequency of a branch changes rapidly along the line and passes through the value $\hbar\omega$, then a neutron group will be observed. Some curves obtained with this method are given elsewhere [9]. For these experiments the method has an important advantage; the pattern is taken at the actual energies desired, while in the constant $\vec{Q}$ (and also the conventional) methods incident energies considerably higher than that corresponding to the peak must be available in the reactor spectrum. The method is also attractive in that the backgrounds tend to be flatter than with the other methods. The method cannot be used however for flat branches such as 3 or 4.

In the crystal spectrometer experiments a magnetic field of about 2800 Oe was applied and the counting rate measured at each point with the field on and off. The field was vertical and thus normal to the plane of the spectrometers, i.e. of $\vec{k}_0$ and $\vec{k}'$. In this geometry the intensities of neutron groups due to magnons are expected to decrease by a factor of (ideally) $4/3$, while the intensities of groups due to phonons should increase if they change at all [16, 6, 17]. Thus magnons can be distinguished from phonons (Fig. 4).

The results of the experiments are shown in Fig. 1; open circles and bars without points represent the results of constant energy transfer measurements, filled circles represent the results of constant $\vec{Q}$ measurements. The error bars represent estimated probable errors.

For most of the acoustic branch the neutron groups were strong and sharp, and unambiguously identifiable as magnons. For optical modes and for acoustical modes near the zone boundary, the intensities were much reduced, but even here the magnetic field effects were sufficiently pronounced to make the identification almost certain. The only observed group not clearly assignable on the spectrum of T.A. Kaplan is that labelled 'h' in Fig. 4(a).

The intensity of this group, relative to group 'g' (assigned as the optical mode 2), was smaller in another similar experiment with somewhat different parameters, and it may be due to some as yet unrecognized spurious effect.

The measurements were corrected for the effect of resolution in Q -space in the following way. The largest contributor to resolution effects is the vertical divergence of the spectrometer beams which introduce a vertical component of the wave vector q . This vertical component has an average value of zero but a finite R.M.S. value $\bar{q}_v$. Thus the average value of the wave vector deduced from the position of a neutron group via Eqs. (1) should be $[q^2 + \bar{q}_v^2]^{1/2}$ instead of the nominal value in the plane. Since it turns out that the acoustic branch is almost isotropic, and therefore depends only on the magnitude of q , the correction can be easily and accurately applied to the extent that the vertical divergences are known. Estimates of the divergences were made and corrections applied to the points of Fig. 1. The dashed line shows the results [9] before application of the correction.

A number of experiments were performed to attempt to detect other branches, without definitive results, probably because of insufficient intensity. Some evidence was observed for an optical mode with $\hbar\omega \sim 0.09$ eV at the $[2, 2, 4]$ reciprocal lattice point.

Experiments were performed to test to what degree the acoustic dispersion curve is isotropic. Constant energy transfer experiments with $\hbar\omega = 0.0493$ eV were made along five lines in Q -space radiating from the $[0, 0, 4]$ reciprocal lattice point in the $[0, 0, 1]$, $[1, 1, 0]$ and $[1, 1, 1]$ directions of the reduced zone. The values for the wave vectors of acoustic magnons of the above energy propagating in these directions were equal, to well within the errors, the mean reduced wave number ($aq/2\pi$) being 0.585 ± 0.015 .

2. TIME-OF-FLIGHT EXPERIMENTS

In order to measure the low energy part of the acoustical branch some experiments were performed under high resolution on the rotating crystal spectrometer. Incident neutrons of $4.059 \text{ \AA}$ were used with the high resolution set of counters described earlier [15]. The vector k' (for the central counter) was directed so that it passed through a reciprocal lattice point of type $[1, 1, 1]$. The vector diagrams for two of the experiments are shown in Fig. 5, and the wavelength distributions in Figs. 6 and 7. In addition to an elastic group E, two sharp neutron groups (a, b, c, d) which result from magnons are seen in each pattern. Groups near 'f' in Fig. 7 are thought to be due to phonons. When plotted in reciprocal space (Fig. 5), the groups are seen to represent solutions to Eqs. (1) on either side of the reciprocal lattice point concerned. After correction for vertical divergence effects (II. 1) the results have been plotted in Fig. 1 as crosses. (It should be noted that for these points q is not in fact in the $[0, 0, 1]$ direction of the reduced zone, although this should not be important because of the isotropy of the dispersion relation.) Without the correction, the dispersion curve would have shown an intercept at $q = 0$ of about 1 meV.

Experiments similar to these have been reported recently by RISTE [8], using the Saclay reactor in France.

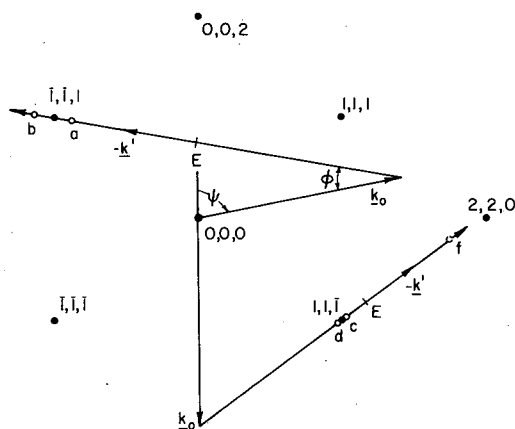
TWO EXPERIMENTS IN THE $(1\bar{1}0)$
PLANE OF A MAGNETITE CRYSTAL

Fig. 5

Reciprocal space diagrams for two time-of-flight experiments.

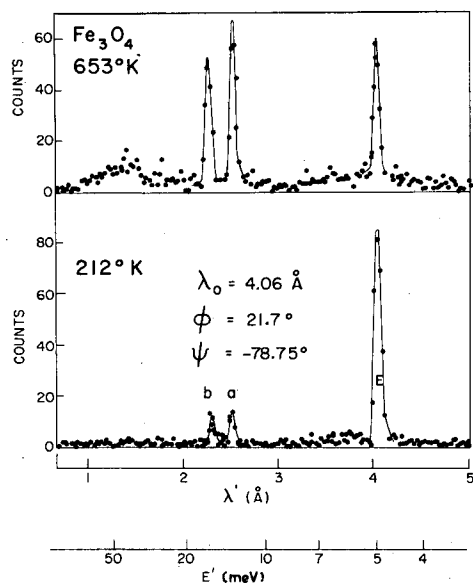


Fig. 6

Wavelength distributions at two temperatures for one of the experiments of Fig. 5.

The temperature dependence of the distributions was studied at four temperatures between 212° and 653°K (Fig. 6). Aside from changes in intensity, which were in agreement with the theory, the major effect of

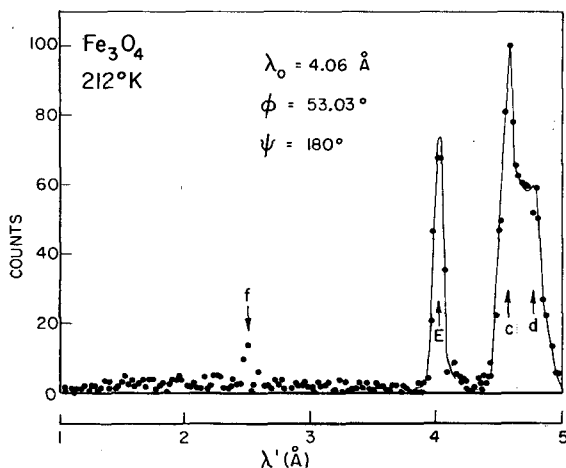


Fig. 7

Wavelength distribution for one of the experiments of Fig. 5.

raising the temperature was to cause the two groups to slightly separate in reciprocal space. If we write the dispersion curve for small q in the form

$$\hbar\omega = \alpha q^2,$$

this effect means that α decreases with temperatures. Let the separation of the two groups in Q -space be δq . Then it is easy to show that, to first order,

$$\alpha \sim (\delta q)^{-2}.$$

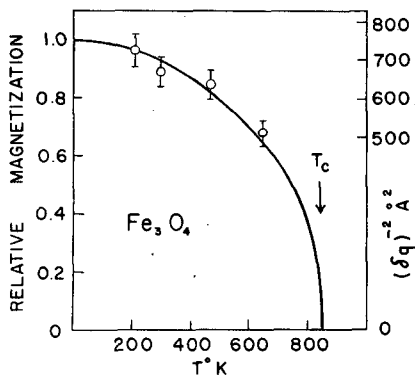


Fig. 8

Comparison of measured peak separations of Fig. 6 with the reduced magnetization [18], as functions of the temperature.

In Fig. 8 the quantity $(\delta q)^{-2}$ for the groups of Fig. 6 ($\hbar\omega \sim 9$ meV) is plotted as a function of the temperature. The reduced magnetization of magnetite [18] is also plotted, the ordinate scales being normalized together at the lowest temperature. The result shows that the "force constant" α varies with temperature somewhat as the magnetization. This result applies also to similar patterns with $\hbar\omega \sim 5$ meV, but for $\hbar\omega \sim 1.3$ meV (Fig. 7) the results were inconclusive.

In all the experiments the neutron groups remained remarkably sharp, and no increase in width with temperature was detected with certainty. Upper limits on the true full widths at half maximum (W) of the groups at 653° K (after correction for resolution by Gaussian unfolding) are: for magnons with $\hbar\omega \approx 1.3$ meV, $W < 0.1$ meV; $\hbar\omega \approx 5$ meV, $W < 0.2$ meV; $\hbar\omega \approx 9$ meV $W < 0.4$ meV. Thus the low energy acoustic spin waves are remarkably well defined at a temperature 75% of the Curie temperature. This observation is in accord with results of RISTE [8].

III. CONCLUSIONS

By comparison of the experimental and theoretical curves of Figs. 1 and 2, we conclude that the exchange integral for Fe atoms on A and B sites, J_{AB} , has the value 2.3 meV with an accuracy of probably better than 10%. (J_{AB} is defined so that the interaction energy is $2J_{AB} \sum_i S_{Ai} \cdot S_{Bi}$.) As noted earlier [6, 9], this is in serious disagreement with conclusions from the specific heat [19].

Much work remains to be done. It is the opinion of the authors that the dispersion curves of Fig. 1 can, with considerable difficulty, be completed and it is hoped that this will be done. This would probably enable the complete set of forces to be deduced.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Dr. T.A. Kaplan for much discussions and correspondence, to Mr. E.A. Glaser and Mr. A.L. Bell for technical assistance, and to Mr. V.A. McCourt of the Mines Branch, Ottawa for cutting the crystals.

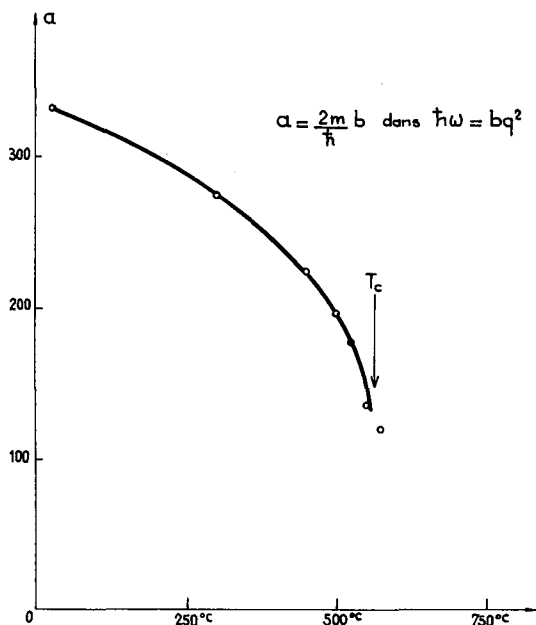
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DISCUSSION

B. JACROT: Last year at Saclay, Riste, Cribier and I studied the energy variation of spin waves in Fe_3O_4 . Our results, shown in the curve below, are in excellent agreement with those of Brockhouse in the zone of recovery. Our results were obtained by techniques identical to his.



T. RISTE: I would only like to add that the magnetization curve has to go to zero at Curie temperature. However, as you see, the spin wave energy stays finite even at this temperature, so there is actually a deviation from the magnetization curve as you go high enough in temperature. But in the lower regions, it seems to be a good fit.

DIFFUSION PAR MnF_2 A L'ÉTAT PARAMAGNÉTIQUE

D. CRIBIER ET B. JACROT
CENTRE D'ÉTUDES NUCLÉAIRES DE SACLAY
FRANCE

Abstract — Résumé — Аннотация — Resumen

SCATTERING BY MnF_2 IN THE PARAMAGNETIC STATE. This small-angle scattering ($<30^\circ$) gives a line which grows in width with the scattering angle. At large angles, the width is constant and the line is Gaussian. From its width we were able to measure the exchange integrals in MnF_2 .

DIFFUSION PAR MnF_2 A L'ÉTAT PARAMAGNÉTIQUE. Cette diffusion aux angles faibles ($<30^\circ$) donne une raie dont la largeur croît avec l'angle de diffusion. Aux grands angles, la largeur est constante, la raie est gaussienne. Sa largeur nous a permis de mesurer les intégrales d'échange dans MnF_2 .

РАССЕЯНИЕ НА MnF_2 В ПАРАМАГНИТНОМ СОСТОЯНИИ. Это рассеяние на малые углы ($<30^\circ$) дает луч, ширина которого увеличивается с углом рассеяния. При больших углах ширина - постоянна, луч - гауссовский. Ширина луча дала возможность измерить обменные интегралы в MnF_2 .

DISPERSIÓN POR MnF_2 EN ESTADO PARAMAGNÉTICO. Esta dispersión en pequeños ángulos ($<30^\circ$) origina una raya cuya anchura aumenta con el ángulo de dispersión. Para ángulos grandes, la anchura permanece constante y la raya asume características gaussianas. Su anchura ha permitido a los autores medir las integrales de intercambio en el MnF_2 .

1. INTRODUCTION

A la température ordinaire, MnF_2 est une substance paramagnétique. Son point de Curie T_c est à 72°K (transition antiferromagnétique). Sa constante de Curie θ est, suivant les auteurs [1] [2], comprise entre 72°K et 113°K . Une valeur de 80°K est la plus vraisemblable [2]. De toute façon la température ordinaire est une température élevée si on la compare à ces températures caractéristiques.

La diffusion des neutrons lents par une substance paramagnétique, où il n'y a pas de contribution orbitale du magnétisme, a été l'objet d'une étude théorique par VAN VLECK [3]. Plus récemment DE GENNES [4] a repris cette étude selon les méthodes introduites par VAN HOVE [5] pour le calcul de la diffusion des neutrons lents par une assemblée de diffuseurs. La section efficace $d^2\sigma/d\Omega dE$ de diffusion des neutrons est la transformée de Fourier par rapport aux variables d'espace et de temps de la fonction de corrélation $\Gamma(r, t)$ entre les centres diffuseurs. Dans le cas où le centre diffuseur est un ion de spin S , cette fonction est la valeur moyenne $\langle S_0(0)S_r(t) \rangle$ du produit scalaire d'un spin de référence à l'instant initial et d'un spin situé à une distance r du premier et considéré à l'instant t . D'après les propriétés d'une transformée de Fourier, la diffusion avec un grand changement de quantité de mouvement du neutron ($ba \gg 1$ où a est une distance interatomique) est déterminée par les corrélations entre voisins rapprochés. Van Vleck et

De Gennes montrent qu'alors la distribution en énergie des neutrons diffusés est voisine d'une distribution gaussienne. Le second moment de cette distribution est, pour un diffuseur polycristallin

$$\langle \omega \rangle^2 = (2/3)(1/\hbar)S(S+1)\sum_j (2J_j)^2 \quad (1)$$

où le changement d'énergie est $\hbar\omega$. J_j est l'intégrale d'échange entre un spin origine et ses voisins de type j qui sont au nombre z_j .

Par contre si l'on considère la diffusion avec de plus petits vecteurs de diffusion, il faut tenir compte des corrélations entre spins éloignés. Contrairement à l'hypothèse implicite de Van Vleck, $\Gamma(r, t)$ n'est pas nul. Dans la limite des tout petits vecteurs de diffusion, De Gennes a montré que la section efficace prend la forme

$$\frac{d^2\sigma}{d\Omega dE} = \left(1, 91 \frac{e^2}{mc^2}\right)^2 \frac{1}{3\pi} \frac{k}{k_0} |f(k)|^2 S(S+1) \frac{2\Lambda k^2}{\omega^2 + \Lambda k^4} \quad (2)$$

où $f(k)$ est le facteur de forme et où Λ est un coefficient de diffusion.

2. CONDITIONS EXPÉRIMENTALES

Nous avons utilisé des neutrons d'une longueur d'onde moyenne 4,27 Å. La largeur à mi-hauteur de leur spectre en énergie est de $1,3 \cdot 10^{-3}$ eV. Les neutrons diffusés sont analysés par leur temps de vol sur une longueur de 3,67 m. La diffusion a été mesurée entre $7^\circ 5'$ et 90° , c'est à dire pour des vecteurs de diffusion moyens compris entre $0,19 \text{ Å}^{-1}$ et $2,08 \text{ Å}^{-1}$. L'échantillon polycristallin a été soigneusement déshydraté pour éliminer une diffusion parasite due à de faibles quantités d'eau. Lors d'une première expérience [6] la présence d'un peu d'eau dans l'échantillon avait eu pour résultat d'ajouter une composante élastique à la diffusion, donc de réduire la largeur aux grands angles. Dans la présente expérience, l'échantillon a été considéré comme sec lorsqu'un traitement thermique à une température plus élevée que le traitement précédent n'a pas modifié le poids de l'échantillon, ni déformé le spectre des neutrons diffusés.

3. RÉSULTATS EXPÉRIMENTAUX

La figure 1 représente le spectre des neutrons diffusés à 45° . On voit clairement que la courbe a deux composantes. La composante élastique assez faible est probablement due à la diffusion incohérente nucléaire de MnF_2 dont la section efficace est de l'ordre de 0,6 b. L'intensité de cette composante est effectivement la même à tous les angles de diffusion. Nous l'avons soustraite de tous les résultats. L'origine magnétique de la raie élargie est confirmée par sa variation d'intensité en fonction de l'angle de diffusion. Le tableau I donne pour chaque angle d'observation l'intensité observée ainsi que l'intensité calculée à l'aide du facteur de forme de l'ion Mn^{++} , normalisées à l'angle 0.

Des courbes analogues à celles de la figure 1 ont été obtenues pour chacun des angles figurant dans le tableau I. On a également mesuré la diffusion en l'absence d'échantillon, et la diffusion par un échantillon de vanadium de même forme que celui de MnF_2 .

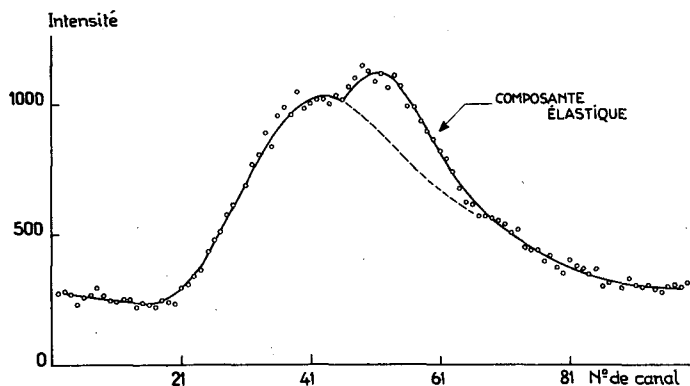


Figure 1

 Diffusion à 45° par MnF_2 .

La figure 2 représente la largeur Γ à mi-hauteur, exprimée en longueur d'onde, de la raie diffusée pour chaque angle de diffusion. Cette largeur est obtenue à partir de la largeur de la raie expérimentale en la corrigeant de la largeur Γ_i du spectre incident. Pour les grands angles on fait cette correction, qui est d'ailleurs faible, en considérant que le spectre expérimental est la convolution de deux gaussiennes.

$$\Gamma^2 = \Gamma_{\text{exp}}^2 - \Gamma_i^2. \quad (3)$$

Le fait d'assimiler le spectre incident à une gaussienne est une bonne approximation. Nous verrons plus loin que la section efficace aux grands angles est effectivement gaussienne.

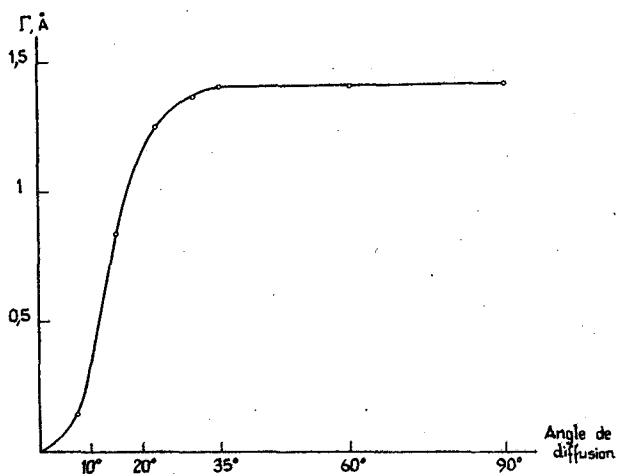


Figure 2

 Diffusion des neutrons de $4,5 \text{ \AA}$ par MnF_2 .

TABLEAU I

INTENSITÉ DIFFUSÉE PAR MnF_2 EN FONCTION
DE L'ANGLE DE DIFFUSION

Angle de diffusion	7°5	15°	22°5	30°	45°	60°	90°
Intensité mesurée	1	0,99	0,945	0,93	0,855	0,71	0,57
Intensité calculée	1	0,98	0,96	0,93	0,86	0,77	0,60

Pour les petits angles on a au contraire supposé qu'il existe une convolution entre une gaussienne (le spectre incident) et une lorentzienne (la section efficace). Pour ce faire, nous avons utilisé la relation suivante due à SARMA [7]

$$D = 2\sqrt{L^2}\Delta + 1,0651\delta + 0,2721\frac{\delta^2}{\Delta} \quad (4)$$

où D est la largeur totale à mi-hauteur de la courbe résultant de la convolution d'une gaussienne $\exp(-x^2/\Delta^2)$ et d'une lorentzienne $(x^2 + \delta^2)^{-1}$. La largeur obtenue par cette méthode à 7°5 est deux fois plus faible que celle que l'on obtiendrait à partir de la relation (3). Mais elle est certainement plus correcte, car nous verrons que l'expérience concorde avec l'hypothèse de la section efficace exprimée en (2) pour les petits angles. Notons que entre 20° et 30°, les deux méthodes donnent sensiblement le même résultat. L'allure générale de la figure 2 est bien celle que l'on attend d'après la théorie de De GENNES [4].

4. DIFFUSION AUX GRANDS ANGLES

A partir de 45° la raie diffusée garde la même forme. Cette forme a été étudiée en détail sur le spectre obtenu à 45° ($k = 1,15 \text{ \AA}^{-1}$).

Le spectre est d'abord corrigé sur la partie de haute énergie d'un léger résidu de la diffusion inélastique dû aux phonons. On corrige ensuite de la variation de l'efficacité des compteurs et du facteur k/k_0 qui figure dans la section efficace. On effectue également une correction pour tenir compte de ce que le facteur de forme n'est pas le même tout le long du spectre. Toutes ces corrections sont faibles, et leur effet global est inférieur à 10%. Le spectre final, représenté sur la figure 3, est comparé au spectre incident. La figure 4 représente encore le spectre sur échelle semi-logarithmique, l'abscisse étant le carré ω^2 des transferts d'énergie. Ceci établit nettement le caractère gaussien de la section efficace. On en déduit le deuxième moment. Le résultat corrigé de la largeur du spectre incident est

$$\langle \omega^2 \rangle^{\frac{1}{2}} = 24^{\circ}6 \text{ k}_B.$$

La précision de ce résultat est de l'ordre de 2%. Ce moment reste constant dans la limite des précisions expérimentales pour des angles de diffusion supérieurs à 45°.

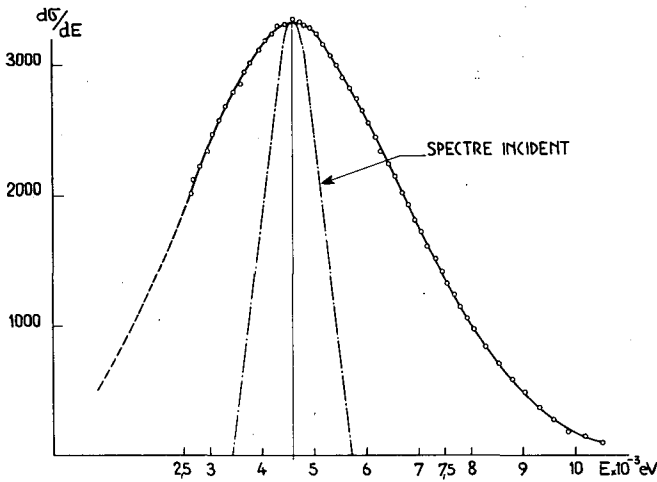


Figure 3

Diffusion à 45° par MnF_2 .

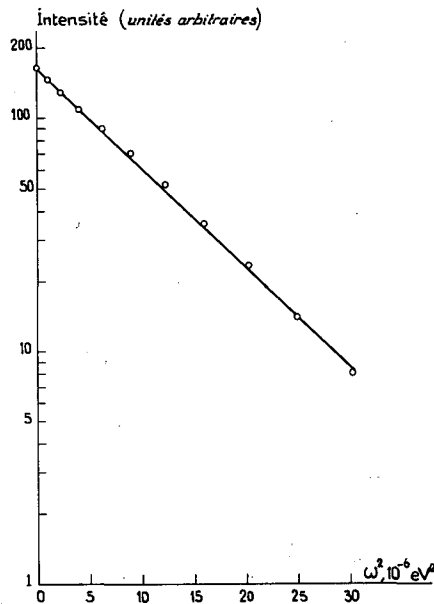


Figure 4

Diffusion à 45° par MnF_2 .

5. DIFFUSION AUX PETITS ANGLES

La largeur de la raie diffusée tend vers zéro avec l'angle de diffusion. Ceci rend les résultats moins précis. Il est difficile d'établir à partir de nos résultats le caractère lorentzien de la section efficace. Mais on peut

constater que la courbe expérimentale a des ailes beaucoup trop importantes pour une gaussienne. Il est alors raisonnable d'admettre une section efficace de la forme (2). Le coefficient de diffusion obtenu à partir du spectre diffusé à $7^{\circ}5$ est $\Lambda = 6 \cdot 10^{-4}$ cgs; à 15° la courbe est déjà nettement plus large que la courbe donnée par la forme (2) avec ce coefficient.

6. DISCUSSION DES RÉSULTATS

MnF_2 est un cristal quadratique centré avec $a = 4,86 \text{ \AA}$ et $c = 3,28 \text{ \AA}$. Les ions Mn sont situés au sommet et au centre du parallélépipède (Figure 5). Au-dessous du point de transition ($T_N = 72^{\circ} \text{K}$) la substance est anti-ferromagnétique avec une maille magnétique identique à la maille cristallographique, l'atome du centre ayant un spin opposé à ceux des atomes placés au sommet. Pour déterminer les diverses interactions entre spins nous disposons grâce à la relation (1) d'une relation indépendante de celle donnant la constante de Curie θ :

$$(3/2)k_B\theta = S(S+1)\sum_j J_j. \quad (5)$$

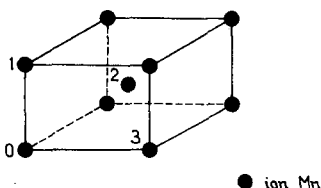


Figure 5

Position des ions de manganèse dans MnF_2 .

Une première analyse peut être faite en introduisant deux intégrales d'échanges seulement. L'une J_2 entre un spin et les huit spins qui lui sont antiparallèles à froid. L'autre J_1 entre ce même spin et ses six voisins parallèles. Les relations (5) et (2) permettent alors de déterminer J_1 et J_2 . On trouve alors $J_2 = 1,79$, $J_1 = -0,08$. Ces valeurs ont été obtenues en prenant pour θ la valeur de 80°K . Ce résultat qui indique une forte prédominance de l'intégrale relative aux spins antiparallèles, est bien en accord avec le fait que T_N est très voisin de θ . Une analyse plus approfondie peut être essayée en introduisant trois intégrales d'échange. On distingue alors l'intégrale J_1 d'interaction avec les deux plus proches voisins, de l'intégrale J_3 d'interaction avec les quatre autres voisins parallèles. On peut alors déterminer J_2 en fonction du rapport J_3/J_1 . Le résultat est donné sur la figure (6). Pour $\theta = 72^{\circ} \text{K}$ on voit que le résultat obtenu plus haut pour J_2 dépend très peu du rapport J_3/J_1 .

Dans une expérience en préparation, utilisant un monocristal de MnF_2 , les intégrales J_3 et J_1 pourront être mesurées séparément.

En ce qui concerne le coefficient de diffusion Λ , DE GENNES [4] en donne l'expression approchée

$$\Lambda = 0,36 a^2 S(S+1) 2J/\hbar.$$

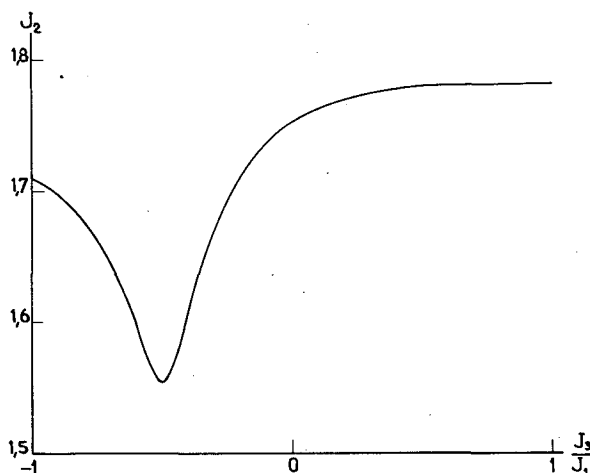


Figure 6

Variation de la valeur obtenue par l'intégrale d'échange J_2
en fonction du rapport des intégrales J_3 et J_1 .

Cette expression est pour un seul type d'interaction avec huit voisins situés à la distance a . Si on utilise pour J la valeur 1,79 trouvée plus haut on trouve $\Lambda = 6,9 \cdot 10^{-4}$ cgs ce qui concorde bien avec la valeur expérimentale de $6 \cdot 10^{-4}$.

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DISCUSSION

B. MOZER: Do the widths that you measure look quite narrow just slightly below the Curie point?

B. JACROT: We have not given any results below Curie point for the line width. We have a lot of data, but it has not yet been used.

DIFFUSION AUX PETITS ANGLES DES NEUTRONS PAR LE FER ET LE NICKEL AU VOISINAGE DU POINT DE CURIE

B. JACROT, J. KONSTANTINOVIC*, G. PARETTE ET D. CRIBIER
CENTRE D'ÉTUDES NUCLÉAIRES DE SACLAY
FRANCE

Abstract — Résumé — Аннотация — Resumen

SMALL-ANGLE SCATTERING OF NEUTRONS BY IRON AND NICKEL CLOSE TO THE CURIE POINT. Recent studies on critical scattering by iron have thrown fresh light on the results obtained previously and shown that:

- (1) At the Curie point, scattering is inelastic. The Lorentzian form of the lines and their angular dependence establish the existence of a scattering process having the diffusion coefficient $2m\Omega/\hbar = 7$.
- (2) At the Curie point, the coefficient K_1^2 is less than $5 \times 10^{-5} \text{ \AA}^{-2}$. Iron and nickel have very different angular distribution. Small-angle scattering below T_C has also been studied.

DIFFUSION AUX PETITS ANGLES DES NEUTRONS PAR LE FER ET LE NICKEL AU VOISINAGE DU POINT DE CURIE. De nouveaux travaux sur la diffusion critique par le fer ont permis de compléter les résultats obtenus antérieurement. Ils établissent les faits suivants:

1. Au point de Curie la diffusion est inélastique. La forme lorentzienne des raies et leur dépendance angulaire établissent l'existence d'un processus de diffusion avec un coefficient de diffusion $2m\Omega/\hbar = 7$.
2. Au point de Curie le coefficient K_1^2 est inférieur à $5 \cdot 10^{-5} \text{ \AA}^{-2}$.

La distribution angulaire est très différente dans le cas du fer et du nickel. On a également étudié la diffusion aux petits angles en dessous de T_C .

РАСSEЯНИЕ НЕЙТРОНОВ ПОД МАЛЫМИ УГЛАМИ ЖЕЛЕЗОМ И НИКЕЛЕМ, БЛИЗКИХ К ТОЧКЕ КЮРИ. Последние работы по критическому рассеянию нейтронов железом дали возможность дополнить полученные ранее результаты. Было установлено:

1. В точке Кюри рассеяние неупруго. Лорентцева форма лучей и их угловая зависимость обосновывают наличие процесса рассеяния с коэффициентом рассеяния $2m\Omega/\hbar = 7$.
2. В точке Кюри коэффициент K_1^2 больше $5 \cdot 10^{-5} \text{ \AA}^{-2}$.

Угловое распределение весьма различно в случае с железом и никелем. Было также изучено рассеяние на малые углы ниже T_C .

DISPERSIÓN DE NEUTRONES EN ÁNGULOS PEQUEÑOS POR EL HIERRO Y EL NÍQUEL CERCA DEL PUNTO DE CURIE. Nuevos trabajos sobre la dispersión crítica por el hierro han permitido completar los resultados obtenidos anteriormente. Dichos trabajos prueban los hechos siguientes:

- 1) La dispersión es inelástica en el punto de Curie. La forma lorentziana de las rayas y su dependencia angular demuestran la existencia de un proceso de dispersión con un coeficiente de dispersión igual a $2m\Omega/\hbar = 7$.
- 2) En el punto de Curie, el coeficiente K_1^2 es inferior a $5 \cdot 10^{-5} \text{ \AA}^{-2}$.

La distribución angular es muy diferente en el caso del hierro y del níquel. Se ha estudiado también la dispersión en pequeños ángulos por debajo de T_C .

INTRODUCTION

L'étude de la diffusion critique par le fer et le nickel près du point de Curie a été l'objet de divers travaux antérieurs [1, 2, 3, 4, 5]. Les résultats

* Adresse actuelle Institut «Boris Kidrich», Belgrade, Yugoslavia.

obtenus avec le nickel [5] montrent une différence importante des interactions dans le fer et le nickel. Par ailleurs, ce travail sur le nickel établit que, contrairement aux prévisions théoriques de VAN HOVE [6], cette diffusion est inélastique même au point de Curie. Comme les travaux antérieurs sur le fer n'avaient pas la possibilité de mettre en évidence cette inélasticité, nous avons entrepris une nouvelle étude de la diffusion aux petits angles par le fer. Faites dans des conditions expérimentales très supérieures aux précédentes, ce travail a permis:

- a) de comparer la diffusion critique par le nickel et le fer,
- b) d'établir l'inélasticité de la diffusion par le fer et de l'étudier quantitativement. L'expérience a permis d'autre part de vérifier par une nouvelle mesure les résultats obtenus par ERICSON et JACROT [3, 4].

1. RAPPELS THÉORIQUES

La diffusion extrêmement forte des neutrons par une substance magnétique près de son point de transition a été expliquée par VAN HOVE [6]. Elle a son origine dans les fluctuations d'aimantation de la substance qui ont un caractère dramatique au point de transition. La section efficace du processus est, suivant VAN HOVE, DE GENNES et ELLIOT [6 - 9] pour une substance ferromagnétique:

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(1,91 \frac{e^2}{\hbar c}\right)^2 \frac{2}{\pi} \frac{k_B T V}{V/\chi + A q^2} \frac{\Lambda q^2}{\omega^2 + \Lambda^2 q^4} \quad (1)$$

q est la longueur du vecteur de diffusion, $\hbar\omega$ est le transfert d'énergie, e , $\hbar$, c , T , k_B ont leur signification usuelle. V/χ est la susceptibilité par unité de volume. Les paramètres A et Λ permettent de rendre compte de la portée et de la relaxation de ces fluctuations. Au lieu de A , Van Hove avait introduit le paramètre K_1 relié à A par

$$A = (V/\chi)(1/K_1^2). \quad (2)$$

La forme de l'équation (1) correspond à des fluctuations dont le comportement spatial à grande distance est en $\exp(-K_1 r)$. K_1^{-1} mesure donc la portée des fluctuations.

Λ est un coefficient de diffusion relié au temps de relaxation des fluctuations par

$$1/\tau_q = \Lambda q^2. \quad (3)$$

Ce coefficient de diffusion a été évalué par DE GENNES [7, 8], MORI et KAWASAKI [10]. De Gennes prévoit un coefficient de diffusion nul au point de Curie (τ_q infini). Mori par contre prévoit un temps de relaxation de la forme

$$1/\tau_q = D[(V/\chi)(1/A) + q^2] q^2. \quad (4)$$

2. CONDITIONS EXPÉRIMENTALES

L'échantillon est un fer Armco de 2 mm d'épaisseur. Il est chauffé sous vide dans un four par rayonnement; les multiples écrans de rayonnement assurent à l'échantillon une homogénéité meilleure que 1°C. Pour les expériences les plus fines (diffusion aux tout petits angles, distribution angulaire), un diaphragme limite le faisceau à une surface de 80 mm² où l'homogénéité est bien supérieure.

Les neutrons utilisés ont une longueur d'onde de 4,75 Å; L'ouverture angulaire totale du faisceau incident est de 0° 9. Les neutrons diffusés sont détectés dans un angle de 0° 5 et analysés après un parcours de 5 mètres.

Un soin particulier a été apporté à la mesure de la température faite par des thermocouples de chromel-alumel de très petit diamètre.

Le champ magnétique utilisé a été obtenu à l'aide de bobines de Helmholtz placées autour du four. La direction du champ est modifiée en faisant tourner l'ensemble four-bobines autour du faisceau incident.

3. ÉTUDE DE LA DISTRIBUTION ANGULAIRE AU-DESSUS DE T_c ET DÉTERMINATION DE K₁²

Si l'on regarde les relations (1) et (2) on voit que le paramètre K₁² apparaît dans un terme $(K_1^2 + k_0^2 \theta^2)^{-1}$ où k₀ est le vecteur d'onde du neutron incident et θ l'angle de diffusion. Lors d'un travail précédent [3, 4], K₁² avait été déterminé en gardant θ fixe et regardant la variation de ce terme avec k₀. Les résultats trouvés étaient très différents de ceux obtenus [1] à partir des distributions angulaires. Pour clarifier cette question nous avons étudié la distribution angulaire au voisinage du point de Curie. Les résultats sont reproduits sur la figure 1. Nous reviendrons plus loin sur l'aspect particulier des distributions en dessous de T_c. Au-dessus de T_c, nous avons, dans un domaine angulaire assez grand, une variation bien linéaire. De ces distributions nous pouvons déduire les résultats suivants:

1. Les valeurs de K₁² ont été déduites pour trois températures. Les résultats sont comparés sur la figure 2 avec les résultats obtenus antérieurement par Ericson et Jacrot. On voit le bon accord.

2. Au point de Curie la précision des mesures permet de dire que K₁² est inférieur à $5 \cdot 10^{-5}$, c'est-à-dire que la portée des fluctuations à T_c est supérieure à 140 Å.

3. Dans le nickel [5], pour interpréter les distributions angulaires, il faut ajouter un terme en q⁴ dans la section efficace. Dans le cas du fer, ce terme est beaucoup moins important.

4. La figure 3 montre que K₁ est très voisine dans le fer et le nickel; ce que nous avons dit au paragraphe précédent signifie que, par contre, dans le cas du nickel, les fluctuations décroissent moins rapidement que e^{-K₁u}.

4. ÉTUDE DE L'INÉLASTICITÉ AU POINT DE CURIE ET AU-DESSUS DU POINT DE CURIE

La figure 4 montre la forme du spectre diffusé par le fer au point de Curie. Ce spectre est pour une diffusion à un angle de 9°. On voit clairement que la diffusion est inélastique. L'étude de la forme de ce spectre

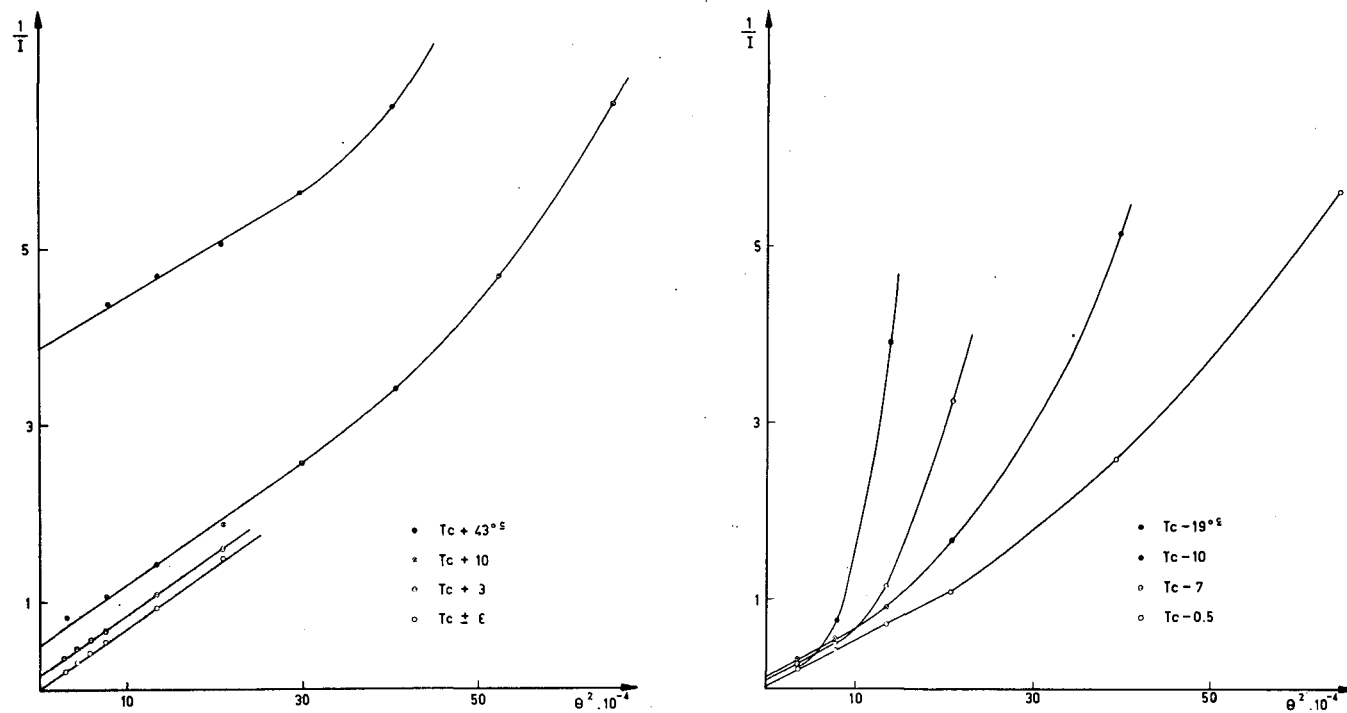


Figure 1

Distribution angulaire des neutrons diffusés par le fer au point de Curie et au voisinage.

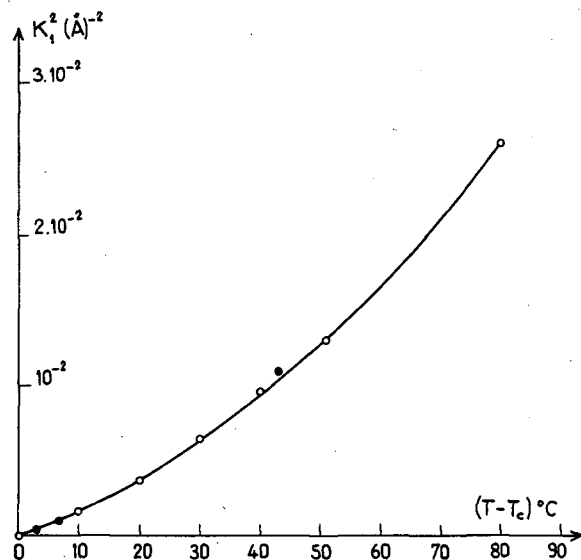


Figure 2

Comparaison des valeurs de K_1^2 obtenues par l'étude des distributions angulaires et par la variation de l'intensité diffusée avec la longueur d'onde.

- Anciennes mesures (ERICSSON-JACROT 1960)
- Valeurs déduites des distributions angulaires.

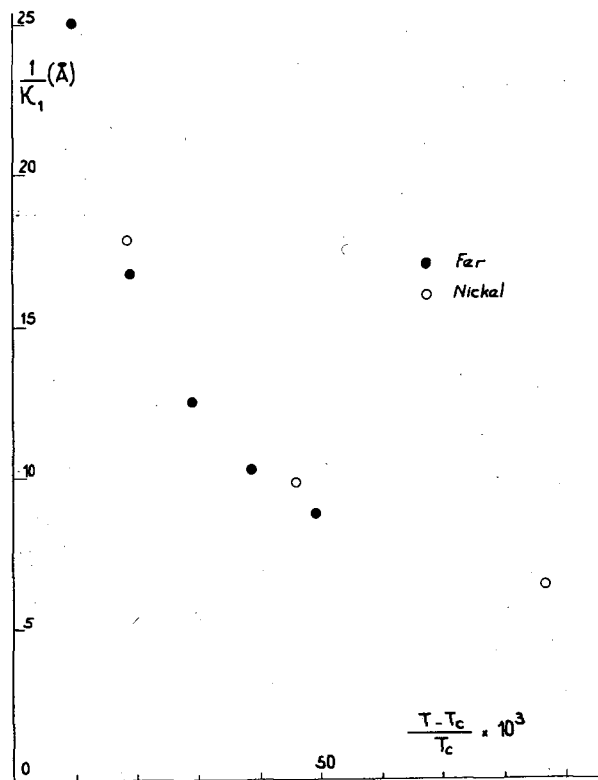


Figure 3

Comparaison de la portée des fluctuations dans le fer et le nickel.

montre qu'il résulte de la convolution d'une section efficace lorentzienne et du spectre incident. Ceci établit la validité de la forma 1 de la section

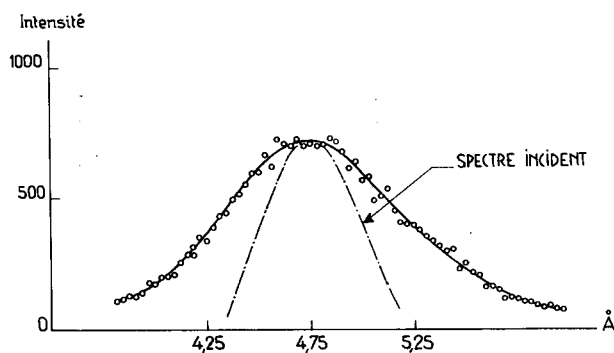


Figure 4

Spectre diffusé au point de Curie par le fer, montrant le caractère inélastique de cette diffusion.

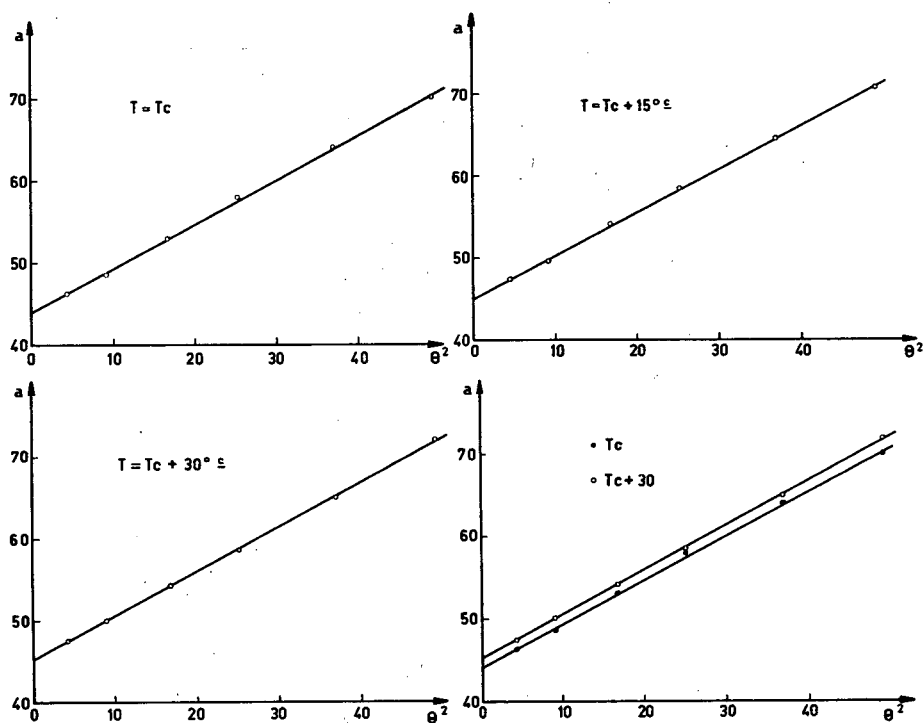


Figure 5

Largeur à mi-hauteur des spectres diffusés en fonction de l'angle de diffusion et de la température. Les largeurs sont exprimées en une unité arbitraire proportionnelle à la longueur d'onde.

efficace. Cela est confirmé par la variation de la largeur de la raie diffusé au point de Curie. La largeur à mi-hauteur varie linéairement avec θ^2 , comme le montre la figure 5. La droite obtenue à T_c est vraie au moins jusqu'à un angle de 9° (limite de l'observation). La pente de cette droite ainsi que la forme du spectre de la figure 4 permettent de déduire le coefficient de diffusion

$$2m\Lambda_{T_c}/\hbar = 7 \quad \text{ou} \quad \Lambda_{T_c} = 2 \cdot 210^{-3} \text{ cgs.}$$

La figure 5 montre également la variation de la largeur de la raie en fonction de l'angle à 15° et 30° au-dessus de T_c . La variation demeure linéaire mais la droite, au lieu de s'extrapoler pour un angle de diffusion nul à la largeur du spectre incident, s'extrapole à des valeurs plus grandes. La diffusion pour $T > T_c$ est légèrement inélastique même pour un angle de diffusion nul.

Ces résultats au point de Curie et au-dessus de T_c sont en contradiction avec les estimations du temps de relaxation (relation 4) que nous avons déduit plus haut du travail de MORI et KAWASAKI [10]. Il semble que le temps de relaxation soit de la forme

$$1/\tau_{q\text{exp}} = D[q^2 + a(T - T_c)]$$

et ne devienne infini que pour $T = T_c$ et $q = 0$.

Les valeurs pour Λ publiées antérieurement [4] étaient obtenues en supposant complètement correcte la théorie de Van Hove. Le travail actuel confirme les valeurs expérimentales des largeurs de spectre, mais montre que l'analyse doit être faite autrement.

5. DIFFUSION EN DESSOUS DU POINT DE CURIE

La figure 6 montre la variation de l'intensité diffusée en fonction de la température pour plusieurs angles de diffusion. (Ces courbes ne sont pas normalisées entre elles.) A 3° l'intensité varie de la même façon que celle observée dans les travaux antérieurs, mais, quand l'angle de diffusion décroît, on voit d'une part, s'affiner le pic de diffusion critique comme le prévoit la forme de la section efficace et, d'autre part, apparaître en-dessous de T_c une nouvelle contribution à la diffusion. Cette diffusion est attribuée aux ondes de spins. La diffusion en avant pour les ondes de spins du fer a déjà été observée par LOWDE [11]. Pour confirmer cette attribution nous avons étudié l'effet d'un champ magnétique. La figure 7 montre l'effet d'un champ de 300 gauss sur l'intensité diffusée. Nous voyons qu'un champ parallèle au vecteur de diffusion augmente la diffusion, alors qu'un champ perpendiculaire la diminue. C'est bien ce qu'on attend de la diffusion par ondes de spins. La figure 8 montre l'action du champ dans la région des bosses de la figure 7.

Au point de Curie on voit que le champ fait décroître l'intensité diffusée quelle que soit sa direction. La variation en fonction de la valeur du champ est une décroissance régulière. VILLAIN [12] a montré que ce com-

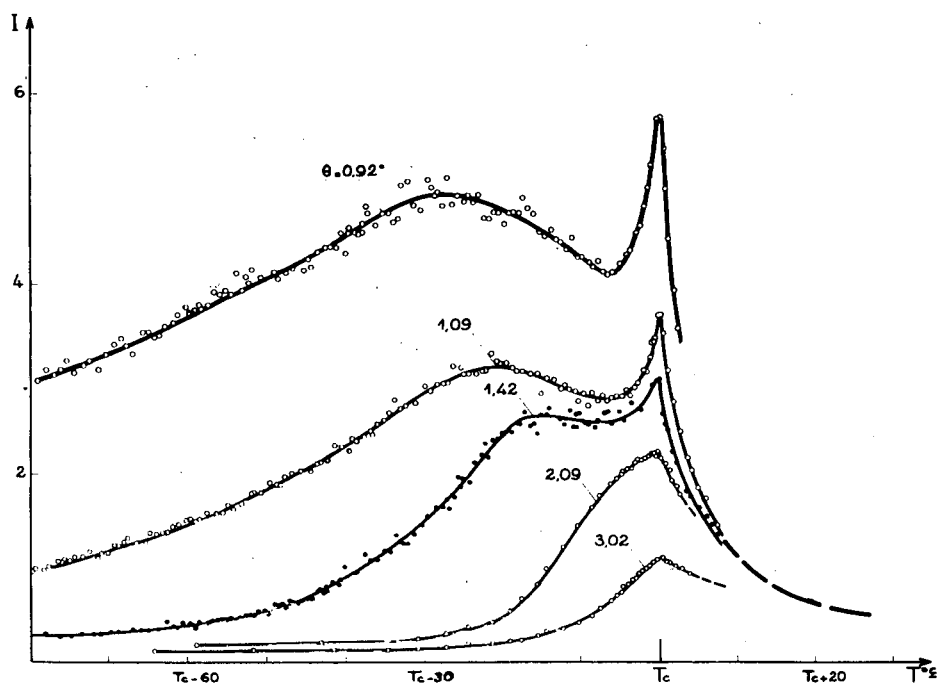


Figure 6

Intensités diffusées en fonction de la température.
Les courbes aux divers angles ne sont pas normalisées.

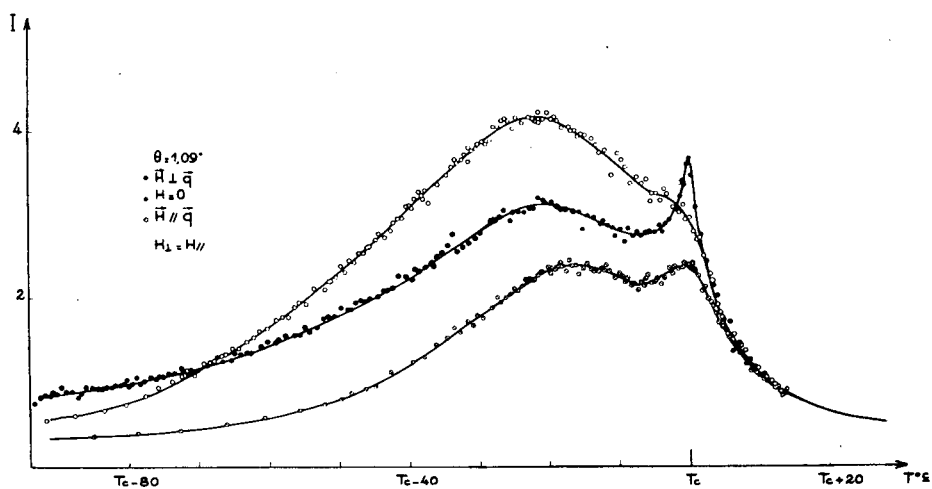


Figure 7

Action d'un champ de 300 gauss sur l'intensité diffusée à 1.09° par le fer.

portement est normal et a pu faire un calcul de champ moléculaire qui rend très bien compte des courbes de la figure 7 dans un domaine de 10° de part et d'autre de T_c .

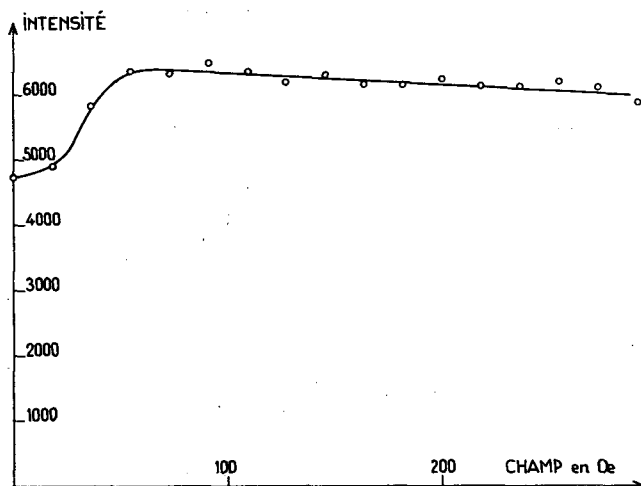


Figure 8

Action d'un champ parallèle au vecteur de diffusion $T_e - T = 25^\circ$.

Un travail d'analyse est en cours pour déduire de la diffusion par ondes de spins à haute température des informations sur le comportement de ces ondes au voisinage du point de Curie. La forme des spectres diffusés par ces ondes de spins a été mesurée pour diverses températures et diverses valeurs du champ appliqué.

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DISCUSSION

J. C. H. VILLAIN: As Dr. Jacrot pointed out in his oral presentation, the increase of intensity with temperature must be due to the increase in the

diameter of the diffusion surface. In calculating this surface, account must be taken of the dipole couplings, because of the small value of the diffusion angle and the diffusion vector $\underline{q}$. The diffusion surface will then be found to be markedly non-spherical, which partly explains the widely differing variation of intensity I with temperature T , according to whether $\underline{q}$ is parallel or perpendicular to the field (Fig. 7). The decrease of I with T towards $T_c - 20^\circ$ is not due to the fact that diffusion processes by a single magnon become impossible; the diffusion "surface" becomes, moreover, increasingly thick.

In the critical range ($T > T_c - 4^\circ$), it is possible to determine, in quasi-static approximation, the intensity as a function of the coefficients APQ in the Landau-Lifschitz formula for the thermodynamic potential:

$$\phi = \iiint d^3r \left[\frac{1}{2} Q M^2 - \underline{M} \cdot \underline{H} + \frac{A}{2} (\nabla M)^2 + \frac{1}{4} P M^4 \right],$$

$$\text{with } \frac{Q}{A} = a(T - T_c) [= k_1^2 \text{ for } T > T_c].$$

Intensity $I(\underline{H}, \underline{q}, T)$ can be easily calculated and depends solely on Q/A , which is known, and on P/A^3 , which may be regarded as constant. Highly satisfactory results will be obtained provided that this constant is calculated on the basis of Dr. Jacrot's experiments rather than from the magnetic data (susceptibility and spontaneous magnetization) which appear to be only imperfectly known.

SOME INVESTIGATIONS OF NEUTRON INELASTIC SCATTERING ON MAGNETICS

SZ. KRAŚNICKI, K. RUTA-WALA AND A. WANIC
INSTITUTE OF NUCLEAR PHYSICS, KRAKÓW, POLAND

A. MURASIK

INSTITUTE OF NUCLEAR RESEARCH, LABORATORY IB, ŚWIERK, POLAND

AND

T. RISTE

INSTITUT FOR ATOMENERGI, KJELLER, NORWAY

Abstract — Résumé — Аннотация — Resumen

SOME INVESTIGATIONS OF NEUTRON INELASTIC SCATTERING ON MAGNETICS. Since crystals of franklinite ($\text{Zn}_{0.75}\text{Mn}_{0.38}\text{Fe}_{1.87}\text{O}_4$) and chromium oxide (Cr_2O_3) were used as samples. Diffuse scattering of neutrons connected with the magnetically active reciprocal lattice points was observed.

In the case of franklinite, the monochromatic beam technique was used. The diffuse scattering at liquid air temperature around $\tau = (111)$ could be explained as magnon scattering. A quadratic dispersion relation of magnons ($W = \hbar/2m \propto q^2$) with $\alpha = 50$ was obtained.

In the case of Cr_2O_3 the critical scattering region was investigated around $\tau = (110)_{\text{homb}}$. The white beam technique was used. The data obtained were compared with those for Fe_2O_3 and expressed by means of Van Hove formalism. Considerable differences were observed.

QUELQUES RECHERCHES SUR LA DIFFUSION INÉLASTIQUE DES NEUTRONS DANS LES CORPS MAGNÉTIQUES. Les auteurs ont utilisé des monocristaux de franklinite ($\text{Zn}_{0.75}\text{Mn}_{0.38}\text{Fe}_{1.87}\text{O}_4$) et d'oxyde de chrome (Cr_2O_3). Ils ont observé une dispersion diffuse des neutrons liée aux points réciproques du réseau magnétiquement actif.

Dans le cas de la franklinite, ils ont utilisé la méthode du faisceau monochromatique. La dispersion diffuse que l'on observe à la température de l'air liquide aux environs de la direction $\tau = (111)$ peut être attribuée à une diffusion de magnons. Les auteurs ont obtenu une relation de dispersion quadratique des magnons ($\omega = \hbar/2m \propto \alpha q^2$) où $\alpha = 50$.

Dans le cas du Cr_2O_3 , la région de diffusion critique a été étudiée aux environs de la direction $\tau = (110)_{\text{homb}}$. Les auteurs ont employé la méthode du faisceau blanc. Ils ont comparé les données obtenues aux données relatives à Fe_2O_3 et les ont exprimées au moyen du formalisme de Van Hove. Des différences considérables ont été observées.

НЕКОТОРЫЕ ИССЛЕДОВАНИЯ НЕУПРУГОГО РАССЕЯНИЯ НЕЙТРОНОВ НА МАГНИТНЫХ ВЕЩЕСТВАХ. В качестве образцов были использованы монокристаллы $\text{Zn}_{0.75}\text{Mn}_{0.38}\text{Fe}_{1.87}\text{O}_4$ и окиси хрома (Cr_2O_3). Были произведены наблюдения над диффузным рассеянием нейтронов, связанным с магнитноактивными противостоящими точками решетки.

Для франклинита был использован метод монохроматического пучка. Диффузное рассеяние при температуре жидкого воздуха около $\tau = (111)$ могло быть объяснено как рассеяние магнонов. Было получено квадратичное соотношение рассеяния магнонов: $W = \frac{\hbar}{2m} \alpha q^2$, при $\alpha = 50$.

Для Cr_2O_3 критическая зона рассеяния была изучена около $\tau = (110)$. Для этого был использован метод белого пучка. Сравнение полученных данных с данными для Fe_2O_3 и выражение их посредством формализма по Ван Гофу показало большие расхождения.

INVESTIGACIONES SOBRE LA DISPERSIÓN INELÁSTICA DE LOS NEUTRONES EN SUSTANCIAS MAGNÉTICAS. Los autores han utilizado como muestras monocristales de franklinite ($\text{Zn}_{0.75}\text{Mn}_{0.38}\text{Fe}_{1.87}\text{O}_4$) y de

óxido de cromo (Cr_2O_3). Han observado una dispersión difusa de neutrones asociada a los puntos recíprocos de la red magnéticamente activos.

En el caso de la franklinita, han empleado el procedimiento del haz monocromático. Han interpretado como dispersión magnones la dispersión difusa que aparece a la temperatura del aire líquido en las proximidades de $\tau = (111)$. Han obtenido una relación cuadrática de dispersión de magnones ($\omega = \hbar/2m \alpha q^2$), siendo $\alpha = 50$.

En el caso del Cr_2O_3 , han investigado la región crítica de dispersión en las proximidades de $\tau = (110)_{\text{rhom}}$, utilizando el procedimiento del haz blanco. Han comparado los datos obtenidos con los relativos al Fe_2O_3 y los han expresado según la formulación de Van Hove. Las diferencias observadas son considerables.

INTRODUCTION

Interaction of neutrons with magnetically-active electrons gives a nique method for investigation of the static and kinetic behaviour of spin systems coupled by exchange forces. Such spin systems are responsible for the magnetic properties of ferro-, ferri-, antiferro or antiferromagnetics. As solids they can form crystals and an ideal sample for neutron investigation should be a monocrystal.

The information about the static of a given spin system is usually derived from the angular pattern and intensity of elastically-scattered neutrons, obtained by means of the Laue or Bragg technique.

Investigation of the kinetics of a given spin system demands in principle the measurements of intensity and energy distributions of monoenergetic neutrons scattered in directions not allowed by simple Bragg law. It is a difficult task because these patterns of magnetic inelastic scattering have very small intensities (total cross-sections of the order of mb) and are superimposed on other types of scattering which cause high background (incoherent elastic scattering, phonon scattering). Fortunately magnetic inelastic scattering is usually concentrated, in reciprocal lattice representation, around the reciprocal lattice vectors which are magnetically active, i. e. which correspond in proper conditions to a high intensity of Bragg reflection of magnetic origin. It helps to localize the sought effect and offers the possibility of deriving valuable information from the angular distribution of magnetically-scattered neutrons only, without analysing their energies. This procedure makes it possible to undertake the experiments even on reactors having a comparatively low flux, down to $\sim 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ if the sample has been delivered in the form of a monocrystal of sufficient dimensions [1, 2].

The aim of the experiments is described below.

In the case of franklinite to investigate whether there a magnon scattering is possible in such a disordered structure and if so, than what is the dispersion law of spin waves (magnons) propagating in it.

In the case of Cr_2O_3 the experiments were made in order to compare the behaviour of the critical scattering of neutrons in Cr_2O_3 with the one previously observed in $\alpha\text{-Fe}_2\text{O}_3$ which is isomorphic with Cr_2O_3 as far as the spatial arrangement of the ions in concerned.

The reported experiments were carried out on the light water-moderated, 2 MW power WWRS reactor in Swierk, Poland with nominal central flux $\sim 2 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$.

MEASUREMENTS AND RESULTS

Franklinite

Experiments were performed on a large single crystal of natural origin with a volume about 5 cm³. Its chemical composition was found to be satisfied by the formula: $\text{Zn}_{0.75}\text{Mn}_{0.38}\text{Fe}_{1.87}\text{O}_4$. The neutron diffraction analysis of a small part cut out from the crystal indicated the following cation distribution among spinel A and B sites: $\text{Zn}_{0.75}\text{Mn}_{0.25/\text{A}}\text{Fe}_{1.87}\text{Mn}_{0.13/\text{B}}\text{O}_4$.

Since the critical point of the sample given by the magnetization *versus* temperature dependence was low, $\sim 230^\circ\text{K}$, the search for magnon scattering of neutrons was made at liquid air temperature. This temperature seems to be sufficiently below the critical point to expect scattering by single magnon processes.

The crystal was contained inside a cryostat mounted on the neutron spectrometer table with two rotational degrees of freedom. In the course of the experiment the [110] axis of the crystal was fixed vertically. Thus diffuse scattering of neutrons around the [111] Bragg reflection could be studied. The large dimension of the sample allowed the use of the monochromatic beam technique. Thus a monoenergetic beam of neutrons obtained by reflection from an aluminium crystal monochromator was directed on to the crystal. With the collimators applied the standard half-width of the [111] Bragg elastic peak of the sample amounted to 42 min.

The measurements consisted in scanning the intensity of the diffuse scattering peak appearing at the position of the (111) Bragg reflection when the crystal was shifted away from the Bragg reflection position θ_B by a known angle $\Delta\theta = \theta - \theta_B$. The diffuse peaks were scanned in the horizontal plane by a high efficiency neutron counter placed inside a heavy shielding on the spectrometer arm. The neutron counter collimator had ~ 40 min collimation angle.

The broad peaks observed proved to be of predominantly magnetic origin, as for sufficiently large $\Delta\theta$ they almost disappeared after heating the crystal to 200°C . A comparison of the magnetic and nuclear structure factors of the (111) reflection revealed that magneto-vibrational scattering at liquid air temperature should be negligibly small. For small $\Delta\theta$ there was observed an admixture of Bragg scattering caused by the mosaic spread of the domains. However, this scattering was restricted to the centre of the diffuse peak only, this being one of the advantages of the monochromatic beam technique over the white beam technique. The wings of the diffuse peaks were free from Bragg scattering. Hence at first the total widths of the diffuse peaks were taken into consideration. For rough instrumental correction the width of the Bragg peak (42 min) was subtracted from each of the apparent total widths. The half of the total width ($1/2 \Gamma_{\text{tot}}$) of the diffuse peaks so corrected could be compared with theoretical calculations based on a quadratic dispersion relation for magnons:

$$\omega = (\hbar/2m_0) \propto q^2 \quad (1)$$

where

q - wave vector of a magnon,

$\hbar\omega$ - energy of a magnon,

α - dispersion constant (dimensionless),

m_0 - neutron mass.

It gives

$$\frac{1}{2} \Gamma_{\text{tot}} = \arcsin \left\{ \frac{1}{\alpha} \left[\frac{k_0^2 (\epsilon \alpha + 1)}{\tau^2 + k_0^2 - 2k_0 \tau \sin \theta} - \epsilon \alpha \right]^{1/2} \right\} \quad (2)$$

where

$k_0 = 1/\lambda_0$ - wave vector of the impinging neutrons,

τ - reciprocal lattice vector,

$\theta = \theta_B + \Delta\theta$,

$\epsilon = \pm 1$.

As may be seen in Fig. 1 the agreement is satisfactory for a dispersion constant $\alpha = 40$. This proved that the results may be interpreted in terms of

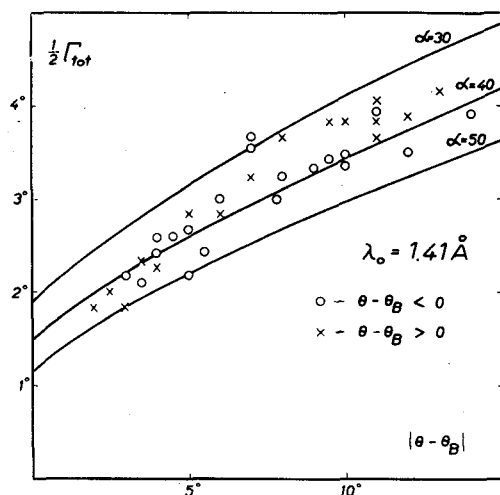


Fig. 1

Width of the magnon scattering peaks versus missetting angle dependence,

— - theoretical curves for quadratic dispersion law for various α 's and for $\lambda_0 = 1.41 \text{ \AA}$
 ○ x - experimental points.

magnon scattering. For a further check an examination of the shapes of the diffuse peaks was undertaken. This was done on the basis of formula (1) and the population factors for magnon states. In this way a number of curves were obtained which represented the shape of the diffuse scattering peak as seen in an experiment with ideal angular resolution. In order to take into account the real angular resolution it was assumed that the shape of the (111) Bragg reflection describes the resolution, i. e. the Bragg peak gives the instrumental curve. The instrumental curve was then folded with the theoretical angular distributions. The resulting curves were compared with experimental ones normalized to the same peak value. This revealed some

discrepancies between their shapes (see Fig.2), the experimental peaks appeared to have wider wings. This limited the accuracy of the estimation of the constant of dispersion α . Therefore it was concluded that $\alpha = 50 \pm 10$.

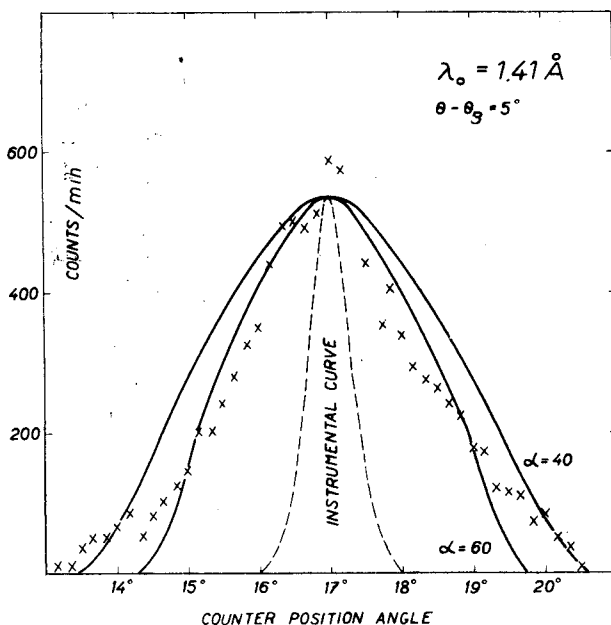


Fig. 2

Shape of the diffuse peak as seen by the rotating counter,

- x x - experimental points;
- - calculated shape;
- - - - instrumental curve.

Cr_2O_3 critical scattering

Cr_2O_3 is antiferromagnetic with critical point $T_N = 35^\circ\text{C}$ and isomorphic to $\alpha\text{-Fe}_2\text{O}_3$.

Experiments were performed on a small ($\sim 0.1\text{ cm}^3$) single crystal artificially grown. Owing to its small dimensions only the white beam technique could be used. The crystal was fastened to the end of a glass rod and mounted on a goniometer head placed on the main table of the Cracow Neutron Spectrometer [3]. The temperature of the crystal could be varied and maintained at a constant value chosen between room temperature and $\sim 90^\circ\text{C}$ with the aid of a thermostat heating and a special double-walled aluminium foil enclosure. A white beam of neutrons, having at most 20 min nominal collimation angle in the horizontal plane, was directed on to the crystal.

The measurements were made on the diffuse streak accompanying the (110) rhombohedral reflection since it possesses the highest value of the magnetic structure factor, and no other (h k l) could give sufficient intensity. They consisted in the scanning of the ridge of the diffuse scattering. The

neutron counter was rotated in a vertical plane. The angle between the direction of the primary white beam and this vertical plane was chosen in such a way that the maximum contribution to the scattered intensity belonged to $\lambda_{\text{eff}} = 1.37 \text{ \AA}$. In such a geometrical situation distinct diffuse scattering peaks were observed and their origin established.

The peaks were strongly temperature-dependent with a sharp maximum of intensity at the critical point of the sample. For a missetting angle of $\theta - \theta_B = 3^\circ$ the intensity almost disappeared when the sample was heated to $\sim 90^\circ \text{C}$. At the critical point temperature the peak intensity showed the predicted inverse quadratic dependence on the missetting angle, the same as was found in the case of $\alpha\text{-Fe}_2\text{O}_3$ [2].

In order to find VAN HOVE's κ_1 parameter [4] the temperature dependence of the diffuse scattering for $\theta - \theta_B = 3^\circ$ was carefully studied. Some of the peaks are shown in Fig. 3. κ_1 was derived from such curves for tem-

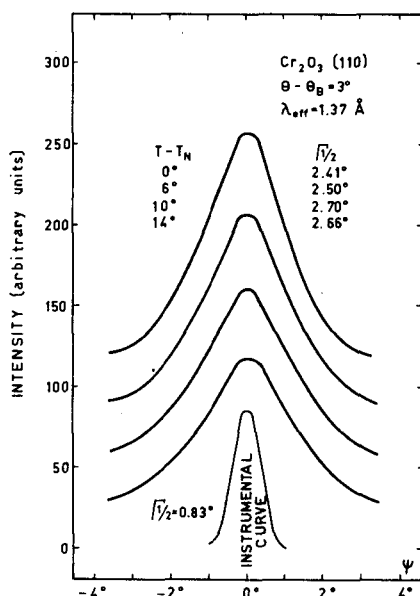


Fig. 3

Shape of the diffuse streak for different temperatures above the Neel Point of Cr_2O_3 , seen by the counter rotating in vertical plane. The curves are shifted upwards only for reasons of clarity; background was nearly the same for all of them.

peratures $T \geq T_N$. The procedure applied was exactly the same as during the work on $\alpha\text{-Fe}_2\text{O}_3$. Even more, the geometry of the scattering was deliberately chosen to fulfil the criterion of similarity:

$$(\Delta\theta \cdot \tau_{(110)} \cdot \lambda_{\text{eff}})_{\text{Cr}_2\text{O}_3} = (\Delta\theta \cdot \tau_{(111)} \cdot \lambda_{\text{eff}})_{\alpha\text{-Fe}_2\text{O}_3} \quad (3)$$

where

$$\Delta\theta = \theta - \theta_B,$$

τ - reciprocal lattice vector,

λ_{eff} - effective wave length of neutrons.

Thus results for Cr_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$ could be compared as shown in Fig. 4 for part of the temperature intervals measured.

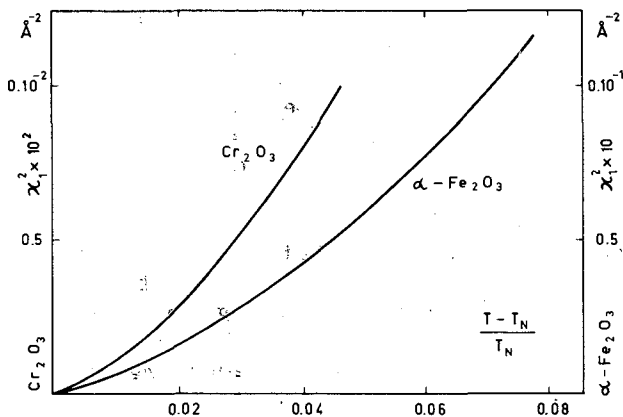


Fig. 4

The experimental curves showing χ^2 temperature dependence in the case of Cr_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$.

As may be seen there is a striking difference between them which up to now has not been interpreted theoretically.

DISCUSSION OF THE RESULTS

In both samples under investigation the magnetic inelastic scattering was found. The angular resolution of the diffraction methods used was improved in comparison with analogous experiments on Fe_3O_4 [1] and $\alpha\text{-Fe}_2\text{O}_3$ [2] by a factor of 2-3.

In the case of franklinite one may expect that the lifetimes of the magnons are rather short due to the low degree of order within the lattice of magnetic ions. At present there is no theory which could deal satisfactorily with such a case.

However, from the general point of view, one might expect an almost quadratic dispersion relation for $q \approx 0$ and a relatively small value of α , which was in fact observed. Up to now, neutron-magnon scattering has been studied only in a few magnetic substances, all with high critical points and comparatively good order:

$$\text{Fe}_3\text{O}_4 : T_C = 855^\circ \text{K}, \alpha \approx 225 \text{ [1, 5] ,}$$

$$\text{Fe} : T_C = 1043^\circ \text{K}, \alpha \approx 135 \text{ [6] ,}$$

$$\text{Co}_{0.92} \text{Fe}_{0.08} : T_C = 1300^\circ \text{K}, \alpha \approx 180 \text{ [7] ,}$$

$$\alpha - \text{Fe}_2\text{O}_3 \quad T_N = 969^\circ\text{K} \quad C_m = 3.8 \times 10^6 \text{ cm/s} \quad [2] ,$$

where C_m - velocity of antiferromagnons.

It would then be useful to obtain more precise data on diffuse scattering geometry for a variety of magnetics in order to have sufficient material for comparison. The shape of the diffuse peaks may eventually give some information on the energy widths of magnon states which should be dependent on temperature and degree of order within the lattice. In some favourable cases measurements on the energy spectrum of scattered neutrons might be feasible in order to check the accuracy of the diffraction methods [8] .

Fig. 4 shows that the range κ^{-1} of the fluctuations in Cr_2O_3 is longer than in $\alpha\text{-Fe}_2\text{O}_3$, when plotted on a reduced temperature scale. This may be taken as an indication that the ions which interact and establish the different antiferromagnetic spin alignments for the two cases are more closely spaced in Cr_2O_3 than in $\alpha\text{-Fe}_2\text{O}_3$. This could be due to a direct antiferromagnetic interaction in Cr_2O_3 , as suggested by GOODENOUGH [8] . So far our calculations, in the molecular field approximation, have not yielded any quantitative agreement for the correlation range.

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DISCUSSION

J. C. H. VILLAIN: What is the distance between the two atoms of chromium which you assumed in your oral presentation to be bound by direct antiferromagnetic exchange? Is it essential to assume the existence of such an exchange? Can the differences between Cr_2O_3 and Fe_2O_3 not be explained by the existence of super-exchange interactions not limited to first neighbours?

T. RISTE: The difference is $2.67 \text{ \AA}$. In a recent paper by OSMOND [Proc. Phys. Soc. 79, (1961) 394] the difference between Cr_2O_3 and Fe_2O_3 has in fact been explained solely on the basis of super-exchange interactions, without reference to antiferromagnetic exchange. In my calculations, however, which were done before publication of Osmond's paper, the range of fluctuations was such that the direct-exchange hypothesis seemed most likely.

SYMPOSIUM ON INELASTIC SCATTERING OF NEUTRONS IN SOLIDS AND LIQUIDS

HELD AT CHALK RIVER, CANADA,
10 - 14 SEPTEMBER 1962

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Editor:	G.R.M. HARTCUP	Division of Scientific and Technical Information, IAEA
Records Officer:	L.S. LIEBERMAN	Division of Languages, IAEA

LIST OF PARTICIPANTS

Name	Institution	Nominating State or Organization
AHMED, N. M.	Pakistan Atomic Energy Commission, Karachi	Pakistan
BERGSMA,	Reactor Centrum Nederland, Petten (N. H.)	Netherlands
BEYSTER, J. R.	General Atomic, Division of General Dynamics Corporation, P. O. Box 608, San Diego, Calif.	United States of America
BOFFI, V. C.	CNEN, 15, via Belisario, Rome	Italy
BROCKHOUSE, B. N.	Department of Physics, McMaster University, Hamilton, Ont.	Canada
CAGLIOTI, G.	CNEN, c/o C. C. R. Ispra (Varese)	Italy
CARTER, R. S.	National Bureau of Standards, Washington, D. C.	United States of America
COCHRAN, W.	Cavendish Laboratory, Free School Lane, Cambridge	United Kingdom
COCKING, S. J.	AERE, Harwell, Didcot, Berks.	United Kingdom
CONNOR, D. W.	Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill.	United States of America
COOTE, G. E.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada
COWLEY, R. A.	Cavendish Laboratory, Free School Lane, Cambridge	United Kingdom
DASANNACHARYA, A.	Atomic Energy Establishment, Trombay, Bombay	India
DE WETTE, F.	Reactor Centrum Nederland, Petten (N. H.)	Netherlands
DOLLING, G.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada
EGELSTAFF, P.	AERE, Harwell, Didcot, Berks.	United Kingdom
ELLIOTT, L.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada
GLÄSER, W.	Institut für Neutronenphysik und Reaktortechnik, Kernforschungszentrum, Karlsruhe	Federal Republic of Germany
GOLDMAN, D. T.	Knolls Atomic Power Laboratory, General Electric, Schenectady, New York	United States of America

LIST OF PARTICIPANTS

337

Name	Institution	Nominating State or Organization
GRIFFING, G.	Phillips Petroleum Co., P. O. Box 2067, Idaho Falls, Idaho	United States of America
HAHN, H.	Institut für Reaktorwerkstoffe, Kernforschungsanlage Jülich des Landes Nordrhein-Westfalen	Federal Republic of Germany
HAUTECLER, S.	Centre d'étude de l'énergie nucléaire, 200, Boeretang, Mol-Donk	Belgium
HAYWOOD, B.	AERE, Harwell, Didcot, Berks.	United Kingdom
HURST, D. G.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada
IYENGAR, P. K.	Atomic Energy Establishment, Trombay, Bombay	India
JACROT, B.	C. E. A., C. E. N. de Saclay, B. P. No. 2, Gif sur Yvette (Seine et Oise)	France
JANIK, J.	Institute of Nuclear Physics, ul. Radzikowskiego, Krakow 23 and Joint Institute for Nuclear Research, Dubna, USSR	Poland
KLEY, W.	EURATOM/C. C. R. Ispra (Varese), Italy	European Atomic Energy Community
KOKKEDEE, J. J. J.	Institute for Theoretical Physics of the University, Maliesingel 23, Utrecht	Netherlands
KOTTWITZ, D. A.	Hanford Labs., General Electric Co., Richland, Washington, D. C.	United States of America
LARSSON, K. E.	Royal Institute of Technology, Institute for Reactor Physics, Stockholm O	Sweden
LEWIS, W. B.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada
MAERKL, H.	Siemens-Schuckertwerke AG., Werner-von-Siemens-Strasse 50, Erlangen	Federal Republic of Germany
MIKKE, K.	Institute for Nuclear Research, Swierk k/Otwocka	Poland
MORALES-AMADO, A.	Comisión Nacional de Energía Nuclear, Insurgentes Sur 1079, Mexico 18, D. F.	Mexico
MORRISON, J. A.	Division of Pure Chemistry, National Research Council, Ottawa	Canada
MOZER, B.	Brookhaven National Laboratory, Upton, L. I., New York	United States of America

LIST OF PARTICIPANTS

Name	Institution	Nominating State or Organization
NIJBOER, B. R. A.	Institute for Theoretical Physics of the University, Maliesingel 23, Utrecht	Netherlands
OTNES, K.	Brookhaven National Laboratory, Upton, L.I., New York	United States of America
PALEVSKY, H.	Brookhaven National Laboratory, Upton, L.I., New York	United States of America
PARKS, D.E.	John Jay Hopkins Laboratory, General Atomic, Division of General Dynamics Corp., P.O. B. 608, San Diego 12, Calif.	United States of America
PETCH, H.E.	Department of Physics, McMaster University, Hamilton, Ont.	Canada
POPE, N.	Department of Mathematics, Royal Military College of Canada, Kingston, Ont.	Canada
QUITTNER, G.	Österr. Studiengesellschaft für Atomenergie G.m.b.H., Lenaugasse 10, Vienna VII	Austria
RISTE, T.	Institutt for Atomenergi, P.O. Box 175, Lillestroem	Norway
ROSENBAUM, M.	Comisión Nacional de Energía Nuclear, Insurgentes Sur 1079, Mexico 18, D.F.	Mexico
SALTER, L.S.	Wabash College, Crawfordsville, Ind.	United States of America
SCHOFIELD, P.	Theoretical Physics Division, AERE, Harwell, Didcot, Berks.	United Kingdom
SINGWI, K.S.	Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill.	United States of America
SJÖLANDER, A.	Institute for Mechanics, Chalmers Institute of Technology, Gothenburg	Sweden
SQUIRES, G.	Cavendish Laboratory, Free School Lane, Cambridge	United Kingdom
STILLER, H. H.	Kernforschungsanlage Jülich, Institut für Reaktorwerkstoffe, Muffeter Weg 3, Aachen	Federal Republic of Germany
STEINSVOLL, O.	Institutt for Atomenergi, P.O. Box 175, Lillestroem	Norway
TCHERNOPEKOV, N. A.	Kurchatov Institute of Atomic Energy, Moscow	USSR
THORSON, I.M.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada

LIST OF PARTICIPANTS

339

Name	Institution	Nominating State or Organization
VERTEBNY, V. P.	Ukrainian Academy of Science, Institute of Physics, Kiev	USSR
VILLAIN, J. C. H.	C. E. A. , C. E. N. de Saclay, B. P. No. 2, Gif sur Yvette (Seine et Oise)	France
VOSKO, S. H.	Department of Physics, McMaster University, Hamilton, Ont.	Canada
WALKER, J.	Physics Department, The University, Birmingham 15	United Kingdom
WALLER, I.	Institute for Theoretical Physics, University of Uppsala, Uppsala	Sweden
WEBB, F. J.	AERE, Harwell, Didcot, Berks.	United Kingdom
WEINZIERL, P.	Österr. Studiengesellschaft für Atomenergie G. m. b. H., Lenaugasse 10, Vienna VIII	Austria
WHITTEMORE, W.	General Atomic, Division of General Dynamics Corporation, P. O. Box 608, San Diego, Calif.	United States of America
WOODS, A. D. B.	Atomic Energy of Canada Limited, Chalk River, Ont.	Canada

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