# Inelastic Scattering of Neutrons in Solids and Liquids

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



NTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA 1963

# INELASTIC SCATTERING OF NEUTRONS IN SOLIDS AND LIQUIDS

Vol.I

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### PROCEEDINGS SERIES

# INELASTIC SCATTERING OF NEUTRONS IN SOLIDS AND LIQUIDS I

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In two volumes

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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.

SIGVARD EKLUND Director General

December 1962

#### EDITORIAL NOTE

The papers and discussions incorporated in the proceedings published by the International Atomic Energy Agency are edited by the Agency's editorial staff to the extent considered necessary for the reader's assistance. The views expressed and the general style adopted remain, however, the responsibility of the named authors or participants.

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

The affiliations of authors are those given at the time of nomination.

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# INTRODUCTION TO THE PROCEEDINGS BY THE SCIENTIFIC SECRETARIES

The Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids consist of the full texts of the papers accepted, in the original language in which they were submitted, together with abstracts of these papers in English, French, Russian and Spanish, and a record in English of the discussions held during the Symposium in connection with the orally-presented summaries of the papers.

The papers have been grouped for the Proceedings in a similar way as for the Symposium. The discussions were edited as little as possible but full use was made of the forms "Participants' Contributions to Discussions" which were completed by the participants themselves. Nevertheless, mainly because the discussion was often so lively that occasionally speakers did not use their microphones, some parts of the discussions have been lost for the Proceedings. It also may happen that the published records contain some inaccuracies due to the fact that in speeding up publication it was not possible to ask the participants to verify their remarks in the proof stage.

It was noted at the Symposium and can easily be seen from the papers that various authors have used different symbols for the same quantity or function, e.g. for the momentum transfer the symbols Q, K,  $\kappa$  may be found. In this connection it should be mentioned that no attempt has been made to standardize notations.

Ι.

# GENERAL PROBLEMS

# THE MÖSSBAUER EFFECT AND DYNAMICS OF ATOMIC MOTIONS IN CONDENSED SYSTEMS\*

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#### Abstract — Résumé — Аннотация — Resumen

THE MÖSSBAUER EFFECT AND DYNAMICS OF ATOMIC MOTIONS IN CONDENSED SYSTEMS. This review deals with those aspects of the Mössbauer effect which concern chiefly the dynamics of atomic motions in solids and liquids. The subject matter is presented in a manner so as to bring out the similarity between the phenomena of slow neutron scattering and y-ray resonance scattering.

EFFET MÖSSBAUER ET DYNAMIQUE DES MOUVEMENTS ATOMIQUES DANS DES SYSTÈMES CON-DENSÉS. Le mémoire traite des aspects de l'effet Mössbauer qui concernent avant tout la dynamique des mouvements atomiques dans les solides et les liquides. L'auteur présente la question de manière à faire ressortir la similarité entre le phénomène de la diffusion des neutrons lents et celui de la diffusion résonante des rayonnements gamma.

ЭФФЕКТ МОСБАУЕРА И ДИНАМИКА ДВИЖЕНИЙ АТОМОВ В КОНДЕНСНЫХ СИСТЕМАХ. Излагаются некоторые аспекты эффекта Мосбауера, связанные, главным образом, с динамикой движения атомов в твердых телах и жидкостях. Цель - выявить сходство явлений рассеяния медленных нейтронов и резонансного рассеяния гамма-лучей.

EFECTO MÖSSBAUER Y DINÁMICA DE LOS MOVIMENTOS ATÓMICOS EN LOS SISTEMAS CONDEN-SADOS. La memoria se ocupa de los aspectos del efecto Mössbauer que interesan especialmente a la dinámica de los movimientos atómicos en los sólidos y líquidos. Los temas se presentan con miras a hacer resaltar la similitud entre los fenómenos de dispersión de los neutrones lentos y la dispersión por resonancia de los rayos gamma.

I intend to confine my talk to those aspects of the Mössbauer Effect which are concerned directly with the dynamics of atomic motion in solids and liquids.

That this is a second international conference on the "Scattering of Slow Neutrons by Solids and Liquids" is an indication of the fact that slow neutron scattering has proved to be a very powerful tool in the study of the dynamics of atomic motion in condensed systems, whereas its rival, the resonance scattering of  $\gamma$ -rays, has still to go a long way to prove its usefulness in this field of investigation. Nevertheless, a comparative study of these two phenomena, which are so closely allied in principle, will be a very useful one and it is to this task I mainly wish to devote myself in this paper.

#### THE MÖSSBAUER EFFECT

Consider a nucleus A at rest which emits a  $\gamma$ -ray of energy  $E_{\gamma}$ .



\* Based on work performed under the auspices of the United States Atomic Energy Commission.

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In the process of emission the nucleus receives a recoil energy R,

$$R = E_{\gamma}^2 / 2Mc^2 , \qquad (1)$$

M being the mass of the nucleus and c the velocity of light. For a 129 keV  $\gamma$ -ray from Ir<sup>191</sup>, the recoil energy R is 0.05 eV (R  $\ll E_{\gamma}$ ). If this  $\gamma$ -ray is to be resonantly absorbed by a similar nucleus B at rest, it has to be supplied with an energy equal to 2R, since energy R is also lost in the process of absorption, i.e. an energy equivalent to 0.1 eV, which would correspond to giving a relative velocity of nearly  $2.3 \times 10^4$  cm/s - an enormous velocity.

If, however,  $2R \leq \Gamma$  the width of the line, the  $\gamma$ -ray will be resonantly absorbed by the nucleus B without giving the latter any velocity. This does not happen in the case of  $\gamma$ -rays because the width  $\Gamma \sim 10^{-5} - 10^{-9}$  eV. For optical transitions the condition  $2R < \Gamma$  is satisfied and we do have resonance fluorescence.

The nuclei are normally not at rest but move with thermal velocities, obeying a Maxwellian distribution. This gives rise to what is known as the Doppler broadening of the resonance line, whose mean value  $\overline{D}$  is

$$\overline{\mathbf{D}} \simeq 2(\overline{\mathbf{c}} \mathbf{R})^{\frac{1}{2}}, \qquad (2)$$

where  $\overline{\epsilon}$  is the mean kinetic energy of the nuclei in the emitter. For nuclear  $\gamma$ -rays  $D \leq R$  for a gas at room temperature. D increases with temperature and this should, therefore, help in bringing about the overlap of emission and absorption lines.

In 1957, Mössbauer was investigating the resonance scattering of 129 keV  $\gamma$ -ray from Ir<sup>191</sup>. For this transition R  $\simeq 0.05$  eV and D  $\simeq 0.1$  eV for room temperature. Thus at room temperature there is a considerable overlap between the emission and absorption spectrum and, therefore, resonance absorption could be observed. To reduce this residual scattering Mössbauer cooled both the source and the absorber and expected a decrease in the effect. Instead he found that resonance absorption increased. Having ascertained that this was not a spurious effect, he started looking for its explanation. A theoretical physicist referred him to LAMB [1] concerning the resonance absorption of neutrons by nuclei bound in a crystal. This hint was sufficient evidence for Mössbauer who then explained his experimental results on the basis of Lamb's theory. In this single beautiful experiment he found two things: (a) that a fraction of 129 keV  $\gamma$ -rays, emitted by the cooled source, did not show a measurable recoil energy loss; and (b) that the very narrow  $\gamma$ -rays did not display Doppler broadening. Their line width corresponded to the natural line width which is  $\sim 5 \times 10^{-6}$  eV. For this important discovery, Mössbauer was awarded the Nobel prize last year.

Mössbauer discovered this important effect in 1957 and his results [2] were published in 1958 in Zeitschrift für Physik. This important discovery remained unnoticed even after the publication of his paper, and even those who noticed it perhaps did not believe in it because, after all, Mössbauer was then an obscure physicist. May I illustrate this by a small personal story. In August 1958 I attended the Second United Nations Conference on the Peaceful Uses of Atomic Energy. I stayed in Europe until the end of March 1959, and during this time I met many physicists but the work of Mössbauer was never mentioned. It was not until April 1959, when I had arrived at Argonne, that I first learned, with considerable surprise, about the Mössbauer Effect after a conversation with Dr. Lipkin. He then went on to explain to me his own simple derivation of the famous Debye-Waller factor [3]. He stressed that it was this factor which is so important in the Mössbauer Effect. After listening to him for some time I had to tell him that nuclear physicists discover things already known to neutron scatterers. This was my first lesson in the Mössbauer Effect. In late 1959 and 1960 there was a flood of letters in the Physical Review about this effect and nobody could have remained ignorant after having read Goudsmit's rejoinder in the Physical Review Letters.

#### THEORY

You are familiar with the derivation of the expression for the crosssection for absorption of a  $\gamma$ -ray of energy E. The formula is given in HEITLER's book [4], and is

$$\sigma_{a}(\mathbf{E}) = \frac{\sigma_{0}\Gamma^{2}}{4} \sum_{\mathbf{n},\mathbf{n}_{0}} \frac{|\langle \mathbf{n} | e^{i\underline{K}} \cdot \underline{\mathbf{R}} | \mathbf{n}_{0} \rangle|^{2}}{(\mathbf{E}_{0} - \mathbf{E} + \epsilon_{n} - \epsilon_{n})^{2} + \Gamma^{2}/4},$$
(3)

where  $E_0$  is the energy difference between the final and the initial nuclear states of the absorbing nucleus;  $\epsilon_n$  and  $\epsilon_{n_n}$  are, respectively, the energies of the states  $|n\rangle$  and  $|n_0\rangle$  of the interacting system of which the nucleus forms part;  $\Gamma$  is the natural width of the excited state of the nucleus and  $g_{no}$  is the statistical weight factor of the state  $|n_0\rangle$ . hK is the momentum of the  $\gamma$ -ray and R is the position vector of the nucleus.  $\overline{\sigma_0}$  is the resonance absorption cross-section.

For reasons which will be obvious from what follows, it is possible to rewrite (4) in a somewhat different form [5] which is

$$\sigma_{a}(\mathbf{E}) = (\sigma_{0}\Gamma/4\hbar) \int_{-\infty}^{+\infty} \exp\left\{i(\underline{K} \cdot \underline{r} - \omega t) - (\Gamma/2\hbar) |t|\right\} G_{s}(\underline{r}, t) d\underline{r} dt, \qquad (4)$$

where  $h\omega = E - E_0$  and  $G_s(\underline{r}, t)$  is VAN HOVE's self-correlation function [6] with which everyone is familiar and which gives in the classical limit the probability of finding a particle at time t at position  $\underline{r}$ , if the same particle was at origin at time, t = 0. The incoherent differential scattering cross-section for slow neutrons is also proportional to the integral in (4) with  $\Gamma = 0$ . Thus we see a close similarity between the two phenomena of slow neutron scattering and  $\gamma$ -ray resonance scattering.

The function  $G_s(\mathbf{r}, t)$  is Gaussian in a solid and in a gas and is probably not far from it in a liquid too.  $G_s(\mathbf{r}, t)$  has, therefore, the form

$$G_{s}(\mathbf{r},t) = (2\pi\gamma(t))^{3/2} \exp\{-\underline{r}^{2}/2\gamma(t)\}.$$
 (5)

 $\gamma(t)$  is the time-dependent width function.  $\gamma(t)$  is known in the case of a gas

and a solid. For liquids  $\gamma(t)$  is not known but can be calculated on the basis of certain models [7].

The mathematical procedure to calculate  $\sigma_a$  (E) from (4) and (5) is exactly the same as we have in the case of neutron scattering and you are all familiar with it. I will, therefore, not repeat it here but simply quote the final result [5].

$$\sigma_{a}(\mathbf{E}) = \frac{\pi\sigma_{0}\Gamma}{2} \left[ \frac{\Gamma}{2\pi} \frac{e^{-2W}}{(\mathbf{E}-\mathbf{E}_{0})^{2} + \Gamma^{2}/4} + \exp(-2W) \cdot \frac{2Wf(|\mathbf{E}-\mathbf{E}_{0}|)}{2(\mathbf{E}-\mathbf{E}_{0})F(\mathbf{T})} \left\{ \operatorname{coth}\left(\frac{\mathbf{E}-\mathbf{E}_{0}}{2k_{B}T}\right)_{1} \right\},$$
(elastic part)
(one phonon part)
+ higher phonon terms ],
(6)

where 2W is the familiar Debye-Waller factor and is given by

$$2W = \frac{1}{2}K^2 \gamma(\infty) = (\hbar^2 K^2 / 2M) F(T).$$
 (7)

$$F(T) = \int_{0}^{\infty} \frac{f(z)}{z} \coth\left(\frac{z}{2k_{B}T}\right) dz$$
 (8a)

$$=\frac{6}{k_{B}\theta_{D}}\left[\frac{1}{4}+\frac{T}{\theta_{D}}\phi\left(\frac{\theta_{D}}{T}\right)\right],$$
(8b)

where

$$\phi(x) = \frac{1}{x} \int_{0}^{x} \frac{y \, dy}{e^{y} - 1} \,. \tag{9}$$

$$F(T) = 3/2k_B\theta_D, \text{ for } T \ll \theta_D, \qquad (10a)$$

and

= 
$$6T/k_B \theta_D^2$$
, for  $T \gg \theta_D$ . (10b)

The first term in (6) gives the cross-section for elastic scattering i.e., for a transition in which the  $\gamma$ -ray has exchanged no phonons with the lattice In other words it gives the probability for the Mössbauer Effect. This probability is proportional to the D-W factor exp(-2W). It would increase as is evident from (7) and (8) and (10) with the decrease in temperature, with the increase in  $\theta_D$  and with the decrease in the recoil energy, which is consistent with observations. The Mössbauer line is Lorentzian in shape with half width  $\Gamma$ . The second term in (6), which corresponds to the wings of the Mössbauer line, is proportional to f( $\omega$ ). Hence a measurement of the wings of the Mössbauer line will give the frequency distribution of the phonons. In the case of neutrons, measurement of f( $\omega$ ) has successfully been achieved but in the case of  $\gamma$ -rays it has so far not been possible to do so because of the very small value of the cross-section. The spread of the phonon spectrum is  $\sim 10^{-2}$  eV and the width of the line  $\sim 10^{-7}$  eV; and therefore to scan this spectrum with such a sharp line would mean a detection efficiency of  $10^{-5}$ . Such an experiment, if not impossible, is very difficult indeed. If, however, the Mössbauer line is broad, like that in Dy ( $\Gamma \sim 10^{-5}$  eV), it would be interesting to explore the singularities in  $f(\omega)$  which might not be possible in the neutron case for lack of good energy resolution.

For high temperatures (T >  $\theta_D/2$ ), it is preferable to write 2W as

$$2W = (K^2 h^2 / M) k_B T \langle 1/\omega^2 \rangle.$$
 (11)

If one measures 2W, (i.e. the recoilless fraction) and plots it as a function of T, any departure from linear dependence on T gives a measure of the temperature dependence of  $\langle 1/\omega^2 \rangle$ . This dependence is connected with anharmonicity.

#### DIFFUSION

The space-time formulation of the absorption probability as expressed by Eq. (4) is particularly suited for the study of the line shape in the presence of diffusion. In the case of simple diffusion

$$\gamma(t) = 2D[t], \qquad (11)$$

D being the diffusion coefficient. The line width is given by [5],

$$\Delta \epsilon = \Gamma + 2\hbar K^2 D. \tag{12}$$

In liquids where  $D \sim 10^{-5} \text{ cm}^2/\text{s}$ , the width due to diffusion is  $10^{-3} - 10^{-4} \text{ eV}$  which is much greater than  $\Gamma$ . It has so far not been possible to observe the Mössbauer Effect in liquids because of the very small value of the probability.

During recent years a study of the "quasi-elastic" scattering of slow neutrons in liquids has led to the belief that the motion of an atom in aliquid is far from a simple diffusing behaviour. Our knowledge in this respect has been limited because of poor energy resolution in the case of neutrons  $(\Delta E \sim 10^{-3} - 10^{-4} \text{ eV})$ , which prevents a detailed study of the line shape. This is, however, not the case with  $\gamma$ -rays for which the energy resolution is very high. In order to learn about the nature of diffusive behaviour, one has to know the line width and shape as a function of  $\underline{K}$ , and for this we will have to do scattering experiments with broad sources like Dy and Tm. In this respect Mössbauer experiments, though difficult, could probably do better than neutrons and it would be worthwhile to do these experiments.

In the case of a solid at ordinary temperatures diffusion is negligible and, therefore, the line broadening due to diffusion is small compared with the natural line width. Very near the melting point diffusion broadening could be of the same order as  $\Gamma$  and even greater. It would be interesting to study the line width as a function of temperature very near the melting point (in fact such a broadening has been observed [8] in the case of  $\operatorname{Sn}^{119}$ ), since it would tell us how the time of residence  $\tau$  of an atom in its lattice site varies with temperature. It should be possible to do such an experiment. Recently an experiment has been done at Mol in Belgium [9] in which  $Fe^{57}$  was diffused in between the layer planes of a single graphite crystal. The  $Fe^{57}$  atoms have comparatively much larger freedom of movement and hence greater diffusion constant in the basal plane than that along the C-axis. A diffusion broadening of the Mössbauer line at not too high temperatures has been observed in this case and also the pronounced anisotropy in the Debye-Waller factor.

#### SECOND ORDER DOPPLER SHIFT

If  $\omega_0$  is the frequency of the  $\gamma$ -ray in the rest frame of the emitting nucleus, the frequency  $\omega_L$  in the laboratory frame is given by

$$\omega_{\rm L} \simeq \omega_0 (1 + \frac{v(t)}{c} \cos \alpha_{\rm L} - \frac{1}{2} \frac{v^2(t)}{c^2} + .),$$
 (13)

where v(t) is the velocity of the nucleus, and  $\alpha_L$  is the angle between  $\underline{v}(t)$ and the direction of emission. Since the period of oscillation of the nucleus is much less than its life time, the second term in (13) averages out to zero. The quadratic term will remain and give rise to a shift in the energy of the  $\gamma$ -ray.

The relative shift is

$$\langle \Delta E_{\gamma}/E_{\gamma} \rangle_{av} = (1/2c^2) \langle v^2 \rangle_{av}$$
 (14)

For a harmonic solid [10] w have

$$(1/E_{\gamma}) (\partial E_{\gamma}/\partial T) = -(1/2Mc^2) C_{\gamma},$$
 (15)

 $C_L$  is the lattice specific heat. Thus knowing the temperature variation of the second order Doppler shift, it is possible to know from (15) the temperature variation of the Debye temperature  $\theta_D$ .

The high temperature limit of (14) is interesting. For  $T \gg \theta_D$ ,

$$\langle v^2 \rangle_{av} \rightarrow 3k_B T/M$$
.

Hence at high temperature the relative shift in the Mössbauer line is proportional to T, the coefficient of proportionality is  $3k_B/2Mc^2$ . This has been verified experimentally [11].

A more interesting case is the one in which the Mössbauer isotope forms an impurity in a host lattice. It can be shown quite generally (without making any assumption of the harmonic nature of the forces) that [12, 7]

$$\langle v^2 \rangle_{av} \simeq \frac{3kT}{M^1} \left\{ 1 + \frac{\hbar^2}{12M^1} \cdot \frac{1}{k_B^2 T^2} \langle \frac{\partial^2 U}{\partial x_0^2} \rangle + 0(T^{-4}) \right\}.$$
 (16)

**M**<sup>1</sup> is the mass of an impurity atom and U is the potential energy of the crys-

tal in the presence of an impurity. From (16) it is evident that a measurement of  $\langle v^2 \rangle_{av}$  from the second order Doppler shift gives the average value of the second derivative of U at the impurity. In the harmonic approximation for a cubic crystal (16) becomes

$$\langle \mathbf{v}^2 \rangle_{av} \simeq \frac{3kT}{M!} \left\{ 1 + \frac{1}{20} \frac{M}{M!} (1 - \gamma) \left(\frac{\theta_{\infty}}{T}\right)^2 \right\} \dots$$
 (17)

where M is the mass of an atom in the host lattice, and  $\gamma$  is a measure of the change in the force constant when an impurity atom is introduced and  $\theta_{\infty}$  is the high temperature limit of  $\theta_D$ . Thus it is possible to measure  $\theta_{\infty}$ directly (assuming  $\gamma = 0$ ), thereby knowing whether the impurity atom is more tightly or less tightly bound in a given host lattice. It has been found [13] that Fe<sup>57</sup> in Be is more tightly bound than Fe<sup>57</sup> in Fe. A full use of Eq. (16) has not yet been made in interpreting the high temperature results of the second order Doppler shift. Anharmonic effects will give a temperature variation of the "generalized force constant"  $\langle \partial^2 U/\partial x_0^2 \rangle$ ".

#### INFLUENCE OF IMPURITY ATOMS ON LATTICE DYNAMICS

It is of interest to know how the dynamical properties of a lattice change with the introduction of impurity atoms, e.g. what are the mean square displacement and the mean square velocity of an impurity atom and how does the frequency spectrum of the normal modes change? Unfortunately, not much experimental and theoretical work has been done in this direction and it is only very recently that attempts have been made. It is obvious that much information in this field can be gained through a study of both neutron scattering and Mössbauer Effect. The former will suffer from the disadvantage that interference between impurities on account of their large number will make the interpretation of the results difficult.

When an impurity atom of mass m' is introduced in a host lattice of atomic mass m, there will in general be a change in the force constants too. If the introduction of an impurity does not change the harmonic character of the forces, the solution of the problem of normal vibration gives a spectrum which is equivalent to that of the perfect host lattice except a set of discrete levels in the case  $m^{i} < m$ , which are thrown out of the continuum [14, 15, 16]. These discrete frequencies have recently been observed [17] through cold neutron scattering. No such experiment has been reported with the Mössbauer Effect. The one phonon spectrum as revealed by the wings. of the Mössbauer line should have a peak corresponding to the impurity mode. However, very high velocities would be needed to produce the required energy shift  $\sim 10^{-2}$  eV. But it would indeed be a pure impurity spectrum. It would also be interesting to measure the width of these localized impurity phonons with the Mössbauer Effect, In these experiments there are many parameters which one could change, such as the impurity concentration and the temperature, and study their effect.

The spatial localization of the oscillations corresponding to these discrete impurity modes has the consequence that a considerable part of the energy of these oscillations is associated with the motion of the impurity atom. On the other hand for a non-localized vibration, the energy assignable to a single atom is of the order 1/N. Thus, in general, the contribution of the discrete levels and the quasi-continuous spectrum to the displacement of the impurity are of the same order. It would, therefore, be interesting to study the probability of the Mössbauer Effect for an impurity atom. The total probability f can be written as a product of  $f_1$  and  $f_2$ , the former corresponding to the continuous part of the spectrum and the latter to the discrete part.

Hence

$$f = f_1 f_2$$
 (18)

Let m<sup>1</sup> be the mass of an impurity atom and m that of the atom of the host lattice. Define

$$\epsilon \equiv ((m-m')/m). \tag{19}$$

Let us assume that the force constant  $A(o, \underline{r}_n)$  between the impurity atom at the origin and any other atom of the host lattice is given in terms of the force constant in the ideal case  $A_0(o, \underline{r}_n)$  by

$$A(o, \underline{r}_{n}) = A_{0}(o, \underline{r}_{n}) (1-\gamma).$$
 (20)

If  $\gamma > 0$ , the force constant decreases and if  $\gamma < 0$  it increases with the introduction of the impurity. Under certain restrictions, it is possible to solve the problem of normal vibrations using a perturbation method. I would only quote a few interesting results [18].

<u>Case (1).</u>  $\epsilon \to 1$  i.e. m' « m;  $\gamma < \epsilon$  (in this case one gets discrete modes) and  $T \to 0$ ,

$$f_2 \simeq \exp\left\{-\frac{E_{\gamma}^2}{2m^{t}c^2} \frac{1}{\hbar \langle \omega_0^2 \rangle^{\frac{1}{2}}} \left(\frac{m^{t}}{m}\right)^{\frac{1}{2}} \frac{1-\gamma}{(\epsilon-\gamma)^{3/2}}\right\}.$$
 (21)

The exponent in (21) varies as  $\sqrt{1/m^4}$  i.e. the probability diminishes as the mass of the impurity decreases. As the temperature increases  $f_2$  falls off much more slowly than  $f_1$ . The reason for this is that since  $\omega_{\text{discrete}} > \omega_{\text{omax}}$ , the temperature excitation of these discrete modes occurs at much higher temperature than does the excitation of continuous spectrum. And

$$f_{1} \simeq \exp\left\{-\frac{E_{\gamma}^{2}}{2mc^{2}} \frac{1}{\hbar(1-\gamma)^{2}} \int_{0}^{\omega_{\text{max}}} d\omega_{0}^{2} \frac{g(\omega_{0}^{2})}{\omega_{0}}\right\}.$$
 (22)

...

 $f_1$  is independent of m'.

<u>Case (II)</u>  $m^* > m$  and  $\gamma = 0$ . In this case f = 1 since there are no discrete states, and for  $T \rightarrow 0$ 

#### MÖSSBAUER EFFECT AND LATTICE DYNAMICS

$$f_1 \simeq \exp\left\{-\frac{E_{\gamma}^2}{2mc^2} \frac{1}{\hbar} \langle 1/\omega_0^2 \rangle^{\frac{1}{2}} |\epsilon|^{-\frac{1}{2}}\right\}.$$
 (23)

The exponent in (23) decreases as  $(1/\sqrt{m^{1}})$  with the increases in mass m<sup>t</sup> of the impurity, thus giving rise to an increase in Mössbauer probability. By putting a heavy Mössbauer isotope like Fe<sup>57</sup> in Be it is possible to increase the Mössbauer probability. Such an increase has indeed been observed [19]. From the study of the second order Doppler shift as we have seen before, it has also been found that Fe<sup>57</sup> is more stiffly bound in a beryllium lattice than in an iron lattice [13]. Since the vibrations of the heavy impurity atom are preferentially in the low frequency range, this enhanced effect disappears with increasing temperature.

Let me remark that by using the standard quantum-statistical perturbation theory it should be possible to calculate  $\langle x^2 \rangle_{av}$  and  $\langle v^2 \rangle_{av}$  much more simply than has hitherto been done [13, 18], without actually solving the dynamical problem. In fact the derivation of Eq. (17) is much simpler than given by MARADUDIN <u>et al.</u> [13].

#### DISPERSION RELATION FOR PHONONS

Everyone is aware of the success of the cold neutron scattering experiments in measuring the dispersion relation  $\omega = \omega(k)$  for the phonons. I think the determination of the dispersion relation has been the greatest contribution of neutron spectroscopy to crystal dynamics. The Mössbauer Effect is an extremely poor rival in this respect. At a first glance it might appear that since the Mössbauer line is very sharp ( $\Delta E \sim 10^{-5} - 10^{-9}$  eV) one would be able to achieve a large energy resolution compared to neutrons, but in actual practice it is not so. For  $\gamma$ -rays the wave number <u>k</u> is much larger than that of neutrons, and hence for a given spread in <u>K</u> = <u>k</u>-<u>k'</u> (i. e. in q, the phonon wave number) a much better collimated beam of  $\gamma$ -rays is needed. This would mean an enormous reduction in intensity compared with neutrons for the same effective energy spread. One should use the Mössbauer Effect where neutrons cannot be used for the reason of high absorption coefficient as in the case of He<sup>3</sup>.

#### SCATTERING OF $\gamma$ -RAYS AND NEUTRONS IN LIQUID He<sup>3</sup>

The most interesting and as yet undiscovered prediction of LANDAU's theory [20] of liquid He<sup>3</sup> is the existence of zero sound [21]. Propagation of ordinary sound for which thermodynamic equilibrium exists over elementary volumes, small in comparison with the wave length of sound, is no longer possible when the mean free path of collision of the particles is  $\gtrsim \lambda_{\text{sound}}$ . In other words the condition of propagation of ordinary sound is

$$\omega \tau \ll 1$$
,

 $\tau$  being the collision time. In practice in all condensed systems condition (24) is always satisfied. To violate (24) exceedingly high frequencies are

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(24)

needed, and that is why the effect has never been demonstrated. But for liquid He<sup>3</sup> the collision time or the mean free path increases as  $(1/T^2)$ . Hence for any given frequency, the wave length and the excitation mean free path will become comparable at some temperature which, though low, is attainable. From heat conductivity measurements  $\tau \sim 6 \times 10^{13} / T^2$ , i.e. equal to  $6 \times 10^{-9}$  s, say for T = 0.01°K.

Therefore

$$\omega \tau > 1$$
, (25)

for  $\omega > 10^8$ /s. Thus for  $\omega \sim 10^8$  s<sup>-1</sup> and temperatures  $\langle 0.01^{\circ}K, \omega\tau \rangle 1$ , collisions can no longer maintain local thermodynamic equilibrium in volume elements small compared to  $\lambda$ . Under these conditions a new sound propagates as has been shown by Landau and called by him as zero sound. Demonstration of this sound would be a great experimental achievement and the verification of Landau's theory of Fermi liquid. Since Landau is seldom wrong, the experimenter can be sure of rewards if successful.

Zero sound is an oscillatory distortion of the Fermi surface. It is a collective oscillation of density exactly analogous to plasma oscillation. Since it is accompanied by density fluctuations, it should be possible to excite zero sound by a piezo electric crystal. The reason why it has so far not been possible to excite this sound is that the frequency needed is very high  $(> 10^9)$  even at very low temperatures of a tenth of a degree absolute.

An indirect method can be proposed to observe the velocity of zero sound. This method is old and is well-known, and consists in observing the Rayleigh scattering of light in He<sup>3</sup>. In addition to the main line one observes satellite lines or what are known as the Brillouin components differing in frequency from the main line by

$$\Delta \omega = \pm 2 \frac{u}{c} \omega \sin \frac{\theta}{2} , \qquad (26)$$

u  $(2 \times 10^4 \text{ cm/s})$  being the velocity of sound and  $\theta$  the scattering angle.

A calculation [22] showed that the scattering of visible light is extremely small and hence the effect will not be detected. However, since the scat tering increases rapidly with frequency as  $\omega^4$  or  $\omega^5$ , it is clear that increasing the frequency of the radiation would considerably enhance the effect. With the discovery of the Mössbauer Effect, it is now possible to use  $\gamma$ -rays for which the scattering will be large because of high frequency and besides the change in frequency  $\Delta \omega$  as given by (26) can be detected accurately. Thus the Mössbauer Effect would provide a possible method to measure the velocity of zero sound [23]. I do not know whether attempts are being made in this direction or not. In my opinion they are worth the effort. As early as 1960, I tried to convince some of my low temperature friends at Argonne about these experiments without much success. With the increase in temperature the attentuation of zero sound will increase and will lead to the broadening of the satellite lines. It would be interesting to know the life time of the zero sound quanta as a function of temperature. It is also possible to excite the zero sound quanta by allowing the neutrons of velocity greater than the velocity of zero sound to be coherently scattered in liquid He<sup>3</sup> at very low temperatures. The scattering crosssection is given by the Fourier transform of the density auto-correlation function which can be computed [24] on the basis of Landau's theory. Unfortunately, in the case of He<sup>3</sup>, the capture cross-section for cold neutrons of energy ~ 1°K is nearly  $10^5 \times 10^{-24}$  cm<sup>2</sup>, whereas the scattering crosssection is only  $10^{-24}$  cm<sup>2</sup>. Because of this, even with the present highest neutron flux available, it is not possible to do the scattering experiment but some day it might be possible.

#### CONCLUDING REMARKS

I do not wish you to have the impression that the achievements of the Mössbauer Effect have after all not been very great. This might be true in the field of lattice dynamics. I would, however, remind you that the Mössbauer Effect is one of the most sensitive tools in Physics, the full potentialities of which still remain to be explored. And let us not forget that, besides other things, it was this Effect which made possible the determination [25] of the gravitational red shift in a terrestrial laboratory and the magnitude and the sign of the magnetic field [26] at the iron nucleus in ferromagnetic iron.

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Note: An excellent review of the Mössbauer Effect is contained in FRAUENFELDER, H., "The Mössbauer Effect", Benjamin, N.Y. (1962)

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# THEORY OF THE INFLUENCE OF PHONON-PHONON AND ELECTRON-PHONON INTERACTIONS ON THE SCATTERING OF NEUTRONS BY CRYSTALS\*

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#### Abstract — Résumé — Аннотация — Resumen

THEORY OF THE INFLUENCE OF PHONON-PHONON AND ELECTRON-PHONON INTERACTIONS ON THE SCATTERING OF NEUTRONS BY CRYSTALS. As predicted by harmonic theory the coherent inelastic spectrum of neutrons, scattered by a single, non-conducting crystal, for a particular angle of scattering consists of a number of delta-function peaks superposed on a continuous background. The peaks correspond to one-phonon processes in which one phonon is absorbed or emitted by the neutron; the background arises from multi-phonon processes. When anharmonic forces (phonon-phonon interactions) are present, the delta-function peaks are broadened into finite peaks, while their central frequencies are shifted with respect to the harmonic values. In the case of a metal there is in addition to phonon-phonon interactions an interaction between phonons and conduction electrons, which also gives a contribution to the displacement and broadening of the one-phonon peaks.

Continuing earlier work of Van Hove ( who considered the relatively simple case of a non-conducting crystal in its ground state ( $T = 0^{\circ}K$ )), we have studied the shifts and widths of the scattering peaks as a result of the above-mentioned interactions by means of many particle perturbation theory, making extensive use of diagram techniques. Prerequisite to the entire discussion is the assumption that, independent of the strength of the interactions, the width of each peak is small compared to the value of the frequency at its centre; only then the peaks can be considered as being well defined with respect to the background to higher order in the interactions. This condition is expected to be fulfilled for temperatures which are not too high and values of the phonon wave vector which are not too large.

Our procedure yields closed formulae for the partial scattering function describing the peaks, which can be evaluated to arbitrarily high accuracy. In particular an expansion for calculating the line shift and line width in powers of u/d and in terms of simple connected diagrams is obtained (u is an average atomic or ionic displacement, d is the smallest interatomic or interionic distance in the crystal). Approximate calculations are performed to give some insight into the orders of magnitude of the effects under study.

THÉORIE DE L'INFLUENCE DES INTERACTIONS PHONON-PHONON ET ELECTRON-PHONON SUR LA DIFFUSION DES NEUTRONS PAR DES CRISTAUX. Comme le prédit la théorie harmonique, le spectre de la diffusion inélastique cohérente de neutrons par un monocristal non conducteur, pour un angle de diffusion donné, se compose d'une série de pics de fonction delta, qui se superposent à un bruit de fond continu. Les pics correspondent à des phénomènes à un phonon, dans lesquels un phonon est absorbé ou émis par le neutron; le bruit de fond provient de phénomènes à plusieurs phonons. Lorsqu'il existe des forces anharmoniques (interaction phonon-phonon) les pics de fonction delta s'élargissent pour former des pics finis et leur fréquence centrale est déphasée par rapport aux valeurs harmoniques. Dans le cas d'un métal il y a, en plus des interactions phonon-phonon, une interaction entre les phonons et les électrons de conduction, laquelle contribue à déphaser et élargir encore davantage les pics à un phonon.

Continuant les travaux de Van Hove (qui avait considéré le cas relativement simple d'un cristal non conducteur à l'état fondamental, soit  $T = 0^{\circ}K$ ) l'auteur a étudié les déplacements et les largeurs des pics de diffusion résultant des interactions indiquées plus haut, à l'aide de la théorie de la perturbation à plusieurs particules, en ayant largement recours à la méthode des diagrammes. Il admet, avant tout examen du pro-

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blème, que quelle que soit la force des interactions, la largeur de chaque pic est petite par rapport à la valeur de la fréquence en son centre; dans ces conditions seulement, on peut considérer que les pics sont bien définis par rapport au bruit de fond, si les calculs d'interaction sont poussés jusqu'aux ordres supérieurs. On estime que cette hipothèse est réalisée tant que les températures ne sont pas trop élevées et que les valeurs du vecteur d'onde des phonons ne sont pas trop considérables.

La méthode appliquée par l'auteur lui permet d'obtenir des formules fermées pour la fonction de diffusion partielle décrivant les pics, qui peuvent être calculées avec une approximation aussi pousée qu'on le désire. L'auteur a obtenu notamment une expression qui permet de calculer le déphasage et la largeur des raies en puissances de u/d et en fonction de diagrammes connectés simples (u étant le déplacement atomique ou ionique moyen et d la plus petite distance interatomique ou interionique dans le cristal). Des calculs approchés donnent une idée de l'ordre de grandeur des effets étudiés.

ТЕОРИЯ ВЛИЯНИЯ ВЗАИМОДЕЙСТВИЙ ФОНОН-ФОНОН И ЭЛЕКТРОН-ФОНОН НА РАССЕЯНИЕ НЕЙТРОНОВ КРИСТАЛЛА-МИ. Как предсказано теорией гармоник, когерентный спектр неупругого рассеяния нейтронов на одиночном непроводящем кристалле при заданном угле рассеяния, содержит пики дельта-функций, наложенных на непрерывный фон. Пики соответствуют однофононным процессам, в которых один фонон поглощается или испускается нейтроном. Фон возникает в результате многофононных процессов. Если присутствуют негармонические силы (взаимодействия фонон-фонон), то дельта-функции уширяются и превращаются в максимумы конечной величины, а их центральные частоты смещаются по отношению к гармовическим значениям. В случае с метадлом, помимо взаимодействий дочерний фонон-фонон, наблюдается также взаимодействие между фононами и электронами проводимости, которое приводит к смещению и уширению однофононных максимумов.

Продолжая более рание работы Ван Гофа (который рассматривал сравнительно простой случай непроводящего кристалла в его основном состоянии (Т = O°K), мы изучили смещения и уширения максимумов рассеяния в результате упомянутых выше взаимодействий методами теории возмущения многих тел, широко используя методы диаграмы.

Полученные результаты обсуждаются на основе предположения о том, что, независимо от силы взаимодействия, ширина каждого максимума мала по сравнению с величиной частоты в его центре. Только в этом случае максимумы могут рассматриваться как хорошо выделяющиеся над фоном при взаимодействиях более высокого порядка. Предполагается, что это условие выполняется для не очень высоких температур и не очень больших значений волнового вектора фонона.

Таким путем мы подучили законченную формулу для функции частичного рассеяния, описывающую максимумы, которые могут быть рассчитаны со сколь угодно высокой точностью. В частности, для вычисления смещения и уширения линий подучены выражения в виде степенной зависимости u/d и в виде простых связанных диаграмы (u - среднее смещение атома или иона, d - наименьшее расстояние между атомами или ионами в кристалле). Выподнены приближенные расчеты, дающие некоторое представление о порядках величин изучаемого явления.

TEORÍA DE LA INFLUENCIA DE LAS INTERACCIONES FONÓN-FONÓN Y ELECTRÓN-FONÓN EN LA DISPERSIÓN DE NEUTRONES POR CRISTALES. Como permite predecir la teoría armónica, el espectro de neutrones dispersados coherente e inelásticamente por un monocristal no conductor consiste, para un ángulo de dispersión determinado, en una serie de picos de functión delta superpuestos a un fondo continuo. Los picos corresponden a procesos en que el neutrón absorbe o emite un solo fonón; el fondo se debe a procesos de varios fonones. Cuando intervienen fuerzas anarmónicas (interacciones fonón-fonón), los picos de función delta se ensanchan, convirtiéndose en picos finitos y sus frecuencias centrales se desplazan respecto de los valores armónicos. En el caso de los metales, además de las interacciones fonón-fonón existe interacción entre los fonones y los electrones de conducción, lo que también contribuye al desplazamiento y ensanchamiento de los picos correspondientes a los procesos de un solo fonón.

Prosiguiendo trabajos anteriores de Van Hove (quien investigó el caso relativamente sencillo de un cristal no conductor en el estado fundamental ( $T = 0^{\circ}$ K)), el autor ha estudiado el desplazamiento y la amplitud de los picos de dispersión resultantes de las mencionadas interacciones aplicando la teoría de las perturbaciones originadas por partículas múltiples y utilizando ampliamente técnicas de diagramas. Un requisito indispensable para dicho estudio es la hipótesis de que, sea cual fuere la intensidad de las interacciones, la amplitud de cada pico es pequeña en comparación con el valor de la frecuencia en el centro; sólo en tal caso puede considerarse que los picos están bien definidos respecto del fondo correspondiente a las interacciones de orden más elevado. Cabe esperar que esta condición se cumpla para temperaturas no demasiado elevadas y valores de vector de onda fonónico no excesivamente grandes.

El procedimiento del autor permite obtener fórmulas cerradas de la función de dispersión parcial que describe los picos; éstos pueden evaluarse con el grado de precisión que se desee. En particular, se obtiene un desarrollo para calcular en potencias de u/d y en función de diagramas simples conectados el desplazamiento y la anchura de las rayas (u es el desplazamiento atómico o iónico medio y d es la distancia mínima interatómica en el cristal). El autor efectúa cálculos aproximados para dar una idea del orden de magnitud de los efectos estudiados.

#### I. INTRODUCTION

In this paper we shall consider the coherent, inelastic scattering of slow neutrons by single, perfect, non-magnetic crystals. In the case of an harmonic, non-conducting crystal (which can be conceived as a system of non-interacting phonons), for a given angle of scattering the outgoing spectrum is a superposition of delta-function peaks, corresponding to one-phonon processes, and a smooth background arising from multi-phonon processes. The one-phonon peaks are particularly interesting from the point of view of crystal dynamics; their locations follow simply from the conservation rules for energy and momentum [1].

In any real crystal, however, anharmonic forces are present, which, if small, can be interpreted as causing an interaction between phonons. In a conducting crystal the phonons interact both with each other and with the conduction electrons. Both types of interactions show up in a most interesting way in the peaks of the scattering spectrum. Their presence results in a shift and broadening of these peaks, the two effects being temperature dependent. In addition to the contributions of the phonon-phonon and electronphonon processes to the frequency shift of the phonons (self-energy effects), there is a temperature dependent contribution arising from thermal expansion. Both contributions are included in the observed shifts.

The above mentioned effects have been investigated experimentally by LARSSON et al. [2] (aluminium) and by BROCKHOUSE et al. [3] (lead) for temperatures well above the Debye temperature.

The aim of the present paper is to study the influence of phonon-phonon interactions and electron-phonon interactions on the displacements and widths of the scattering peaks by means of many particle perturbation theory. VAN HOVE [4] has done this for a non-conducting crystal in its ground state, i.e. at the absolute zero of temperature, using time independent perturbation theory. The present author has extended Van Hove's approach to finite temperatures and to conducting crystals [5,6]. For that purpose time dependent perturbation theory is more suited than the resolvent methods introduced by Van Hove. A treatment of shift and width is of interest in the first place from the point of view of solid state physics as a means of checking its general predictions.

Since we are primarily interested in the peaks of the inelastic scattering spectrum, and not in the complete spectrum, it is important to construct a theory which yields information about the peaks alone. This can only make sense if the peaks are distinguishable from the background. Therefore our treatment is restricted to the case, where, independent of the strengths of the interactions, the width of a peak is small compared to the value of its central frequency. Only then can the peaks be considered as being well defined with respect to the background to higher order in the interactions, and it is possible to isolate a part of the scattering function which can be shown to describe the desired peaks. This case is expected to be realized for temperatures which are not too high (well below the melting point) and values of the phonon wave vector which are not too large. The case of sharply distinguishable peaks is, of course, also the most interesting one from the point of view of the experimentalist,

In the second section we have developed the formalism. For convenience we have restricted ourselves in this section to the case of non-conducting crystals. In the third section, the theory is extended to conducting crystals to include electron-phonon coupling. Extensive use has been made of diagrams to represent the matrix elements. The use of the diagrams is illustrated in the Appendix for the familiar case of scattering by anharmonic crystal. Here we present a simple derivation of the Debye-Waller factor for a harmonic lattice. Finally the end of the Appendix is devoted to some remarks concerning the work of BAYM [7].

#### II. NON-CONDUCTING CRYSTALS

#### 1. The Hamiltonian

Consider a finite, perfect, non-conducting crystal of volume  $\Omega$ , containing N<sub>o</sub> unit cells. Let  $\underline{r}_{sn}$  designate the positions of the atoms in the crystal; each vector  $\underline{r}_{sn}$  is the sum of an equilibrium position vector  $\underline{s} + \underline{R}_{on}$ and a displacement vector  $\underline{u}_{sn}$  where  $\underline{s}$  is a crystal translation vector and  $\underline{R}_{on}$  the equilibrium position vector of atom n in the unit cell containing the origin; n runs from i to  $n_o$ , the number of atoms per unit cell.

The Hamiltonian of the crystal consists of two parts: the kinetic energy of the atoms and a potential energy term. Expanding the potential energy in powers of the displacements of the atoms from their equilibrium positions, we can write the Hamiltonian as follows:

$$H = H^{(2)} + V.$$
 (1)

 $H^{(2)}$ , the harmonic energy, includes all terms through second order in products of the displacements. V, the anharmonic energy, includes all terms of higher order. The solution of the harmonic problem gives a description of the vibrating crystal in terms of independent phonons, where each phonon is characterized by a wave vector  $\mathbf{q}$  and a polarization index j, the vector  $\mathbf{q}$  being defined up to the addition of  $2\pi$  times a vector  $\underline{\tau}$  of the reciprocal lattice. Therefore  $\mathbf{q}$  is restricted to the first Brillouin zone. The polarization index j runs over all positive integers from 1 to  $3n_o$ . We denote the energy of the phonon  $\underline{q}_j$  by  $\hat{\omega}_{\mathbf{q}j}$  (in this section we put  $\hbar = 1$ );  $\omega_{\mathbf{q}j}$  is periodic in  $\underline{q}$ -space with period  $2\pi\underline{\tau}$  and remains unchanged when  $\underline{q}$  is replaced by  $-\underline{q}$ . The excited states (phonon states)  $|\underline{q}_{j}, \underline{q}'_{j'}, \underline{q}'_{j'}, \dots \rangle$  of the harmonic Hamiltonian will be defined by the following equation, which also fixes the normalizing constants:

$$|\underline{\mathbf{q}}_{\mathbf{j}}, \underline{\mathbf{q}}'_{\mathbf{j}'}, \underline{\mathbf{q}}''_{\mathbf{j}''}, \ldots \rangle = \mathbf{A}^*_{\mathbf{q}\mathbf{j}} \mathbf{A}^*_{\underline{\mathbf{q}}\mathbf{j}'}, \mathbf{A}^*_{\underline{\mathbf{q}}\mathbf{j}''}, \ldots \mid 0 \rangle.$$
(2)

Here  $|0\rangle$  designates the vacuum (no phonon) state, defined by  $A_{\underline{q}\underline{j}}|0\rangle = 0$ for all  $\underline{q}_{\underline{j}}$ . We have introduced the creation and annihilation operators  $A^*_{q\underline{i}}$ and  $A_{\underline{q}\underline{j}}$  for the phonon  $\underline{q}_{\underline{j}}$ . They obey the usual commutation rules for bosons. The displacement vector  $\underline{u}_{sn}$  of the atom of type n (mass  $M_n$ ) can be expressed in these operators as follows:

$$\underline{\mathbf{u}}_{\underline{\mathbf{s}}\underline{\mathbf{n}}} = (\mathbf{v}_0 / 16\pi^3 \mathbf{M}_{\underline{\mathbf{n}}})^{\frac{1}{2}} \Sigma_j \int_{\underline{\mathbf{q}}} \omega_{\underline{\mathbf{q}}j}^{-\frac{1}{2}} \left[ \mathbf{A}_{\underline{\mathbf{q}}j} + \mathbf{A}^*_{-\underline{\mathbf{q}}j} \right] \left( \underline{\mathbf{e}}_{\underline{\mathbf{q}}j}^{(n)} - i\underline{\mathbf{f}}_{\underline{\mathbf{q}}j}^{(n)} \right) \exp \left[ i\underline{\mathbf{q}} \cdot \underline{\mathbf{s}} \right].$$
(3)

In this equation  $v_0 = \Omega/N_0$  is the volume of the unit cell; the real vectors  $\underline{e}_{q_j}^{(u)}$  and  $\underline{f}_{q_j}^{(u)}$  determine the polarization and phase of the phonon  $\underline{q}_j$ . The symbol  $\int_{\mathbf{q}}$  stands for  $(\Omega/8\pi^3)^{-1} \Sigma_{\mathbf{q}}$  (summation over one unit cell in reciprocal space), and becomes  $\int \mathbf{q}$  in the limit of an infinite crystal.

If the anharmonic energy V is sufficiently small the notion of phonons is still meaningful and V can be regarded as causing interactions between phonons. The effect of V can in this case be investigated by means of perturbation theory. By substituting (3) in the expansion (1) we obtain for the total Hamiltonian:

$$H = \epsilon_0 + \epsilon_{zp} + H_0 + V, \qquad (4)$$

where  $\epsilon_0$  and  $\epsilon_{zp}$  are the rigid lattice energy and zero point energy respectively and  $H_0$  and V are given by the following equations:

$$H_0 = \Sigma_j \int_{\underline{q}} \omega_{\underline{q}j} A^*_{\underline{q}j} A_{\underline{q}j}; V = \Sigma_{\nu=3}^{\infty} V^{(\nu)}, \qquad (5)$$

with

$$V^{(\nu)} = \Sigma_{\mathbf{j}_{1}} \cdots \mathbf{j}_{\nu} \int \mathbf{q}_{1} \cdots \mathbf{q}_{\nu} \mathbf{B}^{(\nu)}_{\mathbf{q}_{11}} \cdots \mathbf{q}_{\nu j\nu} [\mathbf{A}_{\mathbf{q}_{1j_{1}}} + \mathbf{A}^{*} - \mathbf{q}_{ij_{1}}] \cdots$$

$$[\mathbf{A}_{\mathbf{q}_{\nu} j\nu} + \mathbf{A}^{*} - \mathbf{q}_{\nu j\nu}] \Delta(\mathbf{q}_{1} + \cdots + \mathbf{q}_{\nu}).$$
(6)

$$\mathbf{B}_{\mathbf{q}_{1}j_{1}}^{(\nu)}, \dots, \mathbf{q}_{\nu}j_{\nu} = \left(1/\nu!\right) \left(\frac{1}{2} \operatorname{M}_{\mathbf{n}}\right)^{\frac{\nu}{2}} \left(v_{0}/8\pi^{3}\right)^{\frac{\nu}{2}-1} \left(\omega_{\underline{q}_{1}j_{1}}, \dots, \omega_{\underline{q}_{\nu}j_{\nu}}\right)^{-\frac{1}{2}}$$

$$\sum_{\underline{\mathbf{s}}_{2}} \dots, \underline{\mathbf{s}}_{\nu} \sum_{\mathbf{n}_{1}} \dots, \underline{\mathbf{n}}_{\nu} \sum_{\alpha_{1}, \dots, \alpha_{\nu}} C_{\underline{\mathbf{s}}_{1}}^{(\nu)} - \underline{\mathbf{s}}_{2}, \underline{\mathbf{s}}_{1} - \underline{\mathbf{s}}_{3}, \dots, \underline{\mathbf{s}}_{1} - \underline{\mathbf{s}}_{\nu}, \mathbf{n}_{1}, \dots, \mathbf{n}_{\nu}, \alpha_{1}, \dots, \alpha_{\nu}$$

$$\times \left(\underline{e}_{\underline{q}_{1}\underline{j}_{1}\alpha_{1}}^{(n)} - \operatorname{if}_{\underline{q}_{1}\underline{j}_{1}\alpha_{1}}^{(n)}\right) \cdots \left(\underline{e}_{\underline{q}_{\nu}\underline{j}\nu\alpha\overline{\nu}}^{(n)} \operatorname{if}_{\underline{q}_{\nu}\underline{j}\nu\alpha\nu}^{(n)}\right)$$

$$\times \exp\left[\operatorname{iq}_{2} \cdot (\mathbf{s}_{2} - \mathbf{s}_{1}) + \operatorname{iq}_{3} \cdot (\mathbf{s}_{3} - \mathbf{s}_{1}) + \ldots + \operatorname{iq}_{\nu} \cdot (\mathbf{s}_{\nu} - \mathbf{s}_{1})\right].$$
(7)

in which  $C_{(1)}^{(\mu)}$  is the  $\nu^*$ th order derivate of the potential energy, evaluated for the equilibrium lattice at temperature T. The subscripts  $\alpha_1, \alpha_2, \ldots$ . stand for the x, y, z components. Because of the factor  $(\omega_{q,j}, + \ldots + \omega_{q_yj_y})^{-\frac{1}{2}}$ in eq. (6),  $B_{(1)}^{(\mu)}$  can become infinite when one of the  $\omega_{q_i}$  u becomes zero. However, this situation corresponds to a pure translation of the crystal as a whole and can be excluded explicitly.  $B_{(1)}^{(\mu)}$ , then, turns out to be a finite quantity which in the limit  $\Omega \rightarrow \infty$  is independent of the size of the crystal. Note that the coefficients  $B_{(2)}^{(\mu)}$  and therefore the harmonic frequencies  $\omega_{q_j}$  are temperature dependent as a result of thermal expansion. The generalized delta-function  $\Delta(q_1 + \ldots + q_y)$  occuring in (6) arises from the summation over  $\underline{s}_1$ . In the limit of large  $\Omega$  it can be replaced as follows:

$$\Delta(\mathbf{q}) = \Sigma_{\underline{\mathbf{r}}} \, \delta(\mathbf{q} + 2\pi\underline{\mathbf{r}}), \tag{8}$$

where  $\underline{\tau}$  is a vector of the reciprocal lattice.

The relative strength of the various terms in (4) are measured by the parameter u/d, the expectation value of the  $\nu$ 'th order term  $V(\nu)$  being proportional to  $(u/d)^{\nu-2}$ . Here u is an average atomic displacement for a given temperature and d is the smallest interatomic equilibrium distance in the crystal.

It follows from (6) that each  $V^{(\nu)}$  is a linear combination of products of  $\nu$  annihilation and creation operators, which, when operating on a phonon state, give either another phonon state or zero. Because of the factor  $\Delta(q_1+\ldots+q_{\nu})$  the new phonon state must have the same total wave vector, modulo  $2\pi T$ , as the initial one (conservation of pseudo-momentum).

#### 2. The scattering function

The differential scattering cross-section at temperature T per unit solid angle d $\Omega$  and per unit interval of outgoing energy d $\epsilon$  of the neutron for coherent scattering in the first Born approximation is given by [8]

$$d^{2}\sigma_{T}/d\Omega d\epsilon = a^{2}\left(|\underline{\mathbf{k}}|/|\underline{\mathbf{k}}_{0}|\right) S_{T}\left(\underline{\mathbf{k}}\omega\right) , \qquad (9)$$

in which the scattering function  $S_T(\underline{\kappa}\omega)$ , depending upon  $\underline{\kappa} = \underline{k}_0 - \underline{k}$  and  $\omega$ , the momentum and energy transferred from the neutron to the crystal, has the following form

$$S_{T}(\underline{\kappa}\omega) = Z(\beta)^{-1} \Sigma_{\nu_{0}} \exp(-\beta E_{\nu_{0}}) \Sigma_{\nu} |\langle \psi_{\nu}| T_{\underline{\kappa}} |\psi_{\nu}\rangle|^{2} \delta(\omega + E_{\nu_{0}} - E_{\nu}) .$$
(10)

Here  $|\psi_{\nu_0}\rangle$  and  $|\psi_{\nu}\rangle$  are initial and final excited states of the crystal; they are eigenstates of the total Hamiltonian H, given by (4), with corresponding

eigenvalues  $E_{\nu_0}$  and  $E_{\nu} \cdot Z(\beta) = Tr[exp(-\beta H)]$  is the partition function for the crystal ( $\beta = 1/k_BT$ ). Finally  $T_{\underline{k}}$  represents the operator for the neutron-nucleus interaction:

$$\Gamma_{\underline{\kappa}} = \Sigma_{\underline{s}\underline{n}} \exp\left[i\underline{\kappa} \cdot \underline{r}_{\underline{s}\underline{n}}\right], \qquad (11)$$

The scattering function in the form (10) depends on the exact, but completely unknown, excited eigenstates of the anharmonic crystal. Fortunately we can get rid of this dependence by using the following representation for the delta-function:

$$\delta(\mathbf{x}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-it\mathbf{x}} dt.$$

Using Eq. (4) we then easily find

$$S_{T}(\underline{\kappa}\omega) = (2\pi Z_{\beta})^{\pi-1} \int_{-\infty}^{\infty} dt \exp[-it\omega]$$

$$\times \operatorname{Tr} \{ \exp[-(\beta + \mathrm{it}) (H_0 + V)] T_{\kappa} \exp[\mathrm{it}(H_0 + V)] T_{\kappa} \}$$
(12)

with

$$Z_{\beta} = \exp[\beta(\epsilon_0 + \epsilon_{zp})] Z(\beta) = \operatorname{Tr} \{\exp[-\beta(H_0 + V)]\}.$$
(13)

The variable t in this equation can be interpreted as time [8]. The appearance of the trace in (12) shows that this result does not involve the exact set of states  $|\psi_{\nu}\rangle$ , bearing in mind that the trace is invariant under unitary transformations. In the representation of the phonon states (2) the trace takes the form:

$$Tr \{ \exp[-(\beta + it) (H_0 + V) \quad T_{\underline{\kappa}} \exp[it (H_0 + V)] T_{\underline{\kappa}} \}$$

$$= \sum_{N=0}^{\infty} (N|)^{-1} \sum_{j_1, a, j_N} \int_{q_1 \dots q_N} \langle \underline{q}_{NjN} \dots \underline{q}_{1j_1} | \exp[-(\beta + it) (H_0 + V)]$$

$$\times T_{\underline{\kappa}} \exp[it (H_0 + V)] T_{\underline{\kappa}} | \underline{q}_{1j_1} \dots \underline{q}_{Nj_N} \rangle.$$
(14)

We want to calculate the matrix elements on the right hand side of (14) by means of perturbation theory. For that purpose we need suitable expansions for the various operators occuring in these matrix elements. The following expansions are substituted:

$$U_{t} = \exp[it H_{0}] + \Sigma_{n=1}^{\infty} i^{n} J_{0}^{t} dt_{n} J_{0}^{tn} dt_{n-1} \dots J_{0}^{t_{2}} dt_{1} \exp[it_{1} H_{0}] V \dots$$

$$\dots V \exp[i(t_{n} - t_{n-1}) H_{0}] V \exp[i(t - t_{n}) H_{0}], \qquad (15)$$

$$\mathbf{T}_{\underline{\kappa}} = \Sigma_{\underline{s}_{n}} \exp[i\underline{\kappa} \cdot \underline{\mathbf{r}}_{\underline{s}_{n}}] = \Sigma_{\underline{s}_{n}} \exp[i\underline{\kappa} \cdot (\underline{s} + \underline{\mathbf{R}}_{\mathbf{0}n} + \underline{\mathbf{u}}_{\underline{s}_{n}}7)]$$

$$= \Sigma_{\mathrm{sn}} \exp[i\underline{\kappa} \cdot (\underline{\mathbf{s}} + \underline{\mathbf{R}}_{0n})] [1 + i\underline{\kappa} \cdot \underline{\mathbf{u}}_{\mathrm{sn}} + \ldots + (i^{\mathrm{m}}/\mathrm{m}!) (\underline{\kappa} \cdot \underline{\mathbf{u}}_{\mathrm{sn}})^{\mathrm{m}} + \ldots], \quad (16)$$

with

$$\underline{\kappa} \cdot \underline{u}_{sn} = (v_0 / 16\pi \ \mathbf{M}_n)^{\frac{1}{2}} \Sigma_j \int_{\underline{q}} \omega_{\underline{q}j}^{\frac{1}{2}} [A_{\underline{q}j} + A^*_{\underline{q}j}] \underline{\kappa} \cdot (\underline{e}_{\underline{q}j}^{(n)} - if_{\underline{q}j}^{(n)}) e^{i\underline{q} \cdot \underline{s}} .$$
(17)

and similar formulae for U<sub>-t</sub>, U<sub>0</sub> and T<sub>-K</sub>. We have used the abbreviations  $U_{\pm t} = \exp[\pm it (H_0 + V)]$  and  $U_{\Theta} = U_{i\beta} = \exp[-\beta(H_0 + V)]$ . Substituting the above expansions in the trace on the right hand side of (12), we see that the operator in the matrix element (14) is a linear combination of products of operators V,  $T_{\pm K}$ ,  $\exp[\pm i (t_1 - t_{i-1}) H_0]$  and  $\exp[-(\beta_i - \beta_{i-1}) H_0]$ , while each V,  $T_{\underline{K}}$  and  $T_{-\underline{K}}$  is itself a linear combination of products of creation and annihilation operators,

#### 3. The diagrams

We will represent the matrix elements, occuring in (14), by diagrams and use the following conventions: each operator V, or better a term in some  $V^{(\nu)}$  in the matrix element corresponds to a vertex in the diagram (V-vertex). tex). The vertices occur in the same order from right to the left as the V's in the corresponding matrix element. This order is important; it is given by the ordered integrations in the expansions (15), etc. A phonon will be represented by a line. Each line entering a vertex (coming from the right) represents a phonon which will be annihilated at that vertex, each line leaving a vertex (going to the left) represents a phonon which has been created at that vertex. The total number of lines entering or leaving a V-vertex is equal to the order  $\nu$  of the  $V^{(\nu)}$  which corresponds to that vertex. Other types of vertices, the neutron vertices, are associated with the operators  $T_{\rm K}$  and  $T_{-\rm K}$ . These vertices will be represents the term in  $T_{\pm\rm K}$  proportional to  $(\underline{\kappa} \cdot \underline{u}_{\pm\rm n})^{\rm m}$ , just m phonon lines join. The operators exp[ $\pm i$  (t<sub>i</sub>-t<sub>i-1</sub>)H<sub>0</sub>]





Sample diagram contributing to the matrix element (18).

and  $\exp[-(\beta_i - \beta_{i-1})H_0]$  act on the intermediate states between the vertices. In Fig. 1 we have drawn an example of a diagram corresponding to a particular choice of terms out of the operators V and  $T_{\pm K}$  in the matrix element:

$$\langle \mathbf{q}_{3}\mathbf{j}_{3}, \mathbf{q}_{2}\mathbf{j}_{2}, \mathbf{q}_{1}\mathbf{j}_{1} | \left\{ -\int_{0}^{\beta} d\beta_{1} \exp[-(\beta - \beta_{1}) \mathbf{H}_{0}] \mathbf{V} \exp[-\beta_{1} \mathbf{H}_{0}] \right\} \exp[-it \mathbf{H}_{0}] \mathbf{T}_{-\underline{\kappa}} \\ \times \left\{ \int_{0}^{t} dt_{2} \int_{0}^{t_{2}} dt_{1} \exp[it_{1} \mathbf{H}_{0}] \mathbf{V} \exp[i(t_{2} - t_{1}) \mathbf{H}_{0}] \mathbf{V} \exp[i(t - t_{2}) \mathbf{H}_{0}] \right\}$$
(18)  
$$\times \mathbf{T}_{\kappa} | \mathbf{q}_{1} \mathbf{j}_{1}, \mathbf{q}_{2} \mathbf{j}_{2}, \mathbf{q}_{3} \mathbf{j}_{3} \rangle.$$

By joining the external lines at the left and right of a diagram continuously, as is always possible since the set of initial phonons is identical to the set of final phonons, we can consider each diagram as being rolled onto a cylinder. We define connectedness of a diagram or part of a diagram as connectedness on the cylinder and call a connected part a component. For instance the diagram of Fig. 1 consists of two components. According to a well-known theorem the contribution of a diagram to a matrix element can be simply determined from the contributions of its components. This theorem was formulated for the present case in reference [5], where it was used to prove that the contribution of all components without neutron vertices only cancel the factor  $Z_{\beta}$  in (12). This gives for the scattering function:

$$S_{T}(\underline{\kappa}\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp\left[-it\omega\right] \Sigma_{\delta}^{neutron} T_{T} \left\{ \exp\left[-\left(\beta + it\right)\left(H_{0} + V\right)\right] T_{-\underline{\kappa}} \right\} \times \exp\left[it\left(H_{0} + V\right)\right] T_{\kappa} \right\}_{\delta}, \qquad (19)$$

where the symbol  $\Sigma_{\delta}^{neutron}$  indicates that in calculating the trace only diagrams  $\delta$ , which consist of components containing neutron vertices, must be taken into account.

#### 4. Elastic and inelastic spectrum, one-phonon diagrams

There are still two types of diagrams that contribute to the trace in (19). First, the diagrams that consist of two components, each containing one neutron vertex. These diagrams produce the elastic scattering spectrum. The partial scattering function  $S_T^{(0)}(\underline{\kappa}\omega)$  for elastic scattering, calculated from these diagrams, can be shown to be:

$$S_{T}^{(0)}(\underline{\kappa}\omega) = (8\pi^{3}N_{0}/v_{0}) |\Sigma_{n} \exp(i\underline{\kappa} \cdot \underline{R}_{0n})|$$

 $\times \Sigma_{\nu} Z(\beta)^{-1} \exp(-\beta E_{\nu}) < \psi_{\nu} | \exp(i\underline{\kappa} \cdot \underline{u}_{0_{n}}) | \psi_{\nu} > |^{2} \Delta(\underline{\kappa}) \delta(\omega) .$
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The sum over  $\nu$  of the term in absolute value signs is the Debye-Waller factor at temperature T for the anharmonic crystal. We can at once see from this formula that the Bragg conditions are exactly valid for an anharmonic crystal. Phonon-phonon interactions only affect the elastic scattering intensity.

The second group of diagrams consists of one-component diagrams, each of which contains both of the neutron vertices. These diagrams describe the inelastic spectrum. Here we are not interested in the complete inelastic spectrum, but in studying the scattering peaks. If these scattering peaks are well-defined with respect to the background, i.e. if the width of each peak is small compared to the value of its central frequency, a part of the scattering function can be isolated which will describe the desired peaks.



Fig. 2 General form of the one-phonon diagrams.

This isolated contribution, which will be called  $S_T^{(1)}(\underline{\kappa}\omega)$ , can be obtained by further restricting the summation in (19) to so-called one-phonon diagrams. These one-phonon diagrams have the general form shown in Fig. 2. Each one-phonon diagram consists of a so-called chain of V-bubbles (the shaded areas) connected by single phonon lines (q-lines), a chain beginning and ending at a neutron bubble (the shaded areas containing a neutron vertex). A neutron bubble is not meant to belong to the chain. A bubble is defined as a proper part of the diagram which does not contain any q-line and which is only connected to the rest of the diagram by means of q-lines. In Fig. 1 phonon 3 belongs to the neutron bubble containing  $T_{-\kappa}$ , phonon 1 belongs to the V-bubble between  $t_1$  and  $t_2$ . A chain is broken by cutting one of the qlines; the definition of bubble is chosen in such a way that it is not possible to break the chain by cutting only one line in a bubble. The V-bubbles have a great resemblance to the proper self-energy diagrams in field theory. Indeed, as will be seen later, the V-bubbles describe selt-energy effects which renormalize the energies of the phonons. However, due to the dissipative character of the interaction, they also involve line broadening effects corresponding to finite phonon lifetimes. The desired information about the location and width of the peaks is fully contained in the chains of the one-phonon diagrams and the neutron bubbles only contribute to the scattering intensity. A more detailed discussion of the structure of the one-phonon diagrams can be found in reference [5].

We remark that the term "one-phonon-diagram" is somewhat misleading in the sense that such a diagram generally does not describe a pure onephonon process, in which the neutron excites or absorbs a single phonon in passing through the crystal. The notion of n-phonon process has not such a definite meaning for scattering by an anharmonic crystal as by an harmonic crystal. We speak of one-phonon diagrams because they are the direct generalizations of those diagrams which in the harmonic approximation exactly produces the delta-function peaks in the scattering spectrum. In the latter case  $S_T^{(1)}(\underline{\kappa}\omega)$  describes only the one-phonon processes (see Appendix). In the presence of anharmonic forces  $S_T^{(1)'}(\underline{\kappa}\omega)$  is still expected to describe the peaks correctly, as long as they are distinguishable from the background, however,  $S_T^{(1)}(\underline{\kappa}\omega)$  now describes parts of the smooth background as well.

In order to obtain an expression for the partial scattering function  $S_T^{(1)}$ ( $\underline{\kappa}\omega$ ), which explicitly exhibits the effects we are interested in, we must perform a summation of the one-phonon diagrams in terms of the bubble functions representing the contributions of the bubbles. Although very complicated, this summation can be carried out exactly by extending the methods of DYSON [9] and BELIAEV [10] to the case of arbitrary temperatures. The summation procedure is demonstrated in [ $\overline{5}$ ] for a group of soecial diagrams. We shall not write down the general results here but only consider two special cases where the formulae take simple forms.

(a) Let us first consider the lowest order case. We then find the following set of equations:

$$\mathbf{S}_{\mathbf{T},\mathbf{e}}^{(1)}(\underline{\kappa}\omega) = (\Omega' 8\pi^3) \Sigma_{\mathbf{j}\mathbf{j}} \mathbf{A}(\underline{\kappa}\mathbf{j}) \left[ \mathbf{C}_{(0)}^+ (\omega \underline{\kappa}\mathbf{j}\mathbf{j}') + \overline{\mathbf{C}}_{(0)}(\omega \underline{\kappa}\mathbf{j}\mathbf{j}') \right] \mathbf{B}(\kappa\mathbf{j}')$$
(20)

$$A(\underline{\kappa}_{j}) = Tr \left[ \exp(-\beta H_{0}) T_{\underline{\kappa}_{j}} \right]_{C}$$
(21)

$$B(\underline{\kappa}j') = Tr \left[ \exp(-\beta H_0) T_{\underline{\kappa}j} \right]_C$$
(22)

$$\pm 2\pi i \sum_{j} \left[ \left( \omega_{\underline{k}j} - \omega \right) \delta_{jj'} + G^{\pm}_{(0)} \left( \kappa \omega_{jj'} \right) \right] C^{\pm}_{(0)} \left( \kappa \omega_{j'j''} \right) = \left\{ 1 - \exp\left( -\beta \omega_{\underline{k}j} \right) \right\}^{-1} \delta_{jj''}$$
(23)

The subscripts j and j' in (21 and (22) indicate that the operators  $T_{\underline{K}}$  and  $T_{\underline{K}}$  must create a phonon  $\underline{K}j$  and annihilate a phonon  $\underline{K}j'$  respectively. The subscript C means that only connected diagrams must be considered in calculating the traces. The function  $G^*_{(0)}$  ( $\underline{K}\omega jj$ ) represents the lowest order contribution (i.e. of order  $(u/d)^2$ ) of a V-bubble. To general order this function has the form

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$$G^{\pm}(\underline{\kappa}\omega_{jj}') = i \int_{0}^{\pm} d^{\tau} \exp\left[-i\omega\tau\right] \operatorname{Tr}\left\{U_{\Theta}U_{-\tau}V_{\underline{\kappa}j}U_{\tau}V_{\underline{\kappa}j}'\right\}_{C,nq}$$
(24)  
$$i \int_{0}^{\tau} d^{\tau} \exp\left[i\omega\tau\right] \operatorname{Tr}\left\{U_{\Theta}U_{-\tau}V_{\underline{\kappa}j}U_{\tau}V_{\underline{\kappa}j}\right\}_{C,nq} + \operatorname{Tr}\left\{U_{\Theta}V_{\underline{\kappa}jj}\right\}_{C,nq}$$

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where  $V_{\kappa j}$  contains a creation operator for the phonon  $\underline{\kappa} j$ ,  $V_{\underline{\kappa} j'}$  contains an annihilation operator for the phonon  $\underline{\kappa} j$ , and  $V_{\underline{\kappa} j j'}$  contains both. The subscript C, nq indicates that only connected diagrams involving no q-lines contribute to the traces in (24). Because of the irreducible character of the diagrams contributing to  $G^{\pm}(\underline{\kappa} \omega j j')$ , and expansion of this quantity in powers of u/d converges rapidly for all values of  $\omega$ , while for any particular order only a finite number of essentially different diagrams have to be calculated. To lowest order in the interaction we have for a Bravais lattice

$$G_{(0)}^{\pm}(\underline{\kappa}\omega_{jj}') = i \int_{0}^{\pm\infty} d\tau \exp\left[-i\omega\tau\right] \operatorname{Tr} \left\{ U_{\Theta}^{(0)} U_{-\tau}^{(0)} V_{\underline{\kappa}j}^{(3)} U_{\tau}^{(0)} V_{\underline{\kappa}j}^{(3)} \right\}_{C, nq}$$
(25)  
+ $i \int_{0}^{\pm\infty} d\tau \exp\left[i\omega\tau\right] \operatorname{Tr} \left\{ U_{\Theta}^{(0)} U_{-\tau}^{(0)} V_{\underline{\kappa}j}^{(3)} U_{\tau}^{(0)} V_{\underline{\kappa}j}^{(3)} \right\}_{C, nq} + \operatorname{Tr} \left\{ U_{\Theta}^{(0)} V_{\underline{\kappa}j}^{(4)} \right\}_{C'}$ 

in which  $U_{\tau}^{(0)} = \exp[i\tau H_0]$ , etc.



Fig. 3

Lowest order diagrams contributing to the traces in (24) Strictly speaking, the lines representing the phonons gi and gi do not belong to the diagrams (q is equal to <u>k</u>), they have been drawn to indicate that the appropriate vertices contain creation and/or annihilation operators for these phonons.

The basic diagrams which contribute to the three traces in (25) are represented in Fig. 3a, b and c. In addition to these diagrams, however, there are classes of related diagrams contributing to (25) which can be constructed from the three basic diagrams by breaking an internal phonon line and letting it run around the cylinder an arbitrary number of times ( see Appendix A). By denoting the hermitian and anti-hermitian parts of  $G^{\pm}(0)$  $(\underline{\kappa}\omega_{jj}')$  by  $\Delta_{(0)}$  ( $\underline{\kappa}\omega_{jj}'$ ) and  $\Gamma_{(0)}$  ( $\underline{\kappa}\omega_{jj}'$ ) respectively ( $G^{\dagger}(0) = \Delta_{(0)\pm i}\Gamma_{(0)}$ ), we finally find from this set of diagrams:

$$\Delta_{(0)}(\underline{\kappa}\omega \, jj') = 18 \int_{\underline{q}_1, \underline{q}_2} \sum_{j_1, j_2} \mathbf{B}_{\underline{\kappa}j}^{(3)}, -\underline{q}_1 j_1, -\underline{q}_2 j_2 \quad \mathbf{B}_{\underline{\kappa}j}^{(3)}, \underline{q}_1 j_1, \underline{q}_2 j_2 \quad \Delta(\underline{q}_1 + \underline{q}_2 - \underline{\kappa})$$

$$\{(1 + f_{q_1j_1} + f_{q_2j_2}) [ (\omega - \omega_{q_1j_1} - \omega_{q_2j_2})^{-1} - (\omega + \omega_{q_1j_1} + \omega_{q_2j_2})^{-1} ]$$

+2 
$$(f_{q_1j_1} - f_{q_2j_2})(\omega + \omega_{q_1j_1} - \omega_{q_2j_2})^{-1}$$
P

+12  $\int_{\underline{q}_{1}} \Sigma_{j_{1}} B_{\underline{\kappa}j, -\underline{\kappa}j, \underline{q}_{1}j_{1}, -\underline{q}_{1}j_{1}}^{(4)} \{1 + \exp[-\beta \omega_{\underline{q}_{1}j_{1}}]\} \{1 - \exp[-\beta \omega_{\underline{q}_{1}j_{1}}]\}^{-1}$  (26)

$$\Gamma_{(0)}(\underline{\kappa}\omega \, jj') = 18\pi \int_{\underline{q}_1, \underline{q}_2} \Sigma_{j_1, j_2} \, \underline{B}^{(3)}_{\underline{\kappa}^{j_1}, -\underline{q}_2 j_2} \, \underline{B}^{(3)}_{\underline{\kappa}^{j_1}, \underline{q}_1 j_1, \underline{q}_2 j_2} \Delta(\underline{q}_1 + \underline{q}_2 - \underline{\kappa})$$

$$\times \left\{ (1 + f_{q_1 j_1} + f_{q_2 j_2}) \left[ \delta (\omega - \omega_{q_2 j_2} - \omega_{q_2 j_2}) - \delta (\omega + \omega_{q_1 j_1} + \omega_{q_2 j_2}) \right] \right\}$$

+2 
$$(f_{q_1j_1} - f_{q_2j_2}) \delta (\omega + \omega_{q_1j_1} - \omega_{q_2j_2})$$

with

 $\mathbf{f}_{\underline{q}j} = \left\{ \exp[\beta \omega_{qj}] - 1 \right\}^{-1}$ 

In (26) the subscript P means the Cauchy principal value. The interpretation of the quantities  $\Delta_0 (\kappa \omega j j')$  and  $\Gamma_0 (\kappa \omega j j')$  can be easily read off from Eq. (23). If the anti-hermitian part were zero,  $G^{\pm}_{(0)}(\kappa \omega j j')$  would have real eigenvalues and the functions  $C^{\pm}_{(0)}(\kappa \omega j j')$  would have simple poles at various values of  $\omega$ , giving rise to delta-function peaks in the scattering spectrum at positions  $\omega = \omega_{\kappa j} + \Delta_{(0)} (\kappa \omega j)$ . Because of the anti-hermitian parts, however,  $C^{\pm}_{(0)}(\kappa \omega_{jj'})$  cannot have poles for real  $\omega$  and the delta-function singularities are broadened into finite peaks with widths at half-maximum  $2\Gamma_{(0)}$ . In this case the shifts of the peaks are determined by the hermitian parts, the widths by the anti-hermitian parts of  $G^{\pm}_{(0)}(\kappa \omega_{jj'})$ . In lowest order the two effects are independent of each other. Eq. (20) describe those peaks whose central frequencies occur at positive values of  $\omega$  and which therefore can be considered to correspond to emission of phonons by the neutrons. (Hence the subscript e on  $S_{T,e}(\kappa \omega)$ . Analogous equations hold for the absorption peaks.

The lowest order formulae (26) and (27) for the shift and width of the peaks have recently also been found by KRIVOGLAZ and KASHCHEEV [11] and by MARADUDIN and FEIN [12], using quite different methods. The last mentioned authors have evaluated these formulae for a simple model of a lattice: a face-centered-cubic lattice with central force interactions acting between pairs of nearest neighbours only. This model was used to approximate lead. They obtain the following results for longitudinal phonons propagating in the [100] direction of q-space ( $T = 425^{\circ}K$ ):

 $\Gamma/\omega_{L} = 0.005$  ,  $q = \frac{1}{4} q_{L}$ 

(27)

 $\Gamma/\omega_{\rm L} = 0.007$  ,  $q = \frac{1}{2} q_{\rm L}$ 

 $\Gamma / \omega_{\rm L} = 0.013$  ,  $q = \frac{3}{4} q_{\rm L}$ 

Here  $q_L$  and  $\omega_L$  are the maximum values of the phonon wave vector and frequency respectively. There is order of magnitude agreement between these values and the experimental results of BROCKHOUSE [3], however, adirect comparison is not possible because the present model is too naive to represent lead.

We finally remark, that the lowest order expressions for the shift and width can also be obtained using more intuitive arguments based on the exponential decay of one-particle states [13]. Only to lowest order in the coupling can such simple techniques be expected to be reliable.

There is in addition to the diagrams a, b and c of Fig. 3, a diagram of order  $(u/d)^2$  which contributes to the shift of the peaks (Fig. 3d). However, this diagram involves an intermediate optical phonon with wave vector zero or  $2\pi\tau$ . We omit this contribution because it vanishes for lattices with certain symmetries, for instance for Bravais lattices.

(b) To general order in the interaction Eqs (20-23) must be replaced by more complicated ones [5]. As long as, independent of the strength of the interaction, the widths of the peaks remain small in such a way that the peaks are well-defined and distinguishable from the background, the functions  $G^{\pm}(\underline{\kappa}\omega jj)$  (see (24)) describe the widths and locations of the peaks correctly. However, in higher order in the coupling the shifts and widths are no longer simply the hermitian and anti-hermitian parts of these quantities (compare Eqs (29) and (30)). Moreover the two effects of shifting and broadening become interdependent in this general case.

If we consider a Bravais lattice and drop the polarization indices, the following simple expression for the partial scattering function  $ST^{(1)}(\kappa\omega)$  can be obtained, valid to first order in the parameter  $\Gamma(\omega_q)/\omega_q$ , but to general order in the interaction (we put  $G^{\pm}(\omega) = G$ , etc.)

$$S_{T}^{(1)}(\underline{\kappa}\omega) = \frac{\Omega Q}{(\omega - \omega_{\underline{K}} - \Delta)^{2} + \Gamma^{2}} + \frac{\Omega Q'}{(\omega + \omega_{\underline{K}} + \Delta)^{2} + \Gamma^{2}}, \quad (28)$$

with the abbreviations:

$$\Delta = \operatorname{Re}\left[\omega_{\kappa}\left\{1 + \left(2G^{+}/\omega_{\kappa}\right)\right\}^{\frac{1}{2}} - \omega_{\kappa}\right], \qquad (29)$$

$$\Gamma = \operatorname{Im}[\omega_{\underline{\kappa}}\{1 + (2G^{+}/\omega_{\underline{\kappa}})\}^{\frac{1}{2}} - \omega_{\underline{\kappa}}].$$
(30)

**Q** and  $\mathbf{Q}^{\mathsf{v}}$  are intensity factors of a very complicated form dependent upon  $\mathbf{x}$  and  $\boldsymbol{\omega}$ . Therefore we shall not write down their explicit expressions here. Like  $\Gamma$  and  $\Delta$ , they depend on temperature, but they are independent of the crystal colume  $\Omega$  in the limit of a large crystal. We remark here that for

typographical reasons the temperature dependence of the various quantities  $C^{\pm}$ ,  $G^{\pm}$ , etc. has not been explicitly indicated.

#### III. CONDUCTING CRYSTALS

We will briefly consider in this section the case of a conducting crystal, where, in addition to phonon-phonon interactions, the interaction between phonons and conduction electrons contributes to the displacement and broadening of the scattering peaks.

We accept the following effective Hamiltonian for the electron-phonon system:

$$H = \epsilon_0 + \epsilon_{zp} + H_{op} + H_{oe} + V + W$$
(31)

in which  $\epsilon_0$ ,  $\epsilon_{zp}$ ,  $H_{op}$  and V are given by (4), (5) and (6), while  $H_{oe}$  and W have the following form:

$$H_{oe} = \sum_{\sigma m} \int_{\overline{k}} \epsilon_{\underline{k}m\sigma} \Gamma_{\underline{k}m\sigma}^{*} \Gamma_{\underline{k}m\sigma}, W = \sum_{\nu=1}^{\infty} W^{(\nu)}, \qquad (32)$$

$$W^{(\nu)} = \sum_{\alpha mm' j_1, j_{\nu}} \int_{\underline{k}\underline{k}} \underline{q}_1, \dots, \underline{q}_{\nu} \qquad b^{(\nu)}_{\underline{k}\underline{m}, \underline{k}} \underline{m}, \underline{q}_1 \underline{j}_1, \dots, \underline{q}_{\nu} \underline{j}_{\nu} \quad \Delta \ (\underline{q}_1 + \dots, \underline{q}_{\nu} + \underline{k} - \underline{k}).$$

$$\Gamma_{\underline{k}m\sigma}^{*} \Gamma_{\underline{k}'m'\sigma} \left[ A_{\underline{q}_{\underline{j}}j_{1}}^{} + A_{\underline{q}_{1}}^{*}j_{1}^{} \right] \dots \left[ A_{\underline{q}_{\nu}j_{\nu}}^{} + A_{\underline{q}_{\nu}j_{\nu}}^{*} \right] .$$
(33)

Here  $\epsilon_{\underline{k}\underline{m}\sigma}$  is the energy of a single Bloch electron, characterized by a wave vector  $\underline{k}$ , a spin index  $\sigma$  and an index m distinguishing the Bloch bands.  $\Gamma_{\underline{k}\underline{m}\sigma}^{\underline{k}}$  and  $\Gamma_{\underline{k}\underline{m}\sigma}$  are the creation and annihilation operators for this electron. In the above Hamiltonian  $H_{op}$  and  $H_{oe}$  describe the free phonons and free Bloch electrons and V and W are the phonon-phonon and screened electron-phonon interaction respectively. The relative strength of the various terms in both V and W will be governed by the same parameter u/d. We will not enter into a discussion of the derivation of this Hamiltonian here nor the difficult question of validity (see [6]). We only mention that the foundations upon which the Hamiltonian (31) rests are open to objection and that for this reason it is difficult to decide, for instance, whether or not it makes sense to include terms in the interactions up to general order in the ionic displacements. At any rate we may consider the Hamiltonian as a model Hamiltonian which will describe the system correctly at least in lowest order in the interactions and for wave vectors which are not too small.

The coefficients  $b^{(\nu)}$  with  $\nu > i$  are completely unknown; an expression for the first coefficient  $b^{(1)}_{km,k'm',q'}$  taking into account the screening ef-

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fects, has been derived by BARDEEN [14]. In the limit of small  $\underline{q}$  and considering only electrons within one Bloch band, he finds for a Bravais lattice

$$\mathbf{b}_{\underline{\mathbf{k}},\underline{\mathbf{k}}',\underline{\mathbf{g}}\mathbf{i}}^{(1)} = \mathbf{i}\mathbf{E}_{\mathrm{F}}(\hbar/36\pi^{3}\,\mathrm{M}\rho\omega_{\underline{\mathbf{g}}\mathbf{i}})^{\frac{1}{2}}[\underline{\mathbf{e}}_{\underline{\mathbf{g}}\mathbf{i}}\cdot(\underline{\mathbf{k}}-\underline{\mathbf{k}}')]$$
(34)

where M and  $\rho$  are the mass and number density of the ions,  $E_F$  is the Fermi energy and  $\underline{e}_{dj}$  is a unit polarization vector for the phonon qj.

The formalism developed in Section II for a non-conducting crystal can be extended in a straightforward way to the case of a metal. Using diagram techniques, formulae analogous to those of II.4 are obtained. The bubble function  $G_{\pm}(\underline{\kappa}\omega jj')$ , which describe the positions and widths of the peaks, now has the form:

$$G^{\pm}(\underline{\kappa}\omega jj') = i \int_{0}^{\pm\infty} d\tau \exp[-i\omega\tau] \operatorname{Tr} [U_{\Theta}U_{\tau}(V+W)_{\underline{\kappa}j} U_{\tau}(V+W)_{\underline{\kappa}j}] c, nq$$

$$+ i \int_{0}^{\mp\infty} d\tau \exp[i\omega\tau] \operatorname{Tr} [U_{\Theta}U_{\tau}(V+W)_{\underline{\kappa}j} U_{\tau}(V+W)_{\underline{\kappa}j}] c, nq$$

$$+ \operatorname{Tr} [U_{\Theta}(V+W)_{\underline{\kappa}jj'}]_{C}$$
(35)

with

$$U_{\Theta} = U_{i\beta} = \exp\left[-\beta(H_{op} + H_{oe} + V + W) + \alpha N\right]$$
(36)

$$U_{+\tau} = \exp\left[\pm i\tau \left(H_{op} + H_{oe} + V + W\right)\right]$$
(37)

The electrons are described by means of a grand canonical ensemble; N is the number operator for the electrons and  $\alpha = \mu\beta$ ,  $\mu$  being the chemical potential. The various subscripts in (35) have the same meaning as in (24).

It follows from (35) that in general the contributions to the shift and width of the peaks arising from phonon-phonon interactions and from electron-phonon interactions are not additive. In the calculation of  $G^{\pm}(\underline{\kappa} \omega jj')$  diagrams occur which involve both V-and W- vertices. These contributions are only exactly additive in the case of a Bravais lattice in lowest order in both interactions, i.e. to order  $(u/d)^2$ . In the latter case the contributions to the shift and width of the phonon-phonon interactions are given by (26) and (27). The analogous contributions arising from the electron-phonon interactions can be found to be:

$$\Delta_{(0)}(\underline{\boldsymbol{\kappa}}\boldsymbol{\omega}\boldsymbol{j}\boldsymbol{j}') = \sum_{\sigma} \int_{\underline{\boldsymbol{k}}\boldsymbol{1}, \underline{\boldsymbol{k}}\boldsymbol{2}} b^{(1)}_{\underline{\boldsymbol{k}}\boldsymbol{1}, \underline{\boldsymbol{k}}\boldsymbol{2}, -\underline{\boldsymbol{q}}\boldsymbol{j}} b^{(1)}_{\underline{\boldsymbol{k}}\boldsymbol{2}, \underline{\boldsymbol{k}}\boldsymbol{1}, -\underline{\boldsymbol{q}}\boldsymbol{j}} \Delta(\underline{\boldsymbol{k}} + \underline{\boldsymbol{q}} - \underline{\boldsymbol{k}}) \frac{n_{\underline{\boldsymbol{k}}\boldsymbol{1}\sigma} - n_{\underline{\boldsymbol{k}}\boldsymbol{2}\sigma}}{(\omega + \epsilon_{\underline{\boldsymbol{k}}\boldsymbol{1}\sigma} - \epsilon_{\underline{\boldsymbol{k}}\boldsymbol{2}\sigma})_{P}} + 2 \sum_{\sigma} \int_{\underline{\boldsymbol{k}}\boldsymbol{1}} b^{(2)}_{\underline{\boldsymbol{k}}\boldsymbol{1}, \underline{\boldsymbol{k}}\boldsymbol{1}, -\underline{\boldsymbol{q}}\boldsymbol{j}} n_{\underline{\boldsymbol{k}}\boldsymbol{1}\sigma}$$
(38)

$$\Gamma_{(0)}(\underline{\kappa}\omega jj') = \pi \sum_{\sigma} \int_{\underline{k}_1, \underline{k}_2} b_{\underline{k}_1, \underline{k}_2, -\underline{q}j} b_{\underline{k}_2, \underline{k}_1, \underline{q}j}^{(1)} \Delta (\underline{k}_1 + \underline{q} - \underline{k}_2).$$

$$(n_{k1\sigma} n_{k2\sigma}) \delta (\omega + \epsilon_{k1\sigma} - \epsilon_{k2\sigma})$$

with

$$n_{k\sigma} = \{ \exp[\beta \epsilon_{k\sigma} - \alpha] + 1 \}^{-1}$$

For long wave length acoustical phonons the Bardeen formula in the form (34) is applicable. Neglecting Umklapp-processes and assuming that the phonons are purely longitudinal or transverse, we find for the width of the peak corresponding to a longitudinal phonon:

$$\Gamma_{(0)}(\omega \underline{\kappa}) / \omega_{\underline{\kappa}} = E_F^2 m^{\ast 2} / 9 \pi M \rho s_{\ell} n^3 \qquad \kappa < 2 k_F \qquad (40)$$
$$= 0 \qquad \kappa < 2 k_F$$

Use has been made of the formulae  $\epsilon_{\underline{k}} = \hbar^2 k^2 / 2m^*$  and  $\omega_q = s_{\ell}q$ , where  $m^*$  is the effective mass of the electron and  $s_{\ell}$  the longitudinal velocity of sound;  $k_{\overline{F}}$  is the radius of the (spherical) Fermi surface. Formula (40) gives values for  $\Pi_{(0)}/\omega_{\underline{K}}$  which are of the order  $10^{-3}-10^{-2}$  (in agreement with KRIVOGLAZ [15]) and hence are quite small, presumably much smaller than the values arising from anharmonicities.

If we admit Umklapp-processes,  $\Gamma(0)$  ( $\underline{k}\omega$ ) will display step-discontinuities, not only for  $\kappa = 2k_F$ , but also for those values of  $\kappa$  which satisfy the condition  $|\underline{\kappa} + 2\pi\underline{\tau}| = 2k_F$  for any reciprocal lattice vector  $\underline{\tau}$ . For further details about this question we refer to the recent work of WOLL and KOHN [16].

Concerning the shift of the peaks, we should mention that only the temperature dependent part is observable. It is to be expected that, owing to the nature of the Fermi distribution of the electrons, this temperature dependence of the shift as a result of electron-phonon interactions will be very small and hardly observable.

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#### APPENDIX

In this Appendix we shall illustrate the use of the diagrams introduced in this paper by applying them to the familiar case of an harmonic crystal. At the end of the Appendix we shall devote some words to the work of BAYM [7].

(39)

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For an harmonic crystal (without electron-phonon coupling) the diagrams that contribute to the trace in (19) simply consist of the two neutron vertices and free phonon lines. There are two types of lines, (a) lines which begin and end at the same neutron vertex (loops), and (b) lines which connect the two neutron vertices on the cylinder (b-lines). In both cases the lines may encircle the cylinder an arbitrary number of times; a line which encircles the cylinder n times is said to have n turns. For instance diagram a of Fig. 4 has two b-lines having one and two turns; the loop has one turn. The lines of the diagram shown in Fig. 4b have no turns.



Diagrams contributing to the trace in (19) in the harmonic approximation.

It is convenient to go over to a reduced set of diagrams containing lines without turns. Let us restrict ourselves for a moment to diagrams without loops. Consider the group of all different diagrams with n blines. This group contains just one diagram with no turns. It is now a simple matter to prove that the total contribution of this group of diagrams to ST ( $g\omega$ ) can be obtained by just calculating the diagram without turns but replacing for each b-line in this diagram the factor exp[ $i\omega_{gi}t$ ] by  $D_{\underline{q}j}^{(0)}(t)$ , the unpertubed phonon propagator, which is given by:

$$D_{q,j}^{(0)}(t) = Tr \left\{ exp[ -(\beta + it)H_0] (A_{q,j} + A_{-q,j}^*) exp[itH_0] (A_{-q,j} + A_{q,j}^*) \right\}_C$$
(41)

$$=\frac{\exp[it\omega_{qj}] + \exp[-(\beta + it)\omega_{qj}]}{i - \exp[-\beta\omega_{qj}]}$$
(42)

Further calculation of the diagram with n b-lines with the help of (41) and (42) now leads directly to the n'th term in the well-known phonon expansion, that is the term which corresponds to processes in which only n phonons: are involved per single scattering event.

We now show that the loops on the neutron vertices yield the familiar Debye-Waller factor for an harmonic lattice. For convenience we restrict ourselves to a Bravais lattice. Consider a diagram without loops. Let the contribution of this diagram to  $S_T$  ( $\kappa\omega$ ) be F ( $\kappa\omega$ ). Consider further the group of all different diagrams which aonly differ from the original one in the presence of loops on the  $T_K$  - vertex; the diagram belonging to this group only differ from each other in the number of turns of the loops. The total contribution F' ( $\kappa\omega$ ) of the original diagrams and the associated group of diagrams is (see (16)):

$$F'(\underline{\kappa}\,\omega) = F(\underline{\kappa}\,\omega) \left(i^{2\ell}/2^{\ell}\,\ell!\right) \left[Tr\left\{\exp\left[-\beta H_0\right](\underline{\kappa}\cdot\underline{u}_0)^2\right\}_C\right]^{\ell}$$
(43)

For each loop the exponentials  $\exp [iq \cdot s]$  occuring in (17) cancel out, so that the trace in (43) is independent of <u>s</u> and hence can be taken outside the summation over <u>s</u> ( $F(\underline{\kappa}, \omega)$  contains a summation over <u>s</u>). The factor  $(2^{\ell} \ell!)^{-1}$  is a combinative factor. As before, the subscript C means that in calculating the trace only connected diagrams are involved. Application of the theorem to disconnected diagrams, mentioned in IL 3, gives:

$$F'(\underline{\kappa}\,\omega) = F(\underline{\kappa}\,\omega) (\ell!)^{-1} \left[ -\frac{1}{2} \frac{\operatorname{Tr}\left\{ \exp[-\beta H_0] (\underline{\kappa} \cdot \underline{u}_0)^2 \right\}}{\operatorname{Tr}\left\{ \exp[-\beta H_0] \right\}} \right]^{\ell}$$

$$= F(\underline{\kappa}\,\omega) (\ell!)^{-1} \left\{ -\frac{1}{2} < (\underline{\kappa} \cdot \underline{u}_0)^2 >_{\mathrm{T}} \right\}^{\ell} = F(\underline{\kappa}\,\omega) (-W)^{\ell} / \ell!$$

$$(44)$$

where we have used the familiar notation W for  $\frac{1}{2} < (\underline{\kappa} \cdot \underline{u}_0)^2 > T$ . Summing over  $\ell$  from zero to infinity we get for the total contribution F ( $\underline{\kappa} \omega$ ) of the original diagram plus the group of all different diagrams, which can be constructed from the original one by adding loops to the  $T_{\underline{\kappa}}$  vertex in all possible ways:

$$F''(\underline{\kappa}\,\omega) = F(\underline{\kappa}\,\omega) \exp[-W] \tag{45}$$

A second factor exp[-W] arises from the loops on the  $T_{-\underline{K}}$  vertex. Together this gives the Debye-Waller factor exp[-2W].



Graphic representation of the phonon expansion for scattering by an harmonic crystal.

In Fig. 5 we have graphically represented the phonon expansion for an harmonic lattice. Here each line represents a phonon with propagator function  $D_{10}^{(0)}(t)$ , while a factor  $\exp[-W]$  is associated with each neutron vertex. The first diagram in this expansion, being disconnected, corresponds to elastic scattering. The diagram containing n lines describes the n-phonon processes.

Here briefly we shall consider the work of BAYM[7], who, making use of complicated thermodynamic Green's function methods, has given a formal treatment of neutron scattering by an anharmonic non-conducting crystal. His discussion is based on the approximation that the crystal responds linearly to the forces exerted by the neutron in scattering. This approximation amounts to the assumption that each of the individual phonons created or absorbed by the neutron develop in time in the same way as would a single phonon interacting with the lattice at temperature T. This assumption is easy to translate into the language of the diagrams introduced in this paper. The only diagrams which have to be considered in the calculation of the trace in (19) are composed of neutron vertices and chains (i. e. phonon lines provided with V-bubbles), similar to the way as the harmonic diagrams are composed of neutron vertices and a number of chains which begin and end directly on the neutron vertices. Hence the diagrams shown in Fig. 2 are not included because of the presence of neutron bubbles. From this similarity in structure of both sets of diagrams it follows that the diagrams. The expansion of Baym can be immediately obtained from the diagrams shown in Fig. 5, provided we substitute for each line the perturbed phonon propagator D<sub>clij</sub>(t), given by

$$D_{\underline{q}jj'}(t) = Tr \left\{ exp[ -(\beta + it)(H_0 + V)] (A_{\underline{q}j} + A^*_{\underline{q}j})exp[it(H_0 + V)] (A_{\underline{q}j'} + A^*_{\underline{q}j'}) \right\}_C$$
(46)

and for each neutron vertex a factor exp[-W], with

$$W = \frac{1}{2} \operatorname{Tr} \left\{ \exp[-\beta (H_0 + V)] (\underline{\kappa}_0 \underline{u}_0)^2 \right\} / \operatorname{Tr} \left\{ \exp[-\beta (H_0 + V)] \right\}.$$
(47)

Baym's final result (his formula (45)) then follows after some simple algebra. From (43), (44), (46) and (47) we see that Baym's formula is obtained from the phonon expansion of an harmonic lattice by simple replacing H<sub>0</sub> by H<sub>0</sub>+V (taking into account changes in the polarization indices). Of course, that this must be so can be concluded directly from the underlying assumption mentioned above. An extension of his expression for the scattering function to the case of conducting crystals is obtained by replacing H<sub>0</sub> in the harmonic phonon expansion by H, given by (31).

Finally we should mention that as long as the positions and widths of the peaks are correctly described by the functions  $G \pm (\underline{\kappa} \omega j)$  (see II) Baym's approximation only affects the intensity of the scattering.

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#### DISCUSSION

B.N. BROCKHOUSE: In your expressions for the intensities of the onephonon peaks, you show a quantity Q in the numerator. Is this the same as the expression for the unbroadened phonon and, if so, does it involve  $\omega$ ,  $\omega_{\underline{\kappa}}$ or  $\omega_{\underline{\kappa}} - \Delta$ ?

J.J. KOKKEDEE:  $\Omega Q/\Gamma^2$  is a measure of the height of the emission peak above the background. It should be emphasized, however, that this height is not a well-defined notion, owing to the fact that an exact distinction cannot be made between one-phonon peaks and background. The class of diagrams isolated do describe the peaks but they also describe parts of the background as well. The function Q is a complicated, interaction-dependent quantity which depends on the exact energy  $\omega$ . At lowest order in the interaction, however, it depends on the harmonic (unperturbed) frequencies  $\omega_{\underline{x}}$ at temperature T. At this order, Q is equal to  $\Gamma Q^{harm}$ , where  $Q^{harm}$  is the corresponding intensity factor for the harmonic case.

I. WALLER: I would like to comment on this problem of calculating the width and the shift in the one-phonon lines. As you know, there are two schools of thought regarding the treatment of many-body problems. Some use the method of temperature dependent Green's functions while others work with diagrams. As you mentioned in your paper, Kashcheev and Krivoglaz, using temperature Green's functions, arrived at a similar result for the shift and the width. Where it is a question of going to higher approximations, I think both methods could very well be used, although it does not seem to follow from the paper of Kashcheev and Krivoglaz that their result is valid to the same degree of approximation as that of Dr. Kokkedee. What you really have to calculate to get this shift is the correlation functions of the displacements, taking them at different times. In this approximation, the formula can be written in two parts, one containing the ordinary temperature factor and the other the time correlations between the displacements of two arbitrary nuclei. Of course, you can put it in a somewhat simpler form where you have these correlations in the exponent and then calculate them. It should also be pointed out that there may be other causes for the broadening at high temperatures and that irregularities are introduced in this case, owing to the formation of vacancies. These will certainly be a contributory factor as the melting point is approached.

J.J. KOKKEDEE: As regards your comment on correlation functions, it is true that my trace contains a correlation function, but it is not the correlation function of the displacements. All the diagrams in Fig. 2 of my paper have the same structure, consisting of a chain of self-energy diagrams connected by single lines which are attached to self-energy parts which contain the operator  $T_{\kappa}$ . It is only the chains themselves that are proportional, it is only the chains that contribute to the correlation functions of the displacements. The actual calculation of this correlation function for the anharmonic case, however! requires the solution of the many-body problem and therefore I do not see how it can be done more simply.

I fully agree with Professor Waller that the Green's function method is another effective means of handling a system of interacting excitation, for instance phonons. As to its use by Kashcheev and Krivoglaz in connection with the shift and width of the one-phonon peaks, these authors included only quadratic and cubic anharmonic terms and hence their treatment is a lowestorder treatment. A more general treatment of these effects by means of Green's functions has not yet been made and it is not easy to say which approach is simpler, the diagrammatic method or the Green's function method.

K.E. LARSSON: In the experiment we see a one-phonon line which broadens with temperature. It is always of interest to know what is the real cause of such broadening. Can you, on the basis of your theory and your calculations, estimate how much of the line broadening is due to true lifetime effects and what percentage is attributable to a shift in level distance, i.e. the effect by which the energy distance between "phonon levels" decreases with temperature.

J.J.J. KOKKEDEE: One cannot really speak of two separate and distinguishable effects, as you do. My formalism describes true lifetime effects and includes the second type of effect to which you refer. There may be an influence of the multi-phonon processes, in particular two-phonon processes, on the line shape, but this influence is of quite a different nature. The basic assumption in my calculation is that all the contribution of the shift is a purely lifetime effect of the phonon. Of course, this is true only under certain circumstances, i.e. where the peaks are sufficiently narrow and where the influence of multi-phonon processes on the line shape is small. In other words, it is true only in the case of temperatures which are not too high. For higher temperatures, it would be necessary to construct a more involved theory which would have to include primarily two-phonon processes because, in certain cases, these can provide logarithmic singularities centred on the delta function peaks and actually contribute to the broadening of the peaks. However, we have made no evaluations of this. All I am estimating is the assumption that the broadening of the peak is essentially a lifetime effect of one single phonon.

K.S. SINGWI: I think that what Dr. Larsson means is this: Since you intend to compare the results obtained by theory with those from experiments done at very high temperatures (i.e. near the melting point), you must bear in mind that when you go to such temperatures in an anharmonic oscillator, the phonon levels do not remain separated. The separation diminishes and they come very close together. It is therefore difficult to know whether one is dealing with a pure lifetime effect or with the fact that the density of the levels has increased at high temperature. What you have observed might conceivably be a transition not between two levels which have broadened but between many levels.

# PERTURBATION THEORY OF ANHARMONICITY EFFECTS IN SLOW NEUTRON INELASTIC SCATTERING BY CRYSTALS

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#### Abstract — Résumé — Авнотация — Resumen

PERTURBATION THEORY OF ANHARMONICITY EFFECTS IN SLOW NEUTRON INELASTIC SCATTERING BY CRYSTALS. An earlier perturbation treatment of the corresponding X-ray scattering problem is generalized into a calculation of the effect of vibrational anharmonicity on the scattering of slow neutrons by crystals.

Of an expansion of the lattice potential in powers of the deviations from the thermally averaged sites, the cubic terms are taken into account up to second order; only first order terms are kept in the quartic anharmonicities. All higher terms are neglected. In particular, formulae for the shifts and broadenings of the one-phonon peaks in coherent scattering are derived in terms of the third and fourth order coupling coefficients.

As in X-ray scattering, a simple quadratic relation exists between the shifted "effective frequencies" of the long wavelength lattice vibrations and the isothermal elastic constants of the crystal. The lattice frequencies of the harmonic approximation may be obtained by extrapolating to absolute zero the linear dependence on temperature shown by the shifted frequencies above the Debye temperature.

THÉORIE DES PERTURBATIONS APPLIQUÉE AUX EFFETS D'ANHARMONICITÉ DANS LA DIFFUSION INÉLASTIQUE DES NEUTRONS LENTS PAR DES CRISTAUX. L'auteur calcule l'effet des vibration anharmoniques sur la diffusion des neutrons lents par des cristaux; ce calcul est une généralisation de la théorie des perturbations appliquée précédemment au problème correspondant de la diffusion des rayons X.

Il tient compte des termes cubi ues jusqu'au deuxième ordre dans le développement du potentiel de réseau selon les puissances des écarts par rapport aux positions pondérées thermiquement. Il ne garde que les termes du premier ordre dans les anharmonicités quartiques. Il néglige tous les termes d'ordre supérieur. En particulier, il obtient des formules pour les déphasages et pour l'élargissement des pics à un phonon dans la diffusion cohérente, en fonction des coefficients de couplage des troisième et quatrième ordres. Comme dans le cas de la diffusion des rayons X il existe une relation quadratique simple entre les "fréquences effectives" déphasées des vibrations de réseau à grande longueur d'ondes et les constantes d'élasticité isothermes du cristal. Les fréquences de réseau de l'approximation harmonique peuvent être obtenues en extrapolant jusqu'au zéro absolu la droite représentant les variations des fréquences déphasées en fonction de la température, pour des valeurs supérieures à la température de Debye.

ТЕОРИЯ ВОЗМУЩЕНИЙ ПОД ВЛИЯНИЕМ НЕГАРМОНИЧНЫХ ВОЗДЕЙСТВИЙ ПРИ НЕЙПРУГОМ РАССЕЯНИИ МЕДЛЕННЫХ НЕЙТРОНОВ КРИСТАЛЛАМИ. Для подсчета влияния вибрационной негармоничности на рассеяние медленных нейтронов кристаллами обобщается примененный ранее метод изучения возмущений в соответствующей проблеме рассеяния рентгеновских лучей\*.

При разложении в серию потенциала решетки по степеням отклонения от термических усредненных положений члены третьего ряда учитываются вплоть до второго порядка; что же касается квадратичных негармоничностей, то сохраняются только члены первого ряда. Всеми членами высших рядов пренебрегают.

В частности , выводятся формулы для сдвигов и расширений пиков единичного фонона при когереятном рассеянии, выражаемые в зависимости от коэффициентов связи третьего и четвертого рядов.

Как и при рассеянии рентгеновских лучей, существует простое квадратичное соотношение одвинутых "эффективных частот"длинноволновых вибраций решетки с изотермическими константами упругости кристалла.В гармоничном приближении частоты решетки могут быть получены путем экстраполяции

 <sup>\*</sup> Х.Хан, "Цейттрифт фюр физик", <u>165</u> (1961) 569.

до абсолютного нуля их линейной зависимости от температуры, т.е. зависимости, наблюдаемой для сдвинутых частот за пределами дебаевской температуры.

APLICACIÓN DE LA TEORÍA DE PERTURBACIONES A LOS EFECTOS ANARMÓNICOS EN LA DISPER-SIÓN INELÁSTICA DE NEUTRONES LENTOS POR CRISTALES. El autor generaliza el método de las perturbaciones, anteriormente empleado para estudiar el correspondiente problema de dispersión de rayos X, aplicándolo al cálculo del efecto de anarmonía vibratoria en la dispensión de neutrones lentos por cristales.

El potencial de la red se ha desarrollado en potencias de las desviaciones respecto de los puntos térmicamente ponderados. Los términos cúbicos se consideran hasta el segundo orden; en las anarmonías cuárticas, sólo se conservan los términos de primer orden. Se prescinde de los términos más elevados. En particular, el autor deduce las fórmulas de deplazamiento y ensanchamiento de los picos de un fonón en la dispersión coherente, en función de los coeficientes de acoplamiento de tercer y cuarto orden.

De igual modo que en la dispersión de rayos X, existe una relación cuadrática simple entre las "frecuencias efectivas" desplazadas de las vibraciones reticulares de onda larga y las constantes elásticas <u>isotérmicas</u> del cristal. Es posible obtener las frecuencias reticulares de la aproximación armónica extrapolando hasta el cero absoluto la variación lineal en función de la temperatura que presentan las frecuencias desplazadas por encima de la temperatura de Debye.

#### 1. INTRODUCTION

(a) This is an application of a perturbation method to neutron scattering which has already been used to study the anharmonicity effects on the scattering of X-rays by crystals [1].

During the course of work, two other treatments of the same problem appeared that led to expressions of the shifts and widths of the one-phononpeaks in terms of the third and fourth derivatives of the interatomic potential. They made use of Green's functions methods [2] or of diagram techniques [3]. It was thought worth while, however, to see how much information would be obtained from ordinary perturbation theory.

(b) First, some well-known results shall be recapitulated. According to VAN HOVE [4] the differential cross-section for the scattering of slow neutrons\* by an ideal crystal\*\* is proportional to

$$S(\underline{K}, \Omega) = \frac{N}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{i\Omega t} \sum_{\underline{h}}^{-\infty} e^{i\underline{K}\cdot\underline{q}^{0}(t)} e^{i\underline{K}\cdot\underline{q}^{\underline{h}}(0)} >_{anh.} (1)$$

Here K is the difference between the wave vectors of the ingoing and outgoing neutron waves,  $\hbar\Omega$  the corresponding difference in energy, N is the number of atoms in the crystal,  $q^{\underline{h}}$  (t) is the deviation at time t of the atom "h" from its thermally averaged position Ah, with A the matrix formed out of the three elementary translations of the lattice, and h a vector with integer number components.

 $\langle \rangle_{anh.}$  means the thermal average, taken with the complete anharmonic lattice Hamilton operator, H, which also governs the time dependence of  $\underline{q}^{\underline{h}}$  (t), so that, explicitly,

<sup>\*</sup> The corresponding expression for the scattering of X-rays (see [1]) is given by the integrand of (1) with t = 0.

<sup>\*\*</sup> For the sake of simplicity, only Bravais lattices will be considered here.

PERTURBATION THEORY OF ANHARMONICITY EFFECTS

 $\langle X^{\underline{h}} \rangle_{anh.} = \langle \exp \left[ -i \underline{K} \cdot \underline{q}^{o}(t) \right] \exp \left[ i \underline{K} \cdot \underline{q}^{\underline{h}} \right] \langle o \rangle_{anh.}$ 

$$= \frac{\mathrm{Tr} \{\mathrm{e}^{-\beta \mathrm{H}} \cdot \mathrm{e}^{\mathrm{i} \frac{\mathrm{H}}{\mathrm{h}}} \ \mathrm{e}^{-\mathrm{i} \frac{\mathrm{K}}{\mathrm{h}}} \cdot \underline{\mathrm{g}}^{\mathrm{q}}(0) \mathrm{e}^{-\mathrm{i} \frac{\mathrm{H}}{\mathrm{h}}} \cdot \mathrm{e}^{\mathrm{i} \frac{\mathrm{K}}{\mathrm{h}}} \cdot \underline{\mathrm{g}}^{\underline{\mathrm{h}}}(0)\}}{\mathrm{T}_{\mathrm{h}} \{\mathrm{exp}^{-\beta \mathrm{H}}\}}, \beta = \frac{1}{\mathrm{k}_{\mathrm{B}} \mathrm{T}}.$$
(2)

If the expansion

of the potential energy in powers of the displacement components \*  $q \frac{m}{t}$  etc. is broken off with the second order terms, the so-called "quasi-harmonic" approximation results. In this approximation, the part of the anharmonic effects that arise from thermal expansion is taken into account by means of the temperature dependence of the lattice matrix, A = A(T). In the quasiharmonic case, the expression (2) is known [4] to become

$$\langle X^{\underline{h}} \rangle = e^{-\langle \underline{K} \cdot \underline{q}^{o}(0) \rangle^{2}} + \langle \{ \underline{K} \cdot \underline{q}^{o}(t) \} \{ \underline{K} \cdot \underline{q}^{\underline{h}}(0) \} \rangle, \qquad (4)$$

where  $\langle \rangle$  means the thermal average, taken with the <u>quasiharmonic</u> Hamiltonian, H<sub>0</sub> = E<sub>kinetic</sub> (+  $\phi_0$ ) +  $\phi_2$ , and the <u>quasiharmonic</u> time dependences; this also applies to the following equations.

With the familiar relation

$$\underline{q}^{m}(t) = \sum_{\underline{k},\lambda} \underline{e}(\underline{k},\lambda), \quad \sqrt{\frac{\hbar}{2 NM\omega}} \left\{ b_{\underline{k}\lambda} \cdot e^{i\underline{k}\cdot A\underline{m} - i\omega(\underline{k},\lambda)t} + b_{\underline{k}\lambda}^{+} - i\underline{k}\cdot A\underline{m} + \omega t \right\}$$
(M = nuclear mass) (5)

between the displacements and the (time independent) creation and annihilation operators for the quanta of the quasiharmonic eigenvibrations ("phonons"), plane waves with wave vector  $\underline{k}$ , polarization vector  $\underline{e}$  ( $\underline{k}$ ,  $\lambda$ ) ( $\lambda = 1, 2, 3$ ),  $\langle \chi_{\underline{h}} \rangle$  becomes

$$\left\langle X^{\underline{h}} \right\rangle = e^{\frac{-\Sigma}{\underline{K}\lambda^{2}NM\omega}} \underbrace{\left\langle \underline{K} \cdot \underline{e} \right\rangle^{2}}_{e \underline{k}\lambda} \underbrace{\left\langle 2n+1 \right\rangle}_{e \underline{k}\lambda} \underbrace{\sum_{\underline{k}\lambda^{2}NM\omega}}_{2NM\omega} \underbrace{\left\langle \underline{K} \cdot \underline{e} \right\rangle^{2}}_{\left\{  e^{-i\underline{k} \cdot A\underline{h} - i\omega t +  e^{i\underline{k} \cdot A\underline{h} - i\omega t \right\}}}$$
(6)

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<sup>\*</sup> The first order coefficients vanish whenever each lattice point is a centre of symmetry, e.g. in all Bravais lattices.

with n = ( b+b ) = (e^{\hbar\omega\beta} - 1)^{-1} the average number of phonons k,  $\lambda$  .

The first factor in (4) and (6) is the harmonic Debye-Waller factor. Expansion of the second factor in powers of the exponent, on insertion of (6) into (1), gives rise to the well-known decomposition of the scattering cross-section into its elastic, one-phonon, two-phonon, etc. parts, the one-phonon part being sharply concentrated on the scattering surfaces defined by a product of two  $\delta$ -functions expressing the conservation of energy and quasi-momentum.

The quasi-harmonic results constitute the zeroth order term of the perturbation expansion that is to be described below.

## 2. THE PERTURBATION PROCEDURE

(a) A comparison with experiment of the theory of other anharmonic crystal properties (e.g., the temperature dependence of the elastic constants and the deviations from the rule of Dulong and Petit) has shown that it is a good approximation to neglect the fifth and higher order terms in the Taylor series (3) almost up to the melting point, and to make a perturbation expansion in powers of  $W = \phi_3 + \phi_4$ , in which  $\phi_3$  is taken into account up to second order, while only first order terms are kept in  $\phi_4$ . This corresponds to an expansion in powers of  $\langle q^{02} \rangle^{\frac{1}{2}}/L$  (L = distance between nearest neighbours) up to second order.

As the traces in (2) are invariant with respect to unitary transformations, the unperturbed wave functions may be used in computing them. The perturbation expansion is then simply performed by inserting the following expansions from Dirac perturbation theory into (2)

$$e^{-i\frac{t}{\hbar}(H_0+W)} = e^{-i\frac{t}{\hbar}H_0} \left\{ 1 + \left(\frac{-i}{\hbar}\right) \int_0^t W(t_1) dt_1 + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \widetilde{W}(t_1) \widetilde{W}(t_2) + \dots \right\},$$
(7a)

$$\mathbf{e}^{+i(t/\hbar)(H_0+W)} = \left\{ 1 + i/\hbar \int_0^t \widetilde{W}(t_1) dt_1 + (i/\hbar)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \widetilde{W}(t_2) \widetilde{W}(t_1) + \ldots \right\}$$

Xe<sup>i(t/ħ) H</sup>o.

(7b)

and

$$e^{-\beta(H_0+W)} = e^{-\beta H_0} \left\{ 1 - \int_0^\beta d\beta_1 \widehat{W}(\beta_1) + \int_0^\beta d\beta_1 \int_0^{\beta_1} d\beta_2 \widehat{W}(\beta_1) \widehat{W}(\beta_2) + \dots \right\},$$
(7c)

where

$$\widetilde{W}$$
 (t) = e<sup>i(H\_0/h)t</sup> We<sup>-i(H\_0/h)t</sup> (8a)

and

$$\widehat{W}(\beta) = e^{\beta H_0} W e^{-\beta H_0}.$$
(8b)

and by collecting all terms up to second order in  $\phi_3$  and up to first order in  $\phi_4$ . (Eqs 7c and 8b may be derived from 7a and 8a by replacing it/h by  $\beta$ ).

(b) The main interest is in the elastic and one phonon scattering. The elastic scattering is at once seen from the considerations of VAN HOVE [4] to be given by

$$S_{elastic} (\underline{K}, \Omega) = \delta (\Omega) \cdot N \sum_{\underline{h}} e^{i\underline{K} \cdot A\underline{h}} \cdot \left| \langle e^{i\underline{K} \cdot \underline{q}^{0}(0)} \rangle_{anh.} \right|^{2}.$$

The only effect of the anharmonicity here is to change the vibrational formamplitude  $\langle e^{i\underline{K}\cdot\underline{q}^{0}(0)} \rangle_{anh}$  entering the Debye-Waller factor  $|\langle \rangle_{anh}|^{2}$ . This changes only the intensities of the Laue-Bragg Maxima. The calculation of this effect (for which only the expansion 7c is needed) has already been carried out in connection with the X-ray scattering theory [1] and will not be repeated here. (The Debye-Waller factors for neutron and X-ray scattering are, of course, indentical [4].

(c) In treating the one-phonon-scattering by perturbation theory, one clearly has to assume that the scattering surface of the quasiharmonic theory is in practice still well defined and distinguishable from the background even in the anharmonic case, the anharmonicity inducing only relatively small shifts  $\Delta(\underline{k}, \lambda)$  and broadenings  $\gamma(\underline{k}, \lambda)$  to the  $\delta$ -function peaks that  $S(\underline{k}, \Omega)$  shows as a function of  $\Omega$  in the case of quasiharmonic one-phonon-scattering:

$$\Delta(\underline{k}, \lambda) /_{\omega(\underline{k}, \lambda)} \ll 1, \qquad \gamma(\underline{k}, \lambda) /_{\omega(\underline{k}, \lambda)} \ll 1 \qquad (\mathfrak{g})$$

There is, however, an intricacy that remains to be taken account of when using ordinary perturbation theory. From the analogous situation in the theory of the natural (radiation induced) width of spectral lines, one must expect it to be impossible to obtain the complete shape of the broadened line without taking all orders of perturbation theory into account to some extent. For  $\gamma = \Delta = 0$ ; no "broadened line" function like the Lorentzian

$$L(\Omega) = (\gamma/\pi) \left( \frac{1}{[(\Omega \pm [\omega + \Delta]) + \gamma^2]} \right)$$
(10)

possesses a regular expansion in powers of  $\gamma$  and  $\Delta$ , which quantities one may expect to contain the perturbation at least linearly and in a regular way. However, they do posses a singular expansion in powers of  $\Delta$  if  $\gamma \rightarrow 0$ ,

L 
$$(\Omega) \Big|_{\gamma \to 0} = \delta (\Omega - \omega) \pm \Delta \cdot \delta' (\Omega - \omega) + \frac{1}{2!} \Delta \delta^{*} (\Omega - \omega) \pm \dots$$

which is just the Taylor series description of a shift  $\pm \Delta$  of the  $\delta$ -function

 $\delta (\Omega - \omega)$ . Thus, in the case of a pure shift \* without broadening one would not meet any serious difficulty in contenting oneself with the lowest order of perturbation theory. One would just have to indentify with the frequency shifts the coefficients of the  $\delta$  -functions in the expansions  $\delta (\Omega \pm \omega) \pm c \cdot \delta'$  $(\Omega \pm \omega)$  that one gets from perturbation theory (the lowest order of which will only retain terms at most linear in  $\Delta$ ).

If, on the other hand, there is a (small) finite width  $\gamma$ , then the lowest order terms to appear in the perturbation expansion may, e.g. contain a summand proportional to  $\gamma$ . It is clear that one cannot deduce the complete shape of the broadened curve from this. One can, however, make a reasonable assumption about the form of the function of  $\Omega^{\pm}(\omega + \Delta)$  and  $\gamma$  describing this curve, then make a singular expansion of the assumed function in powers of  $\Delta$  and  $\gamma$  at  $\Delta = \gamma = 0$ , check whether the function (or functional) appearing in this expansion as a coefficient of  $\gamma$  also appears as a factor of the perturbation parameters in the expansion of S( $\underline{k}, \Omega$ ), and determine  $\gamma$  by comparison.

(d) It will be assumed here that the (narrow) peaks proper are of Lorentzian shape. This is an analogy to an assumption familiar from the first treatments of the natural widths of atomic spectral lines, i.e. that the asymptotic time dependence of the coefficients for the unperturbed states must allow for an exponential decay. This means that the phonons are decaying into other phonons as a result of the perturbation and hence (asymptotically for large t) have the time dependence of damped oscillations. (The small-time behaviour is of no interest here, since it only cuts off the outer, long range tails of the Lorentzian and therefore only changes the background intensity).

Bearing in mind that the Fourier transform of the Lorentzian function (10) is

$$e^{\pm i(\omega+\Delta)t-\gamma|t|} \approx (1\pm i\Delta t - \gamma|t|) \cdot e^{\pm i\omega t}$$
, (10a)

one sees that the recipe for obtaining the shifts and widths of the one-phononpeaks is really very simple: 'carry out the perturbation expansion of (2) to order  $\sim \phi_3^2$ ,  $\sim \phi_4$ , collect all terms that are proportional to t or proportional to |t| asymptotically for large absolute values of t and compare to the expressions of type (10a) that are expected to replace the  $\delta$ -function Fourier transforms  $\exp^{(\pm i\omega t)}$  in the one-phonon-term of (6)."

(e) The perturbation calculation itself which is performed by the method already applied to the X-ray case [1] will now be roughly sketched:

(2) can be re-written with (7a-c) up to terms  $\sim \phi_{3}$ ,  $\sim \phi_{4}$ , as

$$\langle \mathbf{X}^{\underline{h}} \rangle_{anh.} = \langle \mathbf{X}^{\underline{h}} \rangle - \left\{ \int_{0}^{\beta} \langle [\hat{\phi}_{3}(\beta_{1}) + \hat{\phi}_{4}(\beta_{1})] \mathbf{X}^{\underline{h}} \rangle d\beta_{1} - \beta \langle \phi_{4} \rangle \langle \mathbf{X}^{\underline{h}} \rangle \right\}$$

\* It will be seen below that this case would be realized to the order  $\langle q^2 \rangle / L^2$  to which the perturbation theory is carried here if there were no  $\phi_*$  terms in (3).

with, e.g.  $\Gamma_{\underline{i}}^{\underline{m}}(t_1, t) = [-i \underline{k} \cdot \underline{q}^0(t), q_{\overline{i}}^{\underline{m}}(t_1)].$ 

(11) is entirely composed of quasiharmonic averages.

 $\tilde{\phi}_3(t_1)$ , e.g. is equal to  $\frac{1}{3!} \Sigma \phi_1^{\underline{m}\underline{n}\underline{0}} \tilde{q}_1^{\underline{m}}(t_1) \tilde{q}_1^{\underline{n}}(t_1) \tilde{q}_k^{\underline{n}} k(t_1) = \phi_3(\tilde{q}(t_1))$ , as may be shown by inserting a factor of  $1 = \exp(iH_0t/\hbar) \cdot \exp(-iH_0t/\hbar)$ between the factors q of the original definition (8a). The analogous equation holds for the  $\hat{\phi}(\beta)$ 's.

The arguments  $\widetilde{q}+\Gamma$  found in some of the terms instead of the  $\widetilde{q}$  arise from the repeated application of

$$e^{-i\underline{K}\cdot q^{0}(t)} q\underline{\underline{m}} (t_{1}) = \left\{ q\underline{\underline{m}} (t_{1}) + \left[ -i\underline{k}\cdot \underline{q}^{0}(t), q\underline{\underline{m}} (t_{1}) \right] \right\} e^{-i\underline{K}\cdot \underline{q}^{0}(t)} ,$$
(12)

which follows from the fact that "all the commutators of the form

$$[\tilde{q}(t_1), \tilde{q}(t_2)]$$
 (or also  $[\hat{q}(\beta_1), \hat{q}(\beta_2)]$ ) [1] (13)

are pure c-numbers" as a consequence of (5) and of the commutation relations

$$[\mathbf{b}_{\underline{k}\lambda},\mathbf{b}_{\underline{k}'\lambda'}^{*}] = \delta_{\underline{k}\underline{k}'}, \delta_{\lambda\lambda'}; \qquad [\mathbf{b}_{\underline{k}\lambda},\mathbf{b}_{\underline{k}\lambda}] = [\mathbf{b}_{\underline{k}\lambda},\mathbf{b}_{\underline{k}\lambda}] = 0.$$

(13) is essential for the calculation of the quasiharmonic averages in (11). They all have the form

(i): 
$$\langle \prod \tilde{q} (t_v) \cdot \prod \hat{q} (\beta \mu) \cdot \chi^{\underline{h}} \rangle$$
 or (ii):  $\langle \prod \tilde{q} (t_v) \cdot \prod \hat{q} (\beta \mu) \rangle$  (14)

(with a separate factor of  $\langle X^h \rangle$ ).

First, because of (13),  $\chi^{h}$  can be written as [4]

$$\chi^{\underline{h}} = e^{-i\underline{K} \cdot \underline{q}^{0}(t)} \cdot e^{i\underline{K} \cdot \underline{q}^{\underline{h}}(0)} = \underbrace{e^{i\underline{K} \cdot \{\underline{q}^{\underline{h}}(0) - \underline{q}^{0}(t)\}}}_{"_{s}\underline{h}(\underline{K}, t)"} \cdot e^{\frac{1}{2}[\underline{K} \cdot \underline{q}^{0}(t), \underline{K} \cdot \underline{q}^{\underline{h}}(0)]}$$
(15)

where the commutator factor is a c-number and hence may be taken out of the averaging brackets, so that the averages remain to be taken with  $s^{\underline{h}}$  instead of  $\chi^{\underline{h}}$ .

Now, as has been proved in [1], from (13) one obtains the equation

$$\hat{\mathbf{q}}_{\mathbf{i}}^{\underline{\mathbf{m}}} (\boldsymbol{\beta}\boldsymbol{\mu}) \cdot \underbrace{\mathbf{e}}_{\mathbf{g},\mathbf{1},\nu}^{\underline{\Sigma}} \kappa_{\mathbf{i}}^{\underline{g}} \cdot \hat{\mathbf{q}}_{\mathbf{g}}^{\underline{g}} (\boldsymbol{\beta}_{\nu})}_{\mathbf{s}(\ldots,\kappa_{\nu}^{\underline{g}},\ldots)^{\mathbf{r}}} = \left\{ \begin{array}{c} \frac{\partial}{\partial \kappa_{\mu}^{\underline{m}}} \\ \frac{\partial}{\partial \kappa_{\mu}^{\underline{m}}} \\ \frac{\partial}{\partial \kappa_{\mu}^{\underline{m}}} \end{array} \right\} - \frac{1}{2} \sum_{\substack{g,\mathbf{1},\nu\\ \overline{\nu} \equiv \mu}} \kappa_{\mu}^{\underline{g}} \cdot \left[ \hat{\mathbf{q}}_{\mathbf{1}}^{\underline{g}} (\boldsymbol{\beta}_{\nu}), \hat{\mathbf{q}}_{\mathbf{1}}^{\underline{m}} (\boldsymbol{\beta}\boldsymbol{\mu}) \right] \right\} \cdot \mathbf{S}$$

$$pure Number \ ^{\mathbf{C}}_{\underline{\mu}}^{\underline{m}}$$

$$(16)$$

In the case of a product of  $\hat{q}$ 's belonging to different  $\beta$ 's, the order of the products must be reversed on replacing the  $\hat{q}$ 's by the operators  $\{\partial/_{\partial\kappa} + C\}$ :

$$\hat{\mathbf{q}}$$
 (1)  $\hat{\mathbf{q}}$  (2) S = { $\partial/_{\partial\kappa}$  + c}<sub>2</sub> { $\partial/_{\partial\kappa}$  + c}<sub>1</sub> S. (16a)

As (16) is also valid for imaginary  $\beta$  and since  $\mathbf{q}(t) = \mathbf{\hat{q}}(\frac{it}{\hbar})$ ; the  $\mathbf{\hat{q}}$ 's may also be treated by (16).

Since the dummy operators  $\{\frac{\partial}{\partial \kappa} + C\}$  are not affected by the average and hence may be taken out of it, all that is necessary in order to compute the averages (14) (with s<sup>n</sup> instead of  $\chi^n$ ) is to apply the substitute product of operators  $\{\partial/\partial_{\kappa} + C\}$  to  $\langle S \rangle$ , where in S,  $\nu$  takes 6 values:

$$\nu = 0 : \beta_0 = 0$$

$$\nu = 1 : \beta_1$$

$$\nu = 2 : \beta_2$$

$$\nu = 3 : it_1/h = \beta_3$$

$$\nu = 4 : it_2/h = \beta_4$$

$$\nu = 5 : it /h = \beta_5$$

and then set  $\kappa \frac{g}{V} = i k_1 (\partial g_k \delta_{\nu 0} - \delta_{g0} \delta_k)$  for (14a),  $\kappa \frac{g}{V} \equiv 0$  for (14b) after all the differentiations have been carried out. The average value  $\langle S \rangle$  needed for this has been shown [1] to be

$$\langle s \rangle = e^{\frac{1}{2} \langle (\sum_{\underline{g} \neq 1} k_{1}^{\underline{g}} q_{1}^{\underline{g}} (\beta_{\nu}))^{2} \rangle}$$

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$$= \exp \left\{ \frac{\frac{1}{2} \sum_{\substack{g,\nu,e \\ g',\nu',e'}} \kappa_{1}^{g} \cdot \kappa_{1'}^{g} \langle \hat{\mathbf{q}}_{1}^{g} (\beta_{\nu}) \cdot \hat{\mathbf{q}}_{1'}^{g'} (\beta_{\nu'}) \rangle \right\}$$

where the averages  $\langle \hat{\mathbf{q}}, \hat{\mathbf{q}}' \rangle$  are easily computed with the aid of the normal coordinate expansion (5) with  $\beta$ 's instead of (it/n)'s. The details of the calculation which is now straight-forward will be emitted here. Only two points may be noted:

(1) The terms in (11) which only contain parts of the e<sup>-bH</sup> expansion can neither shift nor broaden the one-phonon-peaks, since they do not change the harmonic time dependence, i.e. the harmonic energy levels, but only the thermal weightings. They give rise to a temperature-dependent intensity factor that changes the heights of the one-phonon-peaks and is easily computed. This will be given in full in a later paper.

(2) In the calculation of the widths and shifts everything turns out as expected in paragraph 2. d).

# 3. RESULTS

Disregarding some terms that are proportional to t but bear a factor of 1/N when compared to the main terms, one finds for the shifts of frequency  $\omega$  (k,  $\lambda$ )

$$\Delta(\underline{\mathbf{k}}, \lambda) = \frac{1}{4 \operatorname{N}\omega(\underline{\mathbf{k}}, \lambda)} \sum_{\underline{\mathbf{k}}', \lambda'} \phi_{\underline{\lambda}}^{\underline{\mathbf{k}}} - \frac{\underline{\mathbf{k}}'}{\underline{\lambda}'} - \frac{\underline{\mathbf{\epsilon}}(\omega', \mathbf{T})}{\omega'^{2}}$$
(17)

$$+\frac{1}{16 \operatorname{N}\omega(\underline{k},\lambda)} \sum_{\substack{\underline{k}',\underline{k}'\\\lambda',\lambda''}} \frac{\left| \phi_{\lambda} \frac{\underline{k}' \underline{k}''}{\lambda' \lambda''} \right|}{\omega' \omega''} \left[ \left( \frac{\epsilon'}{\omega'} + \frac{\epsilon''}{\omega''} \right) \left\{ \frac{P}{\omega - \omega' - \omega''} - \frac{P}{\omega + \omega' + \omega''} \right\} + 2 \left( \frac{\epsilon'}{\omega'} - \frac{\epsilon''}{\omega''} \right) \cdot \frac{P}{\omega + \omega' - \omega''} \right]$$

Here P/ $\omega$  means the principal value  $\lim_{t\to\infty}$  1/ $\omega$  (1 -  $\frac{\sin\omega t}{\omega t}$ ) of 1/ $\omega$ .

$$\phi_{\lambda}^{\underline{k}} \frac{\underline{k}'}{\lambda'} \frac{\underline{k}'}{\lambda''} = \frac{1}{NM_{2}^{2}} \sum_{\substack{\underline{m} \underline{n} \\ \underline{i} \\ j \\ k}} \phi_{\underline{i} \\ \underline{n} \\ \underline{k} \\ \underline{n} \\ \underline{n}$$

and

$$\phi_{\lambda}^{\underline{k}} \frac{\underline{k}'}{\lambda'} \frac{\underline{k}'' \underline{k}''}{\lambda'' \lambda'''} = \frac{1}{NM^2} \sum_{\substack{\underline{m} \ \underline{n} \ \underline{n} \\ i \ j \ \underline{k} \ \underline{n}}} \phi_{\underline{i} \ \underline{j} \ \underline{k} \ \underline{n}}^{\underline{m} \ \underline{n} \ \underline{n} \underline{p}} e_{\underline{i}} e_{\underline{j}}' e_{\underline{k}}' e_{\underline{i}}'' \cdot e_{\underline{k}}^{\underline{i} (\underline{k} \cdot \underline{A} \underline{m} + \underline{k}' - \underline{A} \underline{n} + \underline{k}'' \underline{A} \underline{p})} (18b)$$

are the Fourier transforms of the third and fourth order coupling parameters.  $\epsilon(\omega, T)$  is Planck's average oscillator energy  $\hbar\omega \langle n \rangle + \frac{1}{2}$ ). For the width of the emission and absorption peaks involving the frequency  $\omega$  (k,  $\lambda$ ) one finds

$$\gamma (\underline{\mathbf{k}}, \lambda) = \frac{\pi}{16 \text{ N } \omega (\underline{\mathbf{k}}, \lambda)} \sum_{\substack{\underline{\mathbf{k}}', \underline{\mathbf{k}}'' \\ \overline{\lambda}', \overline{\lambda}'}} \frac{\left| \frac{\phi_{\underline{\mathbf{k}}} \underline{\mathbf{k}}' \underline{\mathbf{k}}''}{\omega' \omega''} \right|^2}{\omega' \omega''}$$

$$\times \left[ \left( \frac{\epsilon'}{\omega'} + \frac{\epsilon''}{\omega''} \right) \left\{ \delta (\omega - \omega' - \omega'') - \delta (\omega + \omega' + \omega'') \right\} + 2 \left( \frac{\epsilon'}{\omega'} - \frac{\epsilon''}{\omega''} \right) \delta (\omega + \omega' - \omega'') \right]$$
(19)

Here the case of two equal frequencies belonging to the same  $\underline{k}$  but to different polarizations has been excluded for the sake of simplicity. This case only occurs at the exceptional points where two of the quasiharmonic scattering surfaces (or all three of them) intersect. If, however, this intersection is brought about purely by the symmetry of the lattice, there is in general no difficulty even at these points. A more detailed discussion of this point will also be given in a later paper.

It can be seen from (17) and (19) that for a given k,  $\lambda$ , the frequency shift  $\Delta$  as well as the width  $\gamma$  is proportional to T at high temperatures ( $\gamma > \theta_{\text{Debye}}$ ,  $\epsilon \approx \text{k} \cdot \text{T}$ ). So is the part of the quasiharmonic frequencies that depends on temperature, as a result of the effect of thermal expansion. Thus, by extrapolating to absolute zero the linear dependence on T shown by the  $\omega + \Delta$  for  $\text{T} > \theta_{\text{Debye}}$ , one gets the harmonic frequencies  $\omega(\text{k}, \lambda)$ . From these the second order coefficients of the expansion of the lattice potential  $\phi$  in powers of the deviations  $q^{\text{h}}$  from the static equilibium positions Ah (defined by the minimum of  $\phi$ ) can be deduced.

The shifted frequencies  $\omega + \Delta$  found from neutron scattering are in general not identical with those determined from X-rays scattering by the method given in [1]. (There, effective frequencies showing a temperature-dependent shift as compared to the quasiharmonic ones were introduced to describe just the temperature dependent intensity factor coming from the perturbation expansion of  $e^{-\beta H}$  that was omitted here). Yet for small k, i.e. for long wavelength phonons, both the effective neutron and X-ray frequencies become identical. It can be shown by the same method as has been used in [1] that for long wavelengths (j|k|  $\leq \frac{1}{3} k_{max}$ 

$$\rho \cdot (\omega + \Delta)_{\underline{k},\lambda}^{2} \approx \sum_{ij,rs} C^{(isothermal)} (T) e_{i} e_{j} k_{r!} k_{s}$$
(20)

( $\rho$  - macroscopic density N/V<sub>Crystal</sub>), i.e. the squares of the shifted frequencies both in the neutron and in the X-ray case are proportional to the isothermal elastic constants. This prediction is in good agreement with the experiments of HOMRYD, LARSSON and DAHLBORG [5] on aluminium, as shown by Fig. 1.



Fig.1

Temperature dependence of the shifted phonon frequencies  $\omega + \Delta$  according to Eq. 20 and according to [5] at small <u>k</u>.

(\_\_\_\_): C\_{11}^{(adiabatic)} T/C\_{11}^{0} [ + : measurements by SUTTON, P. M., Phys. Rev. <u>31</u> (1953) 516]. (\_\_\_\_\_): the curve computed (from the adiabatic one) for the isothermal constant C\_{11}^{(isotherm)} T, divided by the harmonic value C\_{11}^{0} according to Sutton).

0,\*: points computed from the measurements of LARSSON et al. [4].

### 4. SUMMARY

It has been shown that the shifts and widths of the one-phonon-peaks in neutron scattering induced by the anharmonicity of the lattice vibrations can be obtained from a simple perturbation theory if a reasonable assumption is made about the shape of the peaks, i. e. that this shape is described by a Lorentzian function. Both shifts and widths are proportional to temperature in the high temperature region. One can obtain the temperature independent frequencies that would be seen if all anharmonicities were absent. By extrapolating the linear dependence on temperature shown by the shifted frequencies above Debye temperature, down to absolute zero.

The squares of the shifted frequencies of the long wavelength phonons are proportional to the isothermal elastic constants of the crystal.

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# H. HAHN

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#### DISCUSSION

I. WALLER: I would like to ask whether, using the same method, you could not also get a temperature factor which would contain in its exponent fourth-order terms in the momentum transfers. Have you considered what these terms might be and whether they might be of some importance?

H. HAHN: Yes, this can be done. I have made such a calculation of the temperature factor, especially for the case of elastic scattering, where it is nothing more than an intensity factor. A slightly different factor is involved in the case of one-phonon scattering but the problem is the same and perturbation theory is reasonably applicable. I have also done this calculation in connection with the X-ray scattering work reported in the paper. The Debye-Waller factors are identical for all types of scattered particles and it is true that terms proportional to  $K^4$  are obtained in the exponent of the factor. I have not gone into the problem of the importance of these terms but I recall a remark by Maradudin that they were not very important in a special case that he had calculated. This would be in agreement, with the fact that no-one ever seems to have observed them experimentally.

I. WALLER: It has been pointed out by Singwi and Sjoelander that it could be of interest to investigate the temperature factor in the case of incoherent neutron scattering.

H. HAHN: I agree. As soon as the momentum transfer becomes quite large, those terms would have to be taken into account.

I. WALLER: With reference to your results for the temperature factor, I would like to ask whether you could not get an equally good description of the variations of this factor if you expressed its exponent in the Debye temperature  $\theta$  in the usual way and considered the temperature-dependent  $\theta$ which can be calculated from the measured change of the elastic constants for each temperature T. The Debye temperature might indeed vary with the change in elastic constants in such a way as to give you a somewhat similar result.

H. HAHN: This is certainly true as far as the lower-frequency contributions to the Debye-Waller factor are concerned (with anharmonic contributions up to  $K^2$  only). I am not sure that it is true when you depart from the harmonic theory, because then you get different Debye temperatures.

K.S. SINGWI: I understand that Dr. Lowde and his group at Harwell, working with some alkali halide, have determined the Debye-Waller factor as a function of  $K^2$  and that they see a deviation (a  $K^4$  term).

W. COCHRAN: Speaking as a co-author of the work on LiH to which Dr. Singwi is referring, I do not myself consider that it demonstrates an anharmonic contribution to the Debye-Waller factor.

# THE CALCULATION OF DEBYE-WALLER FACTORS FROM THERMODYNAMIC DATA

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#### Abstract — Résumé — Аннотация — Resumen

THE CALCULATION OF DEBYE-WALLER FACTORS FROM THERMODYNAMIC DATA. Properties of crystals which depend primarily upon the lattice frequency spectrum can be related exactly within the quasi-harmonic approximation. Such properties include thermodynamic quantities, e.g. heat capacity, thermal expansion etc., and the temperature dependence of the intensities of Bragg reflections; the latter is usually expressed as the Debye-Waller factor.

From analyses of appropriate heat capacity and thermal expansion data for simple crystals, it is possible to calculate Debye-Waller factors and their dependences upon temperature and volume much more accurately than they may be obtained by direct measurement. The importance of this is its possible use in the analysis of complicated scattering processes.

An equivalent Debye characteristic temperature,  $\Theta M$ , can be defined for cubic crystals. Its variation with temperature is small: for  $T > \Theta M/3$ ,  $\Theta M$  tends to a constant value which is usually less than characteristic temperatures calculated from heat capacity data at either low or high temperatures. Anharmonic effects appear to be small in the region  $T < 2\Theta M$ .

The general method of analysis will be illustrated with specific examples.

CALCUL DES FACTEURS DE DEBYE-WALLER A PARTIR DES DONNÉES THERMODYNAMIQUES. On peut, grâce à l'approximation quasi-harmonique, établir des relations exactes entre les propriétés des cristaux qui dépend essentiellement du spectre de fréquence du réseau. Ces propriétés comprennent les quantités thermodynamiques suivantes: la capacité calorifique, la dilatation thermique, etc., et les variations des intensités des réflexions de Bragg en fonction de la température; cette dernière propriété est désignée habituellement par le facteur de Debye-Waller.

En se fondant sur l'analyse des données relatives à la capacité calorifique et à la dilatation des monocristaux, il est possible de calculer les facteurs de Debye-Waller ainsi que leur variation en fonction de la température et du volume, d'une manière beaucoup plus précise que par la mesure directe. Ce qui est important, c'est qu'on peut utiliser cette méthode pour l'analyse de processus de diffusion compliqués.

On peut définir une température caractéristique de Debye, équivalente  $\bigcirc M$ , pour les cristaux cubiques. Elle varie très peu en fonction de la température pour  $T > \bigcirc M/3$ ,  $\bigcirc M$  tend vers une valeur constante qui est en général inférieure aux températures caractéristique calculées à partir des données relatives à la capacité calorifique soit aux températures élevées, soit aux basses températures. Les effets anharmoniques semblent être faibles pour T <  $2 \bigcirc M$ .

Les auteurs illustrent la méthode générale d'analyse par quelques exemples particuliers.

ВЫВЕДЕНИЕ КОЭФФИЦИЕНТА ДЕБАЯ-ВАЛЛЕРА ИЗ ТЕРМОДИНАМИЧЕСКИХ ДАННЫХ. Свойства кристаллов, которые в первую очередь зависят от частотного спектра решетки, могут быть точно установлены в пределах квазигармонического приближения. Эти свойства включают терминодинамические величины, такие, как теплоемкость, тепловое расширение и т.д., и температурную зависимость интенсивностей брегговских отражений. Последняя обычно выражается коэффициентом Дебая-Валлера.

Из данных анализов соответствующей теплоемкости и данных теплового расширения для простых кристаллов можно вывести коэффициенты Дебая-Валлера, а также установить их зависимость от температуры и объема более точно, чем они могут быть получены при непосредственном измерении. Главное здесь - возможность использовать их при анализах сложных процессов рассеяния.

Эквивалентная характеристическая дебаевской температуры  $\vartheta^m$ может быть определена для кубических кристаллов. Ее вариации в зависимости от температуры являются небольшими: для  $T > z^m / 3$ ,  $\vartheta^m$  стремится к постоянной величине, которая обычно меньше, чем характеристические температуры, высчитанные из данных по теплоемкости как при низких, так и при высоких температурах. Негармонические эффекты представляются небольшими в районе T < 25<sup>m</sup>.

Общий метод анализа будет проиллюстрирован специальными примерами.

CÁLCULO DE LOS FACTORES DE DEBYE-WALLER A PARTIR DE DATOS TERMODINÁMICOS. Las propiedades de los cristales que dependen principalmente del espectro de frecuencia reticular pueden relacionarse con exactitud dentro de los límites de la aproximación cuasi armónica. Estas propiedades comprenden parámetros termodinámicos como, por ejemplo, la capacidad calorífica y la dilatación térmica, etc., así como la variación en función de la temperatura de la intensidad de las reflexiones de Bragg; esta filtima suele denominarse factor de Debye-Waller.

El análisis de los datos correspondientes a la capacidad calorífica y a la dilatación térmica de monocristales permite calcular los factores de Debye-Waller y sus variaciones en functión de la temperatura y del volumen con una precisión mucho mayor que la alcanzada por medición directa. La importancia de ello estriba en su posible aplicación al análisis de procesos complicados de dispersión.

Para los cristales del sistema cúbico es posible definir una temperatura característica de Debye equivalente $\Theta M$ . Su variación con la temperatura es reducida: para T > $\Theta M/3$ ,  $\Theta M$  tiende hacia un valor constante que suele ser inferior a las temperaturas características calculadas sobre la base de los datos relativos a la capacidad calorífica a temperaturas bajas o elevadas. Los efectos anarmónicos son, al parecer, reducidos en la región T <  $2\Theta M$ .

Los autores aclaran el método general de análisis con ejemplos concretos.

#### I. INTRODUCTION

In the Born approximation the scattering cross-section for a wide variety of processes may be conveniently described in terms of a generalized pair distribution function  $G(\mathbf{r}, t)$  [1].  $G(\mathbf{r}, t)$ , for a monatomic crystal in the harmonic approximation, is essentially determined by the thermal average over all normal coordinates  $\langle u_{\alpha}^{0}(0) u_{\beta}^{e}(t) \rangle_{T}$ ,  $u_{\alpha}^{e}(t)$  is the  $\alpha^{tn}$  cartesian component of the vector displacement u (t) of the  $l^{tn}$  atom from its equilibrium position at time t.  $u^{0}$  is the corresponding vector displacement of a typical atom at a site chosen as the origin of coordinates in the lattice.

A special case of the correlation tensor  $\langle u_{\sigma}^{0}(0) u_{\beta}^{\ell}(t) \rangle_{T}$  is involved in the description of elastic scattering processes in crystalline lattices. The familiar Debye-Waller exponent M(T) is easily shown to be just

$$M(T) = \frac{1}{2} Q_{\alpha} Q_{\beta} \langle u_{\alpha}^{0}(0) u_{\beta}^{0}(0) \rangle_{T}, \qquad (1)$$

with  $Q = \underline{k}_{sc} - \underline{k}_{in}$ ,  $\underline{k}_{sc}$  and  $\underline{k}_{in}$  the wave vectors for scattered and incident waves respectively. (The summation convention is used for Greek subscripts throughout.) Detailed knowledge of M(T) is therefore useful in the design and interpretation of both elastic and inelastic scattering experiments [2, 3]. For a monatomic lattice of cubic symmetry, M(T) is completely determined by the lattice vibrational frequency spectrum [4]. The well known expression is

$$M(T) = \frac{Q^2}{2m} \frac{1}{3N} \int_0^{\omega_m} \frac{G(\omega)}{\omega^2} \epsilon(\omega, T) d\omega, \qquad (2)$$

where:

$$\epsilon (\omega, T) = \hbar \omega \left( \frac{1}{2} + \frac{1}{e \hbar \beta \omega_{-1}} \right).$$

In this expression N is the total number of unit cells in the crystal,  $G(\omega)$  the vibrational frequency distribution function,  $\omega_m$  the maximum lattice eigenfrequency, m the mass of a lattice atom,  $\beta = (k_B T)^{-1}$ . If the lattice has cubic symmetry, but has n atoms per unit cell, then there will be n Debye-Waller factors, i. e.  $M_s$ ,  $s = 1, 2, \ldots n$ . These cannot be individually related to an average over the frequency spectrum, but the latter determines an appropriate linear combination of the  $M_s$  [4]:

$$\frac{1}{n} \sum_{j=1}^{n} \mathbf{m}_{j} \mathbf{M}_{j} = \frac{\mathbf{Q}^{2}}{2m} \frac{1}{3Nn} \int_{0}^{\omega_{m}} \frac{\mathbf{G}(\omega)}{\omega^{2}} \epsilon (\omega, \mathbf{T}) d\omega.$$
(3)

Here  $m_s$  is the atomic mass of the s<sup>th</sup> atom in the lattice unit cell. There is, finally, an appropriate generalization for non-cubic lattices [4], but we shall not consider these in this paper.

It will be noted that both Eqs (2) and (3) involve the integral

$$X(T) = \frac{1}{3 n} \int_0^{\omega_m} \frac{G(\omega)}{\omega^2} \epsilon(\omega, T) d\omega, \qquad (4)$$

hereafter called the "Debye-Waller frequency integral";  $\hbar$  = nN, the total number of vibrating units in the lattice. (We assume in each case that  $G(\omega)$ 

is so normalized that 
$$\int_0^{\omega} G(\omega) d\omega = 3n$$
.)

It follows, therefore, that the sum  $\langle u_{\alpha}^{0}(0) u_{\alpha}^{0}(0) \rangle_{T}$  is an essentially"thermodynamic" quantity, being a temperature dependent average over the lattice frequency distribution, just like the heat capacity, the entropy, etc. This strongly suggests that experimental information on the heat capacity can be correlated with M(T) data for the same substance. In the past, such correlation has been attempted largely through the assumption of the Debye distribution for the lattice frequencies. More recently, lattice dynamical considerations have been used to compute both the heat capacity and the Debye-Waller effect from the same lattice frequency distribution, itself derived either from an assumed lattice dynamical model [5] or from an analysis of inelastic scattering [6]. Our purpose is distinctly different: to use the general theory of lattice dynamics (in the quasiharmonic approximation) to correlate available thermodynamic data with M(T) values. In particular, we shall outline an answer to the following specific question: given thermodynamic data on heat capacity, thermal expansion, elastic constants, etc. for a particular substance (e.g. copper); how can one use that data to accurately estimate M(T), and thence  $\langle u_{\alpha}^{\sigma}(0) u_{\alpha}^{\sigma}(0) \rangle_{T}$ ?

### II. MOMENTS OF THE FREQUENCY DISTRIBUTION

The desired correlation of thermodynamic data with M(T) involves the moments of the frequency spectrum

$$\overline{\omega^{n}} = \frac{1}{3 n} \int_{0}^{\omega_{m}} \omega^{n} G(\omega) d\omega, n \ge 3.$$
 (5)

In the high temperature region the heat capacity can be expanded as a series in powers of  $1/T^2$ , with coefficients involving the positive even moments  $\overline{\omega^{2n}}$  of the frequency distribution [7]. Given heat capacity data of accuracy within 0.5%,  $\omega^2$  may be obtained to an accuracy of about 1%, and  $\omega^4$  and  $\omega^6$ to within two or three per cent [8]. (If anharmonic effects are fairly large, these limits must be increased.) It is perhaps not so well known that appropriate analysis of heat capacity data in the intermediate and high temperature range will yield values of  $\overline{\omega^{-2}}$  and  $\overline{\omega^{-1}}$ , to essentially the same accuracy (often 0.2%) as the original heat capacity data [8]. In addition, low temperature heat capacity data give the first few coefficients of the asymptotic expansion

$$C_v = a T^3 + b T^5 + c T^7 + \dots$$
 (6)

It is not difficult to show that the Debye-Waller frequency integral X(T) possesses low and high temperature expansions whose coefficients can be directly related to certain of the moments  $\omega^n$  and to the coefficients a, b.... of Eq. (6).

1. Low temperatures

$$X(T) = \frac{\hbar}{2} \overline{\omega^{-1}} + \frac{\hbar}{3\pi} \int_{0}^{\omega_{m}} \frac{G(\omega)}{\omega} \left(e^{\beta\hbar\omega} - 1\right)^{-1} d\omega, \qquad (7)$$

where the first term represents the contribution of the zero point energy. The second term may be evaluated in the limit of very low temperature to get the asymptotic expansion for X(T)

$$X(T) = \frac{\hbar}{2} \ \overline{\omega^{-1}} + \frac{1}{3\pi} \left(\frac{\hbar}{2\pi k_{B}}\right)^{2} \ \frac{5}{2} \left[a \ T^{2} + \frac{7}{50} \ b \ T^{4} + \frac{c}{21} \ T^{6} \dots \right]$$
(8)

where a, b, c... are the coefficients in the expansion (6).

2. High temperature

$$X(T) = kT \left[ \overline{\omega^{-2}} + \frac{B_2}{2!} \left( \frac{\hbar}{k_B T} \right)^2 + \frac{B_4}{4!} \left( \frac{\hbar}{k_B T} \right)^4 \overline{\omega^2} + \frac{B_6}{6!} \left( \frac{\hbar}{k_B T} \right)^6 \overline{\omega^4} . \right]$$
(9)

where use has been made of the standard expansion for  $x/(e^x - 1)$  in powers of x; the  $B_{2n}$  are the signed Bernoulli numbers:  $B_2 = \frac{1}{8}$ ,  $B_4 = -\frac{1}{30}$ , ....

### CALCULATION OF DEBYE-WALLER FACTORS

# III. USE OF EQUIVALENT DEBYE CHARACTERISTIC TEMPERATURES

For several reasons it is convenient to make use of the Debye vibrational frequency distribution as a standard reference, thus introducing various characteristic temperatures  $\Theta$  (T, V). The variation of  $\Theta$  with temperature may be related to deviations of the actual lattice  $G(\omega)$  from the Debye distribution and its variation with volume to the effects of thermal expansion of the lattice. Clarity of notation is essential, for there are, of course, many different Debye characteristic temperatures, depending upon which physical property of the lattice is being described. We shall use superscripts to denote the property to which a given  $\Theta$  refers:  $\Theta^{C}$  for the heat capacity,  $\Theta^{M}$  for the Debye-Waller frequency integral, etc. It is convenient to denote the high and low temperature limiting values for the various distinct Debye  $\Theta^{\dagger}$ s. We use subscripts for this purpose: e.g.,  $\Theta_{\alpha}^{C} = \lim_{T \to 0} \Theta^{C}(T)$ ;  $\Theta_{0}^{M} = \lim_{T \to 0} \Theta^{M}(T)$ .)

Unless otherwise specified, all  $\Theta$  values refer to a standard volume, taken as  $V_0 = \lim_{T \to 0} V_T$ .

We define  $\Theta^{M}(T)$  implicitly through the expression:

X(T) = 
$$\frac{9n}{kT} \frac{\hbar^2}{4x} \left[ \frac{1}{4x} + \frac{1}{x^3} \int_0^x \frac{y}{ey - 1} dy \right],$$
 (10)

with  $x = \Theta^{M}(T)/T$ . Equation (10) is just the defining equation for X(T), evaluated for the Debye reference spectrum. Available tables [9] of the function  $x^{-1} \int_{0}^{x} y(ey - 1)^{-1} dy$  may be used to determine M(T) from the  $\Theta^{M}(T)$ .

One further device is useful in working with the moments of the actual frequency spectrum. We define a Debye cut-off frequency  $\omega_D$  (n) such that, for a given moment  $\overline{\omega^n}$  of the actual frequency spectrum, a Debye distribution with this cut-off will yield the same  $n^h$  moment, i.e.

$$\overline{\omega^{n}} = \frac{3}{n+3} \left[ \omega_{D} (n) \right]^{n}, \text{ or } \omega_{D}(n) = \left[ \frac{n+3}{3} \overline{\omega^{n}} \right]^{\frac{1}{n}}, \begin{array}{c} n > -3, \\ n \neq 0. \end{array}$$
(11)

(The limits  $\omega_D(-3) = \lim_{n \to \infty} \omega_D(n)$  and  $\omega_D(0) = \lim_{n \to \infty} \omega_D(n)$  exist.)

For any frequency distribution, a graph of  $\omega_D(n)$  against n can be determined, and the deviation of this curve from a horizontal straight line reflects the departure of the lattice  $G(\omega)$  from the reference  $(\omega^2)$  distribution. Figure 1 shows the  $\omega_D(n)$  curve for a well known model of the f. c. c. lattice, LEIGHTON's[10] one parameter nearest neighbour model. The ratios  $\omega_D(n)/\omega_m$  are actually shown,  $\omega_m$  being the maximum allowed frequency of the lattice. Also shown in Fig. 1 are five of the  $\omega_D(n)$  values as determined for copper from available thermodynamic data. (A somewhat arbitrary estimate  $\omega_m = 4.5 \times 10^{13} \text{ s}^{-1}$  has been assigned for convenience of representation.) It is significant that  $\omega_D(-2)$ and  $\omega_D(-1)$  may be determined with great precision (~0.3%) from the thermodynamic data.

We use the fact that limiting values of the different  $\Theta$  (T) at high and low temperatures are determined by particular  $\omega_D(n)$ :

$$\mathbf{k}_{\mathbf{B}}\Theta_{\mathbf{0}}^{\mathbf{C}} = \hbar \omega_{\mathbf{D}} (-3) ; \ \mathbf{k}_{\mathbf{B}}\Theta_{\infty}^{\mathbf{C}} = \hbar \omega_{\mathbf{D}} (2).$$
(12)





(b) Copper, determined from thermodynamic data 4.

It follows immediately from Eqs (8), (9), and (10) that we can add to this list:

$$\mathbf{k} \ \Theta_0^{\mathbf{M}} = \hbar \ \omega_{\mathbf{D}} \ (-1) \ ; \ \mathbf{k}_{\mathbf{B}} \Theta_{\infty}^{\mathbf{M}} = \hbar \ \omega_{\mathbf{D}} \ (-2).$$
 (13)

We now use Equation (10) and the  $\omega_D$  (n) to obtain high and low temperature expansions for  $\Theta^M$  (T), which are most useful for the final estimation of M(T) values from thermodynamic data. Using the fact that the leading coefficient **a** in the heat capacity expansion (6) is a =  $(12/5) \pi^4 n k_B (\Theta_0^C)^{-3}$ , with  $k_B \Theta_0^C = \hbar \omega_D (-3)$ , we obtain an asymptotic low temperature expansion, the first two terms of which are

$$\Theta^{M}(\mathbf{T}) = \Theta_{0}^{M} \left[ 1 + 6.580 \left\{ 1 - \left( \Theta_{0}^{M} / \Theta_{0}^{C} \right)^{3} \right\} \left( \mathbf{T} / \Theta_{0}^{M} \right)^{2} \dots \right].$$
(14)

At high temperatures we get the rapidly converging expansion

$$\Theta^{M}(\mathbf{T}) = \Theta^{M}_{\infty} \left[ 1 + \frac{1}{7200} \left\{ \left( \Theta^{C}_{\infty} / \Theta^{M}_{\infty} \right)^{2} - 1 \right\} \left( \Theta^{M}_{\infty} / \mathbf{T} \right)^{4} + \frac{1}{423360} \left\{ \left[ \left( \omega_{D}(4) / \omega_{D}(-1) \right)^{4} - 1 \right\} \left( \Theta^{M}_{\infty} / \mathbf{T} \right)^{6} + \dots \right] \right\}.$$
(15)

The expansions (14) and (15) determine  $\Theta^{M}(T)$ , within their regions of convergence, and the use of Equation (10) yields M(T). Note that (15) is significantly more rapidly convergent than is the corresponding high temperature expansion for X(T), Eq. (9), or the corresponding expansion for  $\Theta^{C}$  (T) [11]. In fact, for lattices which have been so far investigated,  $\Theta^{M}(T)$  is within

1% of  $\Theta_{\infty}^{M}$  for temperatures down to about  $\Theta^{M}/3$ . This is a relatively low temperature for a solid, with the zero point energy typically several times the thermal energy at such a temperature. We conclude that it is safe to interpolate between the high and low temperature expansions to get  $\Theta^{M}(T)$  in the intermediate temperature region. It should be noted that the situation is quite different for  $\Theta^{C}(T)$  in the comparable temperature region, for which the corresponding interpolation requires great care.

# **IV. APPLICATIONS**

It is of interest to apply the procedure as outlined to the Leighton nearest neighbour model of the f.c.c. lattice, for which the moments are known[11]. The variation of  $\Theta^C$  (T) and  $\Theta^M$ (T) is shown in Fig. 2. It is convenient to employ  $\Theta_m = \hbar \omega_m \ /k_B$  as a reducing parameter, so that  $\Theta(T)/\Theta_m$  is plotted against  $T/\Theta m$ .





 $\Theta^{c}(T)$  and  $\Theta^{M}(T)$  for Leighton's model of face-centred cube.

$$----- \frac{\Theta^{M}(T)}{\Theta_{m}} \operatorname{against} \frac{T}{\Theta_{m}}$$
$$---- \frac{\Theta^{c}(T)}{\Theta_{m}} \operatorname{against} \frac{T}{\Theta_{m}}$$

One feature noted in the figure should be quite generally true: the temperature variation of  $\Theta^{M}(T)$  this is much less marked than that of  $\Theta^{C}(T)$ . The general nature of this conclusion is supported by the shape of the  $\omega_{D}(n)$  curves of Fig. 1, which are quite typical. The high and low temperature limiting values of  $\Theta^{M}(T)$  are determined by  $\omega_{D}(-2)$  and  $\omega_{D}(-1)$  respectively, while the corresponding values of  $\Theta^{C}$  (T), on the other hand, are determined by  $\omega_{D}(2)$  and  $\omega_{D}(-3)$ . Several conclusions follow: (a) If one insists on describing the vibrational spectrum of an actual lattice by a one parameter Debye spectrum, the error involved in the description of elastic scattering processes (X-ray, neutron) will be less than that for the description of heat capacity; (b) Elastic scattering data on M(T) will yield less detailed information about the actual frequency spectrum G( $\omega$ ) than will heat capacity data.

We next discuss an application of the procedure to an actual case of some interest: copper. (The applicability of the quasiharmonic description of lattice vibrations to a metallic crystal may be questioned; one can only say that metals seem to behave, in their gross vibrational properties, in a similar fashion to insulators.)

In dealing with experimental data for actual crystals, correction must be made for the effects of thermal expansion. This is most conveniently done by considering the volume dependence of  $\Theta^{M}(T)$ . For  $T < 0.3 \ \Theta^{C}$ , the effects of thermal expansion are small, and it will suffice to consider the volume







dependence of  $\Theta_\infty^M$  . This is described [12] by the Grüneisen parameter  $\gamma$  (-2), where

$$\gamma$$
 (n) =  $-\frac{1}{n} \nabla \frac{d}{dV} \ln \overline{\omega^n}$ ;  $\gamma(-2) = -\nabla \frac{d}{dV} \ln \Theta_{\infty}^{M}$ .

 $\gamma$  (-2) can be calculated from thermal expansion data [13] to within a few per cent. We thus calculate the  $\omega_D$  (n) from experimental data at fixed volume  $V_0$ , and then modify the resulting  $\Theta^M(T, V_0)$  values by using  $\gamma$  (-2) and the relation:

$$\Theta^{M}(\mathbf{T}, \mathbf{V}_{\mathbf{T}}) / \Theta^{M}(\mathbf{T}, \mathbf{V}_{0}) = (\mathbf{V}_{0} / \mathbf{V}_{\mathbf{T}})^{\gamma}, \gamma = \gamma (-2)$$
(16)

The results of the calculation for Cu are shown in Fig. 3. The  $\omega_D(n)$  were calculated using heat capacity data [14, 15], thermal expansion data [16-18] and compressibility data [19]; they are shown in Fig. 1. The resulting  $\Theta^{\dot{M}}$  (T, V<sub>0</sub>) curve for fixed volume V<sub>0</sub> is shown as the dotted curve in Fig. 3; after correction for thermal expansion, using  $\gamma$  (-2) = 1.9, we obtain the final  $\Theta^{M}$ (T, V) curve as shown by the solid curve in Fig. 3.

A test of the thermodynamically predicted  $\Theta^{M}(T)$  function for Cu is provided by available X-ray data [5, 20, 21]. The experimental points are also shown in Fig. 3. The agreement is well within the experimental error. We may also conclude that anharmonic effects (which would vitiate some of the general conclusions reached in the foregoing analysis [22]) appear to be small for temperature  $T < 2\Theta^{M}$ .

Finally, we would emphasize that in this example and in others not here discussed the Debye-Waller exponent M has been obtained much more precisely from good thermodynamic data than from direct elastic scattering measurements. Such precise estimates should help to remove some of the uncertainty in the interpretation of scattering measurements both with X-rays and with neutrons.

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# DIELECTRIC CONSTANTS AND LATTICE VIBRATIONS IN IONIC CRYSTALS

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# Abstract — Résumé — Аннотация — Resumen

DIELECTRIC CONSTANTS AND LATTICE VIBRATIONS IN IONIC CRYSTALS. A number of relations have been derived between the static and high-frequency dielectric constants of crystals and the frequencies and polarization properties of optic phonons of small wave-number. The concept of "apparent charge" is important in this connection. It is a quantity which can be measured experimentally but is not the same as ionic charge. It should be possible to determine apparent charges by a combination of the results of measurement of reflectivity in the infra-red, and of neutron inelastic scattering.

CONSTANTES DIÉLEC TRIQUES ET VIBRATIONS DE RÉSEAUX DANS LES CRISTAUX IONIQUES. Les auteurs ont obtenu un certain nombre de relations entre les constantes diélectriques statiques et les constantes de haute fréquence des cristaux et entre les fréquences et les propriétés de polarisation des phonons optiques ayant un nombre d'ondes faible. A cet égard la notion de«charge apparente»est très importante. C'est une quantité que l'on peut mesurer expérimentalement mais qui n'est pas la même que la charge ionique. Il devrait être possible de déterminer la charge apparente en combinant les résultats de mesures de réflectivité dans le domaine infrarouge et de mesures de la diffusion inélastique de neutrons.

ДИЭЛЕКТРИЧЕСКИЕ ПОСТОЯННЫЕ И ВИБРАЦИИ РЕШЕТКИ В ИОННЫХ КРИСТАЛЛАХ. Был выведен ряд соотношений между статическими и высокочастотными диэлектрическими постоянными кристаллов и частотами и свойствами поляризации оптических фонов с небольшим волновым числом. В этой связи имеет значение общее представление о "кажущемся заряде", представляющем собой величину, которая может быть измерена экспериментально, но не является зарядом иона. Представляется возможным определить кажущийся заряд посредством комбинации результатов измерений коэффициента отражения инфра-красных лучей и неупругого рассеяния нейтронов.

CONSTANTES DIELÉC TRICAS Y VIBRACIONES RETICULARES EN CRISTALES IÓNICOS. Los autores establecen una serie de relaciones entre las constantes dieléctricas estáticas y de alta frecuencia de cristales y las frecuencias y propiedades de polarización de los fonones ópticos de bajo número de onda. A este respecto, es importante el concepto de "carga aparente". Es una cantidad que puede medirse experimentalmente, pero que no coincide con la carga iónica. Los autores estiman que debería ser posible determinar las cargas aparentes combinando los resultados de la medición de la reflectividad en la dispersión infrarroja con los de la dispersión inelástica de neutrones.

The dielectric properties of a crystal are closely related to the characteristics of optic modes of vibration for which the wave vector  $\underline{q}$  is close to zero. For example, for a cubic crystal such as an alkali halide,

$$\frac{\epsilon}{\epsilon} \frac{(0)}{(\infty)} = \frac{\omega_{\rm L}^2}{\omega_{\rm L}^2} \left[ \epsilon (0) / \epsilon (\infty) \right] = \left[ \omega_{\rm L}^2 / \omega_{\rm T}^2 \right]$$
(1)

where  $\epsilon$  (0) and  $\epsilon$  ( $\infty$ ) are the static and high frequency dielectric constants, and  $\omega_L$  and  $\omega_T$  are the frequencies of longitudinal and transverse optic modes
for which  $q \rightarrow 0$  (LYDDANE et al.[6]). It has been verified by neutron spectroscopy that this result holds for potassium bromide (WOODS et al. [9]), and for calcium fluoride (CRIBIER et al. [4]). Generalisations of Eq. (1) have been made by various authors, COCHRAN [1], KUROSAWA [5], COCHRAN and COWLEY [2]. In this paper we shall merely quote relevant results, with some extensions, and show how they may be used to relate measurements made by two techniques, infrared spectroscopy and neutron spectroscopy.

For simplicity we consider crystals whose symmetry is such that there are modes of vibration in which all atoms move in a unique direction, such as [100] for a cubic crystal. This reduces the problem to a one-dimensional one. The equations of motion for an undamped free vibration become

$$\omega 2m_{k}U(k) = \sum_{k'} M(kk') U(k') - Z_{k}E$$
(2)

where

 $U(\kappa) \exp i (q \cdot r - \omega t)$ 

is the displacement of an atom of type  $\kappa$ , ( $\kappa = 1 \dots n$ ),

 $\mathbf{E} \exp i (\mathbf{q} \cdot \mathbf{r} - \omega \mathbf{t})$ 

is the macroscopic electric field, and

P exp i (q  $\cdot$  r -  $\omega$ t)

is the polarization, assuming throughout that  $q \rightarrow 0$ . Polarization, macroscopic field and atomic displacements are related by

$$\mathbf{P} = \frac{(\epsilon(\infty) - 1)}{4\pi} \mathbf{E} + \frac{1}{v} \sum_{\mathbf{k}} Z_{\mathbf{k}} \mathbf{U}(\mathbf{k})$$
(3)

where v is the unit cell volume. The quantity  $Z_k$  appearing in Equations (2) and (3) may be called the apparent change, depending on the ionic charge of an atom, its polarizability, and on the short range forces between the atoms. In the general case, not considered here, the apparent charges are not scalar but tensor quantities (COWLEY [3]). Only for the unrealistic "rigid ion" model of a crystal, for which  $\epsilon(\infty) = 1$ , is  $Z_k$  equal to the ionic charge.

For transverse modes E = 0, so from Eq.(1) the transverse frequencies  $(\omega_T)_j$  are the n roots of the equation

Det. 
$$(M - m\omega^2) = 0$$
 (4)

where M is a matrix of order n whose elements are the M(kk') and m is a diagonal matrix formed from the atomic masses. Let  $U_j(k)$  and  $P_j$  specify the atomic displacements and polarization for a mode whose frequency is  $(\omega_T)_j$ , subject to the normalizing condition

$$\sum_{\mathbf{k}} \mathbf{m}_{\mathbf{k}} \left| \mathbf{U}_{\mathbf{j}} \left( \mathbf{k} \right) \right|^{2} = \sum_{\mathbf{k}} \mathbf{m}_{\mathbf{k}} = \mathbf{m} .$$
 (5)

Let  $\epsilon(\omega)$  be the dielectric constant for any frequency  $\omega$ . The following results can then be derived:

(i) The classic dispersion formula is obtained as

$$\epsilon(\omega) = \epsilon(\omega) + \frac{4\pi v}{m} \sum_{j=2}^{n} \frac{P_j^2}{((\omega_T)_j^2 - \omega^2) + i\gamma_j \omega}$$
(6)

This is usually written as

$$\epsilon (\omega) = \epsilon (\omega) + \sum \frac{\frac{4\pi\rho_{j}}{(1 - \omega^{2}/(\omega_{T})_{j}^{2})}$$
(7)

where  $\rho_j$  is the oscillator strength, and each damping factor  $\gamma_j$  is assumed to be very small.

(ii) Eq. (1) is generalized to

$$\frac{\epsilon(0)}{\epsilon(\infty)} = \prod_{j=2}^{n} \frac{(\omega_{\rm L})_{j}^{2}}{(\omega_{\rm T})_{j}^{2}}$$
(8)

Furthermore, Kurosawa has shown that

$$\frac{\epsilon(\omega)}{\epsilon(\infty)} = \prod_{j=2}^{n} \frac{(\omega_L)_j^2 - \omega^2}{(\omega_T)_j^2 - \omega^2}$$
(9)

It follows that

$$\epsilon((\omega_1)_{i_1}) = 0 \tag{10}$$

(iii) The apparent charges satisfy a sum rule

$$\frac{4\pi}{v}\sum_{k}\frac{Z_{k}^{2}}{m_{k}}=\frac{4\pi v}{m}\sum_{j}P_{j}^{2}=\epsilon(\infty)\sum_{j}((\omega_{L})_{j}^{2}-(\omega_{T})_{j}^{2}) \qquad (11)$$

In these equations j = 1 denotes the acoustic mode, which does not contribute.

It is well known that for an alkali halide there is a band of high reflectivity in the infra-red between  $\omega_T$  and  $\omega_L$ . In other crystals the extent of the splitting of the various transverse and longitudinal modes may be expected to be a measure of the strengths of the various resonances. This may be given quantitative expression by combining Equations (7) and (9), to give

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$$\frac{4\pi\rho_{i}(\omega_{T})_{u}^{2}}{\epsilon(\infty)} = \frac{\prod_{i=1}^{l} \{(\omega_{L})_{i}^{2} - (\omega_{T})_{i}^{2}\}}{\prod_{i=1}^{l} [(\omega_{T})_{j}^{2} - (\omega_{T})_{i}^{2}]}$$
(12)

Since neutron spectroscopy can in principle give all the frequencies, it follows that oscillator strengths and the static dielectric constant can be derived directly from the neutron measurements. Both the real and imaginary parts of the dielectric constant as a function of frequency could be obtained, provided that the damping factor associated with each transverse optic mode could be measured from the neutron energy spread.

It has generally been assumed that infra-red measurements give only the frequencies  $(\omega_T)_j$ . But if the  $\rho_j$  are also measured, the frequencies  $(\omega_L)_j$  can be derived by combining Eqs. (7) and (10). Recently careful measurements of the infra-red reflectivity of BaTiO<sub>3</sub> and of SrTiO<sub>3</sub> have been made (SPITZER et al. [7]). The following Table gives the frequencies  $(\omega_T)_j$ and oscillator strengths  $4\pi\rho_j$  which they found, and the frequencies  $(\omega_L)_j$ which we have derived from their results. Frequencies measured by neutron spectroscopy of SrTiO<sub>3</sub> (the subject of a separate paper by R.A. Cowley) are given in brackets. The modes labelled  $(\omega_T)_4$  and  $(\omega_L)_3$  are degenerate, so that  $(\omega_T)_4$  is not infra-red active.

### TABLE I

BaTiO <sub>3</sub>				SrTiO <sub>3</sub>		
j	( <i>w</i> <sub>T</sub> )j	4 <sup>πρ</sup> j	(ω <sub>L</sub> ) <sub>j</sub>	( <sub><i>w</i><sub>T</sub>)<sub>j</sub></sub>	$4\pi\rho_{\mathbf{j}}$	$(\omega_L)_j$
2	34 cm <sup>-1</sup>	2000	180	88(92)	300	175(168)
3	183	2.0	-	178(170)	3.6	- (267)
4	-	0	463	-(267)	0	460
5	510	1,0	735	546	1.9	810

#### MEASURED FREQUENCIES AND OSCILLATOR STRENGTHS

If is of some interest to consider how apparent charges might be measured. In an alkali halide, the apparent charge is related to the effective charge e\* introduced by SZIGETI [8] by

$$\ddot{Z} = \frac{1}{3} (\epsilon (\infty) + 2) e^*$$

Numerical values quoted by Kurosawa are a little greater than the electronic charge. Kurosawa has also attempted to calculate the  $Z^{15}$  for for BaTiO<sub>3</sub> In this type of crystal there are four independent values of  $Z_k$ , for although the three oxygen have equal ionic charges, they are not all equivalent for displacement in a particular direction. (Only two of  $Z_{xx}$ ,  $Z_{yy}$  and  $Z_{zz}$  are equal for each oxygen). Equation (11) supplies one relation,

and the condition  $\sum Z_k = 0$  supplies a second. Further relations can in principle be found by measurement of neutron inelastic scattering cross-section for modes of wave number zero. The scattering cross-section in directly proportional to  $|G_1(Q)|^2$ , where

$$QG_{j}(\underline{Q}) = \underline{Q}\sum_{k} U_{j}(k) b(k) \exp (i\underline{H} \cdot \underline{r}(k))$$
(13)

where  $\underline{Q}$  is the scattering vector, b(k) the scattering length (including the appropriate Debye-Waller factor) and  $\underline{H}$  is a vector of the reciprocal lattice. When each atom is situated on a centre of symmetry, the  $U_j(k)$  are entirely real and can be deduced from the measured cross-sections. The  $Z_k$  may in principle then be deduced from the equations

$$\mathbf{P}_{j} = \frac{1}{v} \sum_{k} Z_{k} U_{j}(k).$$

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## DISCUSSION

H. HAHN: I seem to recall a paper by Maradudin on the influence of anharmonicity on the dispersion relations. I would have expected his theory to give a damping factor something like the one you assume.

W. COCHRAN: I think you are referring to a paper by Maradudin and Wallace. I have not studied it very closely, but I have not been able to get their result into the form of the simple classical dispersion formula which I have shown.

# PRACTICAL ANALYSIS OF NEUTRON SCATTERING DATA INTO SELF AND INTERFERENCE TERMS

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### Abstract — Résumé — Аннотация — Resumen

PRACTICAL ANALYSIS OF NEUTRON SCATTERING DATA INTO SELF AND INTERFERENCE TERMS. Van Hove's original work emphasized the physical significance of the division of neutron scattering data into two parts - one due to the motion of single atoms (self term) and the other due to the time dependence of the well known pair correlation (interference term). Vineyard further emphasized the significance of the "Gaussian" component of the self term. In this paper practical methods, involving modern computing techniques, are discussed by means of which these divisions may be accomplished.

Examples will be quoted from the "scattering law" analysis of Be, Be O, graphite, heavy water, liquid tin and snatowax including the derivation of the generalized frequency function. The direct interpretation of the scattering law in terms of the physical behaviour of the scattering system can then be demonstrated.

ANALYSE PRATIQUE DES DONNÉES SUR LA DIFFUSION DES NEUTRONES EN FONCTION DES TERMES PROPRES ET DES TERMES D'INTERFÉRENCE. Dans ses travaux, Van Hove a insisté sur la signification physique de la division des données sur la diffusion des neutrons en deux catégories : la première concernant les mouvements des atomes individuels (terme propre) et la deuxième les variations de la corrélation de paires bien connues en fonction du temps (terme d'interférence). Vineyard a insisté d'autre part sur la signification de la composante gaussienne du terme propre. Dans son mémoire l'auteur examine les méthodes pratiques (supposant l'emploi de calculatrices modernes), permettant de faire ces divisions.

Il cite des examples de l'étude, du point de vue de la loi de diffusion, de Be, de BeO, du graphite, de l'eau lourde, de l'étuain liquide et du santowax, y compris la détermination d'une fonction de fréquence généralisée. Il peut alors donner une interprétation directe de la loi de diffusion en fonction du comportement physique du système diffuseur.

ПРАКТИЧЕСКАЯ РАЗБИВКА ДАННЫХ ПО РАССЕЯНИЮ НЕЙТРОНОВ НА САМОСТОЯТЕЛЬНЫЙ И ИНТЕРФЕРЕНЦИОННЫЙ ЧЛЕНЫ. В основном труде Ван Гофа подчерживается значение разбивки данных относительно рассеяния нейтронов на две части: одна из них касается данных о движении отдельных атомов (самостоятельный член), а другая - хорошо известной парной корреляции, в зависимости от времени (интерференционный член). Более того, Вайнярд подчерживал значение гауссовой составной части самостоятельного члена. Обсуждаются практические методы, основанные на использовании современных счетно-решающих машин и позволящие произвести такую разбивку.

Приводятся примеры анализа "закона рассеяния" Ве, ВеО, графита, тяжелой воды, жидкого слова и "снатовакса", включая вывод обобщенной функции частоты. Это позволяет выявить возможность непосредственного толкования закона рассеяния, в зависимости от физического поведения рассеивающей среды.

SEPARACIÓN PRÁCTICA DE LOS DATOS RELATIVOS A LA DISPERSIÓN DE NEUTRONES EN TÉRMINOS PROPIOS Ý TÉRMINOS DE INTERFERENCIA. Van Hove destacó en su trabajo original la importancia que reviste desde el punto de vista práctico, la separación de los datos relativos a la dispersión de neutrones en dos partes: una debida al movimiento de los átomos (término propio) y otra debida a la variación en función del tiempo de la conocida correlación de pares (término de interferencia). Vineyard, por su parte, subrayó la importancia de la componente "gaussiana" del término propio. En la presente memoria el autor examina procedimientos prácticos para efectuar esas separaciones utilizando modernos métodos de cálculo.

Expone ejemplos del análisis de la "ley de dispersión" del Be, Be O, grafito, agua pesada, estaño liquido y Santowax, incluyendo la determinación de la función de frecuencia generalizada, lo que permite explicar la interpretación directa de la ley de dispersión en función del comportamiento físico del sistema.

## 1. INTRODUCTION

VAN HOVE [1] has given a general interpretation of neutron inelastic scattering by solids and liquids. The first step in his method is to isolate a scattering law which is a function only of the momentum and energy transferred in the scattering process. The function is then related via a double Fourier transformation to functions representing the motion of the atoms in the scatterer. The Van Hove transformation yields the so-called "spacetime correlation" functions,  $G_s(\mathbf{r}, t)$  and  $G_d(\mathbf{r}, t)$ ; the former corresponds to the motion of a single atom while the latter corresponds to the relative motion of a pair of atoms. Normally the sum of these two functions would be obtained from the neutron scattering data. For the sake of clarity the physical meaning of these functions is given in the Appendix.

The method of data analysis suffers from two disadvantages. First, both the G functions and the original S functions have a complicated form and cannot be understood without reference to a dynamical model of the scatterer; consequently there has been no real advance through the transformation from one function to the other.\* Secondly, when dealing with experimental data a Fourier transformation is equivalent to an analysis in terms of moments and a moment analysis is unsuitable for functions of arbitrary shape. In particular it leads to errors when analysing non-periodic functions with several maxima, such as frequency distributions.

Thus the merit of Van Hove's work lies in two features. First, it emphasizes that the function defined by the neutron cross-sections is the scattering law; and secondly, it provides a framework within which the relationship between dynamic models of the scatterer and the scattering law may be established (it should be noted that the Fourier transformation of a complete theoretical function does not involve the errors which arise in the transformation of experimental data). The procedure adopted here, therefore, is to analyse the scattering law in terms of dynamic (or structural) features of the scatterer.

The major step in this direction is to separate the self and distinct or interference functions. This branch of neutron scattering theory rests upon the assumption of the independence of nuclear and atomic motions. Consequently the scattering lengths of the target atoms can be considered as variables not affecting the atomic motions, and the separation into self and interference terms is a priori possible and reasonable. The difficulty in making this separation is that it is not possible, at present, to control the nuclear scattering lengths and therefore the method must rest upon an adequate theoretical understanding of the two functions. It is the purpose of this paper to discuss how this step may be made within the framework of existing knowledge and experimental results. Once the separation has been accomplished, a more detailed discussion of each function is justified in terms of specific dynamic features of the scatterer (see for example EGEL-STAFF [2, 3].

The method of calculating the self term will be described in Section 2 and the problems which arise when fitting the calculation to experimental

<sup>\*</sup> In this connection it is useful to consider the analysis of scattering by a single crystal where the G functions are not used and all the work is related to dynamic models of the crystal.

data will be discussed. The following two sections will be devoted to a discussion of the interference term and properties of it which are important in fitting to experimental data. The final justification of the numerical separation of observed data into these two parts is the success which these methods have in explaining the measured scattering law, and so far a reasonable degree of success has been achieved as is illustrated in companion papers [7, 8] and the later sections of this paper.

The notation used in the following sections follows that given in [2].

## 2. THE EVALUATION OF THE SELF FUNCTION

The structure of the self term has been discussed by VINEYARD [4] who suggested that  $G_s$  might be represented as a Gaussian function of r having a time dependant width  $[W(t)]\frac{1}{2}$ . It can be shown (e.g. SCHOFIELD [5]) that this is equivalent to assuming that the atoms move in a symmetrical parabolic potential. The terms in  $G_s$  caused by departures from this simple potential do not seem to contribute greatly to the magnitude of the scattering law, and consequently the Gaussian approximation to  $G_s$  is often taken as the leading term in an expansion of the self function. EGELSTAFF[2] shows how W(t) is related to a "generalized frequency distribution"  $p(\beta)$  which may be derived in principle from experimental data by the relationship:

$$\operatorname{Lim}\left[\frac{S_{s}(\alpha,\beta)}{\alpha}\right]_{\alpha \to 0} = p(\beta)/\beta^{2}$$
(1)

EGELSTAFF and SCHOFIELD[6] show how  $S_{\varsigma}(\alpha,\beta)$  can be calculated from  $p(\beta)$  and the Gaussian approximation and in practice their method of calculation is used in an iterative procedure to find  $p(\beta)$  from the experimental data. A computer programme LEAP has been written by McLatchie to evaluate  $S_{\varsigma}(\alpha,\beta)$  from  $p(\beta)$ .

In using Eq. (1) to obtain an initial estimate of  $p(\beta)$  from the data, a reliable technique of extrapolation to  $\alpha = 0$  is required. One method is to use a representation in which a straight line extrapolation is possible. Under the Gaussian approximation the scattering law is a Fourier transform of an exponential function and, if the distribution  $p(\beta)$  is confined to a limited range of  $\beta$  values, the scattering law will be nearly exponential too. Thus in many cases it is convenient to plot log  $(S/\alpha)$  versus  $\alpha$  and make a nearly linear extrapolation to the origin.

A linear extrapolation of this kind is valid for  $\beta$  values at which  $p(\beta)$  is non-zero; for larger  $\beta$  values the value of S comes from "multiphonon" contributions and a graph of log  $(S/\alpha)$  versus  $\alpha$  will include a maximum and then tend to zero as  $\alpha \rightarrow 0$ . A liquid diffusion scattering law always includes significant "multiphonon" terms (since for diffusion  $p(\beta)$  has its maximum value at  $\beta = 0$ ) and consequently in this case, as  $\alpha$  tends to zero, log  $(S/\alpha)$  passes through a maximum and approaches a constant value at  $\alpha = 0$ . For this reason it is unwise to use the extrapolation technique for the interpretation of "quasielastic" peak data on liquids and alternative methods have been discussed by EGELSTAFF[3].

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Sometimes  $p(\beta)$  for non-zero values of  $\beta$  may be composed of two fairly distinct regions, denoted in the following by the subscripts 1, and 2. In this case it is convenient to write:

$$S_{s}(\alpha,\beta) = (1/2\pi) \int e^{i\beta t} e^{-a \left\{ W_{1}(t) + W_{2}(t) \right\}} dt$$
$$= \int S_{1}(\beta^{1}) S_{2}(\beta - \beta^{1}) d\beta$$
$$= e^{-\alpha(\lambda_{1} + \lambda_{2})} \left\{ \delta(\beta) + E_{1}(\beta) + E_{2}(\beta) + \int E_{1}(\beta^{1}) E_{2}(\beta - \beta^{1}) d\beta \right\}$$
(2)

where  $\lambda$  is the Debye-Waller constant and the function  $E_n$  represents the inelastic part of the scattering law  $S_n$ . Consequently both the terms  $E_1$  and  $E_2$  will produce peaks in S if plotted as a function of  $\alpha$ . At values of  $\beta$  which correspond to the second part of  $p(\beta)$  it is better to extrapolate S/ $\alpha$  from a straight line region due to  $E_2$  at large values of  $\alpha$ , and ignore the "multiphonon" part of  $E_1$  occurring at lower values of  $\alpha$ . A numerical calculation of this kind is shown in Fig. 1 which illustrates the points made above.\*



Fig. 1

Illustration of the type of scattering law which is obtained for a two component  $\rho(\beta)$ .

- (a) The  $\rho(\beta)$  function employed is shown by the solid line while the dotted line shows the  $\rho(\beta)$  that would be deducted if the data at a > 1.5 only were used.
- (b) The scattering law at  $\beta$  values corresponding to the peaks and the trough in  $\rho(\beta)$ .
- (c) The  $\log S/\alpha$  plot for these  $\beta$  values.

<sup>•</sup> It is convenient to discuss such calculations in terms of a normalized frequency function  $\rho(\beta)$  which has unit area, and is given by  $\rho(\beta) = (2/\beta)$  Sin h ( $\beta/2$ ) p( $\beta$ ).

ing effect which can arise if: (i) The large  $\alpha$  part only is used i.e.  $\alpha > 1.5$  in this example; and (ii) Single values of  $\alpha$  are used together with a calculated extrapolation, e.g.  $\alpha = 1$  with calculation for Debye type of  $p(\beta)$ . In (i) the frequency function obtained would approximate to the dotted line in Fig. 1a which is similar to the original curve if considerably broadened. In (ii) the same type of result is obtained but the broadening is greater than for (i) in this example.

From an initial estimate of  $p(\beta)$  and a calculation of the corresponding  $S/\alpha$  curves, it is necessary, by comparison with the data, to derive a more accurate distribution. Two factors have to be considered in doing this: one is the resolution broadening effect discussed above and the other is the effect produced by area conservation of the frequency distribution. The latter factor means that to compensate for an error in the S calculated from the initial estimate of  $p(\beta)$  a correction is needed to  $p(\beta)$  which is considerably larger than the percentage error in S. Thus both of these factors imply that the structure in  $p(\beta)$  will be underestimated by the initial estimate. Another factor is that sometimes only part of the  $\beta$  range is covered by the experimental data. This occurs for example in many experiments on the scattering by hydrogenous molecules when vibrational levels are not observed. In such cases the area due to the vibrational levels (if their energy is known from other data) can be found from the slope of the curves at large a through the method discussed by EGELSTAFF et al. [7]., (e.g. from the slope of Fig. 1c curves at  $\alpha$  from 2 to 4).

Thus the 'recipe' for finding  $p(\beta)$  in each case depends upon the nature of this function. In the cases of Be and Be0 (SINCLAIR [8]  $p(\beta)$  has a fairly simple shape and a satisfactory fit to the data was obtained after one iteration. In the case of graphite (see Section 3 and Fig. 2) two iterations were needed because, in addition to the shape, the range of  $p(\beta)$  has to be found. This is equivalent to saying that for Be the amplitude of the S/ $\alpha$  curves had to be adjusted to fit the data whereas in the case of graphite both the amplitude and slope had to be adjusted.

A more complicated case is that of water discussed by EGELSTAFF et al.[7], where initial calculations were required to establish the magnitude of the vibrational component. Of similar kind is the data on Santowax obtained by BRUGGER [9]. The slope of the lines on the  $S/\alpha$  plot required -80% of the area of  $p(\beta)$  to be associated with vibrational modes. The part of the distribution at lower  $\beta$  values has a shape similar to Fig. 1a. A high peak near the origin was required to produce the wide separation between the low  $\beta$  curves observed by Brugger (c.f. separation between  $\beta = 0.5$  and  $\beta = 0.1$  curves in Fig. 1b). The general level of observed intensity between  $\beta = 1$  and 2 required a similar region in  $p(\beta)$ . It is interesting that curves of the shape for  $\beta = 1$  in Fig. 1b have been observed by Brugger [9] for Santowax at low temperature. After the main features of the distribution have been established in this way, two or three iterations may still be needed to get a reasonable fit in such complicated cases [7].

The discussion so far has concerned the fitting of the data to the Gaussian approximation for  $G_s$  and it has been shown that a wide variety of different observed shapes can be explained on this basis. However, in no case so far studied has unambiguous evidence been obtained that the an-





(a) The structure factor  $I_d^0$  for graphite averaged over the *a*-resolution used in the inelastic scattering experiments of Ref. [12] and [13].

(b) The damping term in the approximate interference calculation for the case of room temperature graphite, evaluated using Eq. (6).

harmonic or nonsymmetrical terms in the potential are significant. Positive evidence is required that no matter what shape of  $p(\beta)$  is employed, the experimental data cannot be fitted. The evidence available at present [see e.g. papers by BROCKHOUSE [10], BRUGGER [9] and EGELSTAFF et al. [7] ] suggests that the anharmonic terms may be most important at low values of  $\alpha$  and contribute no more than - 10% of the scattering law at higher values of  $\alpha$ . To settle this question more precise data and further computations are required.

## 3. THE EVALUATION OF THE INTERFERENCE TERM USING ASYMP-TOTIC FORMULAE

The majority of observed scattering laws contain a significant contribution from the interference term  $S_d$ . Thus although the calculated and experimental of  $S_s$  are in fair agreement, a reasonable account of the interference term is required to confirm that conclusion.

VINEYARD [4] and EGELSTAFF [2] have considered the asymptotic forms of  $S_d$ . These limiting forms will be combined in this Section into one formula and compared to experimental data for polycrystalline materials. The formula will, however, be written in a general form.

It is convenient to write the asymptotic formula in terms of the intermediate scattering functions  $I_s$  and  $I_d$ . Vineyard's formula is:

$$I_{d}(\alpha) = I_{d}^{0}I_{s}(\alpha)$$
(3)

where  $I_0^{0} = \int S(\alpha,\beta) d\beta - 1$ , and is derived on the assumption that the motion of a pair of atoms is not correlated. This assumption is valid for atoms an infinite distance and time apart and thus (3) is valid in the limit  $\alpha \rightarrow 0$ ;  $t \rightarrow \infty$ . Egelstaff's formula is valid for near classic systems and any $\alpha$  in the limit  $t \rightarrow 0$ . It is based on the fact that in forming the function  $G_d(\mathbf{r}, t)$  the initial motion of the "distinct" atom is not important; since it only exists statistically as a thermal cloud the  $t^2$  term is missing (this contrasts with the formation of  $G_s$  where the initial motion of the atom at the origin sets up the thermal cloud and gives the term proportional to  $t^2$  in  $G_s$ ). Further, the motion of the thermal cloud will be the same at first for both the "self" and "distinct" atoms - this leads to an identification of the coefficients of  $t^4$  in  $G_s$  and  $G_d$ . EGELSTAFF [2] writes his formula in terms of a time variable y which includes the effect of quantum mechanical terms in the G function. Thus he writes:

$$I_d(\alpha, y) = I_d^0 \exp(-Cy^4/12)$$
 (4)

where  $\overline{C} = \int_{0}^{\infty} \beta^{2} \cosh(\beta/2) p(\beta) d\beta$ .

Equations (3) and (4) may be combined into one equation if the Gaussian approximation for  $G_s$  is employed, i.e.

$$I_{d} = I_{d}^{O} \exp \{-\alpha f(y)\}$$
(5)

where f(y) takes the form in (4) as  $y \rightarrow 0$  and becomes the width function defined in Section 2 as  $y \rightarrow \infty$ . To obtain the correct width function in this limit it is necessary to make f(y) approach a "diffusion" width function and to fix the Debye-Waller factor  $\{e^{-\alpha\lambda}\}$  at its known value from the self term. At shorter times f(y) should exhibit a behaviour similar to the solid. Thus the difference between two Gaussian functions is chosen to yield the limit (4) and, since this involves two parameters (which have to be determined from the values of C and $\lambda$ ), there are no disposable constants. If the diffusion width function is of the type employed by EGELSTAFF and SCHOFIELD[6] the assumed form for f(y) is:

$$f(y) = 2d(y^{2} + c^{2})^{\frac{1}{2}} - 2dc + (4g/\beta_{1}^{2}) \{1 - \exp(-y^{2}\beta_{1}^{2}/4)\} + (4/\beta_{2}^{2}) \{\exp(-y^{2}\beta_{2}^{2}/4)^{-1}\}$$
(6)

and

$$\beta_{2}^{2} = (u/2g) \left\{ \left[ \left( 1 + \frac{1 - g^{2}}{uv} \right)^{2} + \frac{4}{uv} g^{2} \right]^{\frac{1}{2}} - \left( 1 + \frac{1 - g^{2}}{uv} \right) \right\}$$
(7a)  
$$\beta_{2}^{2} = (u/2g) \left\{ \left[ \left( 1 - \frac{1 - g^{2}}{uv} \right)^{2} + \frac{4}{uv} \right]^{\frac{1}{2}} + \left( 1 - \frac{1 - g^{2}}{uv} \right) \right\}$$
  
$$g = 1 - d/c; \ u = 2\overline{C}/3 + d/c^{3}; \ v = (\lambda + 2dc)/4$$

where d is the diffusion constant and c is the time delay for the diffusion process both of which are determined by the self term. It is a simple matter to Fourier transform Eq. (5) using this form for f(y) and a double series of Gaussian terms is obtained. A computer programme SLIM has been written by Heard to evaluate  $S_d$  on this approximation using as input data the  $p(\beta)$  employed for the self term and a tabulation of  $I_d^0$ .

An alternative method of specifying  $\beta_1$  and  $\beta_2$  has some merits. The term in (6) containing  $\beta$  is similar to the analogous term in the width function, and by comparing it with the width function, a value of  $\beta_1$  could be chosen to give the best fit. It is likely that this choice would be equivalent to making the coefficient of y<sup>4</sup> the same in both cases, and from this assumption alternative definitions of  $\beta_1$  and  $\beta_2$  are obtained, i.e.:

$$\beta_1^2 = \frac{u}{g}.$$
(7b)
$$\beta_2^2 = \frac{4}{2}\overline{C}$$

The use of (7b) allows the Debye-Waller facor to take on the value:

$$\lambda = 4g^2/u - 3/\overline{C} - 2dc$$
 (7c)

For the solid this reduces to  $\lambda \overline{C} = 3$ , which is reasonably accurate in the high temperature (i.e. classic) limit - for a Debye solid and an oscillator the actual values are 3.6 and 2 respectively. This difference is probably indicative of the accuracy to which the formula (6) represents the asymptotic formulae (3) and (4).

The sum  $S_s + S_d$  has been calculated using the LEAP and SLIM computer programmes and compared with experiment in several cases. An example, for room temperature graphite, is shown in Figs. 2 and 3. Figure 2a is a curve of  $I_d^o$  (ref. [11]) averaged over the  $\alpha$ -resolution function used in the experiments; the zero level in this diagram is somewhat arbitrary and comparison with the inelastic scattering suggests that it may have been set too high. Figure 2b is the damping factor which multiplies  $I_d^o$  to give  $S_d$ . The self term  $S_s$  has been calculated by the method described in the previous section and an example is given in Fig. 3. Also shown in the figure is the



Comparison of calculation with experiment for the case of room temperature graphite; this figure verifies that the use of Eq. (5) and (6) overestimates the amount of structure in the inelastic spectrum.

sum of self and interference terms compared to the data of EGELSTAFF and COCKING [12] and of HAYWOOD and THORSON [13]. Clearly the data and calculation disagree.

There are several qualifying comments to make about this result. First, a recalculation using the (7b) definitions gave a 30% larger discrepancy; secondly, readjustment of the base line of Fig. 2a could reduce the discrepancy by 30%, and, thirdly, atomic motions in room temperature graphite are not "classical" as required by the theory. However, none of these factors seem likely to eliminate this discrepancy altogether; similar discrepancies are observed at other  $\beta$  values for room temperature graphite and also in the case of heated graphite [12]. The same calculation has been made for Be and compared to the data of SINCLAIR[8] but similar discrepancies are observed. It is concluded that the asymptotic formulae allow too much structure to appear in the inelastic spectrum. In the next Section an explanation of this effect for polycrystalline samples will be considered and liquid samples will be considered in later sections.

The physical effect being demonstrated here is that the damping with time of the structure observed at t = 0 as a result of the correlated motion of atoms can be observed in the experimental data and is not confused with the damping implied by the asymptotic results. It should be noted also that

the De GENNES [14] narrowing effect is derived theoretically by the moment method and hence is equivalent to the asymptotic damping discussed here. Thus the present result is equivalent to saying that the De Gennes narrowing does not account quantitatively for the observable narrowing in coherent scattering data. An experimental test on this point would be, in fact, the same as the test made above.

The virtue of the method described in this Section is that it ensures that the moments of  $S_d$  are given correctly, even though it disagrees with experiment over the region covered in Fig. 3. In the following Section another method will be described which does not satisfy the moment theorems, but gives a reasonable latitude over the experimental range of  $\alpha$  and  $\beta$ .

### 4. ONE PHONON CONTRIBUTION TO THE COHERENT TERM FOR POLY-CRYSTALS.

The region of the scattering law covered by the data shown in Fig. 3 is dominated by the one phonon term in the phonon expansion for crystal scattering. Thus the reason for the discrepancy illustrated by that Figure can be understood by reference to a simple one-phonon calculation.

EGELSTAFF [15] has calculated the one-phonon coherent scattering law for a polycrystal and shown that for simple crystals it is the product of the self term and a type of structure factor (Z). His formula reads:

$$Z = \frac{\Sigma}{\pi} \left[ \pi F(\tau) / 2B\tau Qq \right]$$
(8)

When  $F(\tau)$  is the usual X-ray crystal structure factor for the reciprocal lattice point  $\underline{\tau}$ , B is the volume per nucleus, q is the wave number of the phonon, and hQ is the momentum transferred in the scattering process. In order to conserve momentum the range of Q over which scattering is allowed to take place is:

$$2\pi\tau - q \le Q \le 2\pi\tau + q \tag{9}$$

Since a range of Q is allowed by (9) the scattering from each reciprocal lattice point will be spread along the axis of  $\alpha$  in Fig. 3. This means that the peaks in the function  $I_d^0$  are smoothed out over the range given by (9). In effect this reduces  $I_d^0$  to a value rather close to its average value of zero.

Vineyard's asymptotic limit corresponds to  $\alpha \rightarrow 0$ , which causes the onephonon term to be dominant, and in addition to  $\beta \rightarrow 0$ , which causes the range of Q in (9) to approach zero. Egelstaff's limit corresponds to the opposite situation where  $\alpha \rightarrow \infty$  multiphonon terms are dominant and the integral of S<sub>d</sub> with respect to  $\beta$  is all that can be observed. Thus the above remarks express the fact that the range of momentum transfer is restricted by the limiting conditions themselves, and, as conditions are varied away from either limit, a finite range of Q space becomes available.

The quantitative effect of the condition (9) can be seen from the figures in EGELSTAFF's paper [15]. The sum at (8) produces a rather smooth curve (variations - 15%) except where only one or two values of  $\tau$  are allowed. At large Q many values of  $\tau$  enter the sum and as Q is decreased the number becomes less; thus at large  $\alpha$  the scattering law is smooth and as  $\alpha$  is decreased it remains smooth until a point is reached where large steps appear. The data of Fig. 3 are in the region where smooth behaviour is expected; the steps are expected to occur in the region  $\alpha \leq 0.05$ .

The behaviour of the sum at (8) will be considered in the region of large Q where it gives a relatively smooth function. Since many values of  $\tau$  enter the sum in this region a uniform distribution of reciprocal lattice will be assumed. In this limit the sum may be replaced by an integral viz:

$$Z = \frac{Q_0}{2q} \int \frac{dQ}{Q} \text{ (with limits } Q_0 \pm q) \tag{10}$$

The mean value of Q is written  $Q_0$  and from (9) it is equal to  $2 \pi \tau$ . Carrying out this integration:

$$Z = \frac{1}{2x} \log \frac{1+x}{1-x} = 1 + \frac{x^2}{3} + \frac{x^4}{5} + \text{ etc.}$$
(11)

where  $q \leq Q_0$  and  $x = q/Q_0$ .

The derivation of this expression involves the implicit step of averaging over the range  $Q_0^{\dagger}$  q; and thus when  $Q \rightarrow q$  the sum diverges. In practice because of the close spacing of planes, averaging will normally take place over a smaller interval and the asymptotic limit -  $1 + x^2/3$  - will be valid until Q approaches the difference between neighbouring values of  $2\pi\tau$ . Several such expressions should be written down, one for each branch of the dispersion law. However, this expression will be compared to data taken at a fixed energy transfer and hence a fixed phonon frequency, and for that frequency a suitable average q could be defined which is related to the frequency by a suitable average velocity V.

This ratio x can be given in terms of V, as:

$$x^{2} = (\beta^{2}/\alpha)(kt/2MV^{2})$$
(12)

where M is the mass of an atom in the system. The appearance of  $^{1}/V_{2}$  in this formula implies that the average velocity is weighted towards those for the transverse branches of the dispersion law. (In some circumstances this may provide a method of measuring the velocity of sound as a function of frequency.)

The formulae (11) and (12) give the expected fractional deviation of the one phonon coherent term from the one phonon self term. Two examples of the fit of this expression to the scattering law for Be[8] are given at Fig. 4. The agreement with regard to shape is fair and the values of V used to obtain the fit are somewhat lower than those measured on a single crystal of Be by SCHMUK et al. [16] for these energy transfers. However the increase in the average velocity between  $\beta = 7.5$  and  $\beta = 2.5$  is expected since the transverse modes have energies  $\beta < 2$ . Thus the separation, via these calculations, of the self and interference terms has been more successful in this case than for the previous one.

In concluding this Section it should be pointed out that the damping function of Fig. 2b tends to zero at values of  $\alpha$  and  $\beta$  near the limits of the range covered by the one phonon term. This shows that although it is necessary, in principle, to switch from the methods of this Section to those of the previous one at large  $\alpha$  and  $\beta$ , only a small error would be found in using for51.1



Fig.4

Comparison of calculation with experiment for the case of room temperature Be; this figure verifies that the use of the smoothed coherent correction Eq. (11) gives a reasonable estimate of the difference between the LEAP output and the observed coherent scattering law.

mula (11) with the total self term for comparison with most data. Some care is required at high  $\beta$  in the use of (12), because at sufficiently high values the  $\beta^2$  factor should be offset by the damping effect of Fig. 2b.

In applications where the moments of  $S(\alpha,\beta)$  are important, it will be necessary to take account of these small discrepancies because the positive and negative components in the damping function (Fig. 2b) cancel to make the first moment of  $S_d$  equal to zero.

## 5. APPLICATION OF PREVIOUS DISCUSSION TO LIQUIDS

The general features of the foregoing discussion are applicable toliquid data. Calculations of the self term proceed from the Gaussian approximation through the methods described by EGELSTAFF and SCHOFIELD [6], and the iterative procedure discussed in Section 2. The asymptotic formula of Section 3 is applicable to liquids and when its predictions are compared to the experimental data on heavy water [17], liquid tin [18] and sodium[ 19], the results are essentially the same as those of Fig. 3. Thus momentum damping in the intermediate region of momentum transfer is important for liquids as well as for solids.

Damped phonon models for liquids have been suggested several times and the discussion of Section 4 would be applicable to these models. The comparison of the neutron scattering by solid and liquid sodium by COCKING [19] and solid and liquid tin by COCKING and GUNER [18] has shown that a broad region exists where the scattering laws for the two states are very similar. In this region the formulae (11) and (12) should be adequate to discuss the coherent effects and may give a measure of the velocity of sound in liquids at high frequencies. However tests on this point have not yet been made.

A preliminary calculation of the type shown in Fig. 4 has been carried out for heavy water and is given in Fig. 5. The data in this figure have been taken from Fig. 9 of reference [17b]. It shows that this technique gives an account of  $S_d$  for a liquid, but so far the calculation has not been extended to all  $\beta$  values and therefore the general validity for heavy water is not tested.



Comparison of experiment with a calculation for the case of room temperature heavy water, using the method employed for solids.

## 6. CONCLUSIONS

The calculation of the self and interference parts of the scattering law has been considered. In the case of the self part an iterative procedure has given reasonable fits to the experimental data and yielded frequency distributions for a number of materials. A simple approach to the interference effect involving the behaviour of the one-phonon term has been shown to be successful for polycrystals. The preliminary indications are that it should also be successful for some liquids. An asymptotic formula was developed from earlier work, but this can be shown to exaggerate the effect of the structure in the interference term. However, it has the merit of satisfying the moment theorems and hence may be of merit in applications (such as the calculation of neutron spectra) where the moments are important and some smoothing is implicit elsewhere in the calculations.

In this attempt to analyse the components of the scattering law, two parts of the work can be identified:

(i) The physical properties which give major contributions to the cross-sections are identified; and

(ii) These properties are studied individually, so enabling the neutron data to be properly used and to be linked to information obtained from other sources. As a result of the complex nature of neutron data, most of the conclusions have to be tested by numerical calculations using a large computer. Thus the use of these techniques is related to available computing techniques, the results, however, are sufficiently encouraging to warrant further studies on the same lines.

### 7. ACKNOWLEDGEMENT

It is a pleasure to acknowledge the able assistance of Mr. C. Heard and Mrs. B. Brooks in the many computations upon which this report is based.

### APPENDIX

## PHYSICAL MEANING OF THE CORRELATION FUNCTIONS FOR ISOTOPIC SAMPLES, USED IN THE ANALYSIS OF NEUTRON INELASTIC SCATTERING DATA

1. The self functions

S<sub>5</sub>(p, E) - the scattering law:

If momentum p is absorbed by the scatterer,  $S_s$  is the probability that an energy  $E(\frac{1}{2})$  will be demanded from the same source.

Is(p, t) - the intermediate scattering function:

If momentum p is given to an atom at time t = 0,  $I_s$  is the fraction of that momentum still residing on that atom at time t.  $I_s$  is the Fourier transform of  $S_s$  with respect to E and is related to it in the same way as a decay function is to a line shape.

G<sub>s</sub> (r, t) - the space-time correlation function:

If an atom is at the origin at time t = 0,  $G_s$  is the probability that it is at a distance r from the origin at time t.  $G_s$  is the Fourier transform of  $I_s$  with respect to p.

The parameter p is conveniently expressed in terms of the neutron energy and mass, in this case it is related to the non-dimensional variable  $\alpha as_1 = p^2/2 AT$ , where A is the ratio of nuclear to neutron masses and T is the temperature in energy units,  $\alpha$  is the square of the momentum transferred, expressed as a change in the translational energy of the struck atom. The energy transfer E can also be given in non-dimensional units as  $\beta = \frac{E}{T}$ .

2. The interference functions

 $G_d(\mathbf{r}, t)$  - the space time correlation function:

If the origin is assumed to be on a given atom at time t = 0,  $G_d$  is the probability that any other atom is at a distance r from the origin at time t.

Id (Q, t) - the intermediate scattering function:

If the sample is thought of as an atomic grating, then  $I_d$  is the scattering pattern of this grating as it is seen from the above origin at time t. It is obtained from G by a Fourier transform with respect to r. In the case of the interference functions, it is convenient to use a variable different from the actual momentum p because in this case distances across the grating are being represented. The variable Q is given in Å-1 and is related to p by MQ = p.

 $S_d(Q,\omega)$  - the scattering law:

Correlation term to be added to the self term, necessitated by the fact that the scattered neutron, which has transferred momentum p to the scatterer, is being observed through an atomic grating. In line with the change of momentum variable, it is conventional to use  $\omega$  for the energy transfer where  $\omega = E$ . This function is the Fourier transform of  $I_d$  with respect to t.

### 3. The coherent function

 $(S_s + S_d)$ :

The sum  $S_s + S_d$  has valuable properties in certain limited cases. A typical example is that of scattering by single crystals where  $S_d = -S_s$  over a large range of the variables, so making the coherent function zero. This property is used in the measurement of dispersing laws. Similar properties of this function can be used in the interpretation of liquid scattering (e. g. EGELSTAFF, these proceedings).

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## DISCUSSION

N.A. TCHERNOPLEKOV: Could you clarify the physical meaning of the function  $p(\beta)$  for substances like BeO? To what extent does this function correspond to the frequency distribution function?

P. EGELSTAFF: In such cases  $p(\beta)$  is the Fourier transform of the weighted sum of the velocity correlations for the two different atoms. It does not reduce to the frequency distribution of normal modes except in special cases. However, it has the character of such a distribution. Moreover, if it can be separated by theory into the contributions from each type of atom, enough information is available to carry out calculations of the kind described in the paper.

B.N. BROCKHOUSE: Are you saying that there are separate  $p(\beta)$  functions for beryllium and oxygen in the example chosen?

P. EGELSTAFF: This depends on what you believe to be the dynamics of beryllium oxide. I was not referring to beryllium oxide in particular but to diatomic molecules in general or to systems involving two atoms. In principle, you have a different frequency distribution for the two atoms. In certain special cases, it will be the same.

K.E. LARSSON: For a very large group of materials, namely solids, it would seem that the phonon expansion formula should give accurate results for  $p(\beta)$ . I am thinking in particular of the hydrogenous scatterers in the solid state. Do you consider that your method of treating data, involving the trouble of extrapolating to zero, is necessary and that it offers anything new in these cases?

P. EGELSTAFF: This method is essential for coherent scattering solids. In the case of incoherent scattering solids (such as the ones you

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mention), it provides a check upon the normal phonon expansion and can, in principle, check the validity of the harmonic approximation.

K.S. SINGWI: You have a very simple expression for the interference term obtained, by replacing the sum over  $\tau$  by an integral. As you know, this is true only for a very large value of  $\Pi Q^2$ . Therefore, what do you do in the region where you make these extrapolations and where  $\Pi Q^2$  is not very large?



P. EGELSTAFF: I will reply by reference to the following diagram: We consider only the data in the unshaded region of the diagram, and here  $\Pi Q^2$  is large enough for simple formula to be valid. Thus the interference term is calculated and subtracted from the measured coherent term to give the self term. The problem is now to extrapolate the self term through the shaded region to  $\alpha = 0$ . This problem was considered in the first half of this paper. The behaviour of the coherent term in the shaded region of the diagram is a separate question and will be considered in another paper we are presenting at this Symposium entitled "Theory and interpretation of coherent neutron scattering by liquids". EXPERIMENTAL TECHNIQUE

ΊI

# THE PERFORMANCE AND AUTOMATIC OPERATION OF THE LIQUID HYDROGEN COLD NEUTRON SOURCE IN DIDO

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### Abstract — Résumé — Аннотация — Resumen

THE PERFORMANCE AND AUTOMATIC OPERATION OF THE LIQUID HYDROGEN COLD NEUTRON SOURCE IN DIDO. A brief description is given of the design and operation of the liquid hydrogen cold neutron source in the Dido reactor. Cold neutron gain factors under various conditions have been measured, and the performance relative to the Bepo and EL 3 sources will be discussed. After initial cooling of the refrigerator this source is operated automatically for periods of several days. The problems met in doing this and the techniques employed will be described.

COMPORTEMENT ET FONCTIONNEMENT AUTOMATIQUE DE LA SOURCE DE NEUTRONS RALENTIS DANS L'HYDROGÈNE LIQUIDE, DU RÉACTEUR DIDO. Les auteurs décrivent brièvement l'agencement et le fonctionnement de la source de neutrons ralentis dans l'hydrogène liquide, du réacteur Dido. Ils ont mesuré les facteurs de gain de neutrons lents pour diverses conditions, et examinent le rendement par rapport aux sources Bepo et EL 3. Après un refroidissement initial du fluide réfrigérant, la source fonctionne automatiquement pendant des périodes de plusieurs jours. Les auteurs exposent les difficultés qu'ils ont rencontrées et les techniques qu'ils ont employées pour parvenir à ce résultat.

ХАРАКТЕРИСТИКА И АВТОМАТИЧЕСКОЕ ДЕЙСТВИЕ ЖИДКОВОДОРОДНОГО ИСТОЧНИКА ХОЛОДНЫХ НЕЙТРОНОВ В "+ АКТОРЕ "ДИДО". Дается краткое описание устройства и работы жидководородного источника холодных нейтронов реактора "ДИДО". Измерены данные процесса получения холодных нейтронов в раздичных условиях, обсуждаются характеристики источников, полученых на реакторах ВЕРО и ЕІЗ. После пенвоначального охлаждения с помощью холодильника этот источник работал автоматически по нескольку дней. Дано описание проблем, возникающих в процессе работы.

CARACTERÍSTICAS Y FUNCIONA MIENTO AUTOMÁTICO DE LA FUENTE DE NEUTRONES FRÍOS DE HIDRÓGENO LÍQUIDO DEL REACTOR DIDO. Los autores describen brevemente las características y funcionamiento de la fuente de neutrones fríos de hidrógeno líquido instalada en el reactor Dido. Han medido los factores de ganancia de los neutrones fríos en diversas condiciones y examinan las características de las fuentes en relación con los reactors Bepo y EL 3. Después del enfriamiento inicial del refrigerador, la fuente funciona automáticamente durante varios días. Los autores describen los problemas que se plantean y las técnicas experimentales utilizadas para resolverlos.

## 1. INTRODUCTION

Cold neutrons are commonly defined as those having energies below 0.005 eV. As the thermal neutron spectrum of a reactor is a Maxwell distribution corresponding to the temperature of the reactor moderator there will be only a very small component of cold neutrons perhaps 1 or 2% of the total thermal neutron flux. With such low fluxes of cold neutrons only low resolution experiments are possible. An obvious way to increase the cold neutron flux is to cool the moderator of the reactor, or part of it. Fig.1 shows the calculated neutron fluxes which would be obtained at four different



Fig.1

Maxwell distributions of neutron flux.

neutron wavelengths as a function of moderator temperature, assuming the total neutron flux is constant and is in thermal equilibrium with the moderator. These curves have been drawn for an experiment with constant resolution, that is  $\Delta t \infty t$ , not for a constant time-of-flight interval  $\Delta t$ . This is a more realistic picture for an experiment using, say, a rotor running at various speeds as monochromator. The maximum flux which can be obtained at any wavelength is the same, provided that the moderator temperature can be adjusted to the optimum value.

In practice one has to insert the cold moderator in an existing hole of a reactor, so its volume will be severely limited and the neutrons are not likely to reach thermal equilibrium with the cold moderator. In addition it is not simple to vary the moderator temperature to any precise value for a particular experiment. However, experiments with liquid hydrogen moderator in a 4-in hole in the reactor Bepo [1] showed that a useful increase of cold neutron flux could be achieved. The gain of 5Å neutrons was a factor 7, while at longer wavelengths the factor rose to 25. Such increases are most valuable for cold neutron scattering experiments, even though they are much lower than the maximum theoretically possible, and so a second liquid hydrogen moderator was designed and installed in the reactor Dido.

## 2. GENERAL DESCRIPTION

The layout of the equipment is shown in Fig. 2, and details of the section inside the reactor in Fig.3. The moderator chamber is a cylindrical vessel A, with one end convex and one end concave, containing a cooling coil B. Liquid and gaseous hydrogen from the refrigeration plant is circulated through







Fig.3

The liquid hydrogen loop in Dido.

the cooling coil, keeping the chamber near 20°K, while the main volume of the chamber is filled with liquid hydrogen by condensation of gaseous hydrogen under 70 psig pressure from a cylinder. The moderator chamber is enclosed by a vacuum case C to provide thermal insulation and also it is strong enough to contain any possible explosion of the liquid hydrogen. As the vacuum case is thick-walled, nuclear heating amounts to some 500 W, concentrated mainly in the end nearest the reactor core; to remove this heating a stream of carbon dioxide E is circulated round the tip of the apparatus. Keeping the vacuum case cool is necessary not only to preserve its strength and to prevent grain growth, but also to reduce the thermal radiation heating of the surface of the moderator chamber.

The vacuum case acts as an evacuated flight path for neutrons scattered from the moderator chamber in the direction of the reactor face. These neutrons pass through a collimator, through beryllium and bismuth filters G, and through a second collimator to the scattering apparatus [2] outside the reactor. The liquid and gaseous hydrogen lines are conveyed out of the vacuum case separately along side tubes F, curved to reduce radiation streaming. The beryllium filter G is mounted on a turret, so that it can be moved out of the neutron beam and replaced by open hole H, or by shielding material to cut off the beam. The beryllium is cooled by liquid nitrogen to 77°K to improve its transparency to cold neutrons; to convey liquid nitrogen into the turret (which has to be rotated through 245° between its extreme positions) eight turns of coiled pipes I are employed- the coils wind up as the turret is rotated to one extreme and unwind as it is rotated to the other.

The refrigeration plant is situated in a building outside the reactor containment building. A Corblin 2CV250 diaphragm compressor takes hydrogen at 5 psig from a static gasholder of 200 ft<sup>3</sup> volume, and delivers the gas at 1500psig and a flow of 20 ft<sup>3</sup>/min to the liquefier. The liquefier of the Joule-Thomson type, expands the high pressure gas to 15 psig and the whole mixture of gas and liquid from the expansion valve passes along the pipeline 60 ft long to the reactor, through the cooling coil of the moderator chamber and back to the liquefier. Most of the liquid hydrogen evaporates as it travels round the circuit, but the cold gas returning to the liquefier passes back through the low pressure sides of the heat exchangers. Thus the liquefier operates as a balanced refrigerator, not as a conventional liquefier in which the total heat of the evaporated hydrogen is discarded. Liquid nitrogen for the liquefier is supplied continuously from a 450 gal(imp) tank. To reduce thermal radiation heating of the long pipeline the section outside the reactor building is surrounded by a radiation shield cooled by the cold nitrogen gas evaporated by the liquefier. The section inside the reactor building has a similar radiation shield cooled by cold nitrogen gas evaporated by the beryllium filter.

### 3. SAFETY

The principal disadvantage of using liquid hydrogen as a cold neutron source is its inflammability; the possibility of an explosion inside the reactor must be given serious consideration. A possible mechanism for an explosion could be that air leaks slowly into the vacuum case and solidifies on the moderator chamber: under irradiation the solid oxygen is converted to ozone, which is unstable. Spontaneous detonation of ozone could fracture the moderator chamber and initiate a hydrogen explosion. (Such ozone explosions have occurred in liquid nitrogen loops in reactors where oxygen has been present as an impurity). A second possible mechanism could be a fracture of the vacuum case admitting air suddenly; the liquid hydrogen in the moderator chamber would boil violently and might build up sufficient pressure to burst the chamber. An explosion could be initiated by a static electrical discharge produced by the bursting chamber. To render the system safe so that the reactor cannot be damaged, it is necessary to ensure that no air can enter the vacuum case to come in contact with hydrogen and form an explosive mixture, or to make the vacuum case strong enough to contain any possible explosion. The former remedy unfortunately becomes very complicated in practice, so the latter remedy is adopted and the walls of the vacuum case are made strong enough to contain any possible explosion. Tests in which 300 cm<sup>3</sup> of liquid hydrogen was exploded with various amounts of solid air in an 8-cm diam. tube showed that pressures up to 75 atm were developed [3]. To contain such explosions safely the vacuum case was made of magnesium-zirconium alloy ZA with walls 6 mm thick.

If there is a sudden burst of air into the vacuum case, the maximum amount that will condense in the cold parts of the apparatus (i. e. the moderator chamber and the hydrogen circulating pipes) is limited by the amount of liquid hydrogen in the chamber.  $250 \text{ cm}^3$  of liquid hydrogen boiling off will condense only 10 g of solid air, which is only a few per cent of the stoichiometric mixture to give complete combustion. An explosion under these conditions would be very much less severe than those obtained in the tests. On the other hand a small air leak into the vacuum case might pass unnoticed, as the air would condense on the cold parts of the system without appreciably affecting the vacuum. If the apparatus were run for a long time in this condition a considerable quantity of solid air might collect, even exceeding the stoichiometric amount, and similar pressures to those measured in the tests might be developed if an explosion were initiated.

To avoid such a large explosion a monitoring system is employed. The diffusion pump which evacuates the vacuum case pumps into a closed 21 volume. Though most constituents of any air leaking into the vacuum case will solidify on the cold parts of the apparatus, the helium, hydrogen and neon in the atmosphere will not condense, but will be pumped out into this closed 21 volume. The pressure of helium, hydrogen and neon which collects in the closed volume will therefore be a measure of the amount of solid air which has solidified inside the vacuum case. A **Pirani gauge connected** to a simple transistor amplifier closes down the whole hydrogen loop if the pressure in the closed volume rises above 250  $\mu$ m. This corresponds to about 7 g of solid air (depending on the amount of hydrogen in the atmosphere locally); this amount of air is so small that the closed volume may be evacuated several times during a long run without warming up the hydrogen system to evaporate the air and the system will still be perfectly safe.

As an additional safeguard to prevent the compressor pumping hydrogen into the reactor building if the hydrogen lines were broken by some accident, isolation values are provided on the lines where they enter the reactor building. There are four values, one on the inlet and one on the outlet hydrogen lines on each side of the wall. These values are opened pneumatically and closed by springs; they close automatically if the vacuum fails.

### 4. PERFORMANCE ON AUTOMATIC CONTROL

The liquid hydrogen loop has been run for a total of more than twelve hundred hours. Before the loop can be started up the charcoal cleaners of the liquefier have to be regenerated for at least 12 h, and it takes 4 h from first admitting liquid nitrogen to the liquefier before the loop is in a steady state with the moderator chamber full of liquid hydrogen, ready for use as a cold neutron source. It is intended to close down not more than once a week, and eventually only once a month when the reactor is shut down, so that cold neutrons will be available for all the time the reactor is running. So far the longest run has been 200 h with the plant running on automatic control, being left unattended overnight. At the end of such a period the plant closes itself down without attention.

The requirements for such a piece of equipment to run automatically are that it needs no adjustment, it feeds itself with hydrogen and liquid nitrogen, and that it is safe if any mishap occurs, such as a blockage or an electricity failure. To reduce the need for adjustment the expansion valve of the liquefier is made in the form of a capillary, 0.3 mm internal diameter, instead of the more usual needle valve. As the bore of the capillary is much larger than the annular gap of a needle valve to provide the same flow resistance, there is less chance of its becoming blocked during the run. A bypass needle valve is incorporated in parallel with the capillary (this is necessary for the initial cooling down of the loop) and this valve may be adjusted from day to day to compensate for any partial blockage of the capillary.

The hydrogen loop being a closed circuit there is no need to add hydrogen gas to the system once it has cooled down and reached its steady operating conditions. The feed of liquid nitrogen comes from a 450 gal (imp) storage vessel, and is controlled by a vapour pressure bulb at the top of the liquid nitrogen bath of the liquefier. In case any mishap occurs when the loop is running unattended, relief valves are provided on all sections of the circuits so no dangerous high pressures can build up. The most common fault is a blockage in the loop, restricting the flow of liquid hydrogen. This causes the loop to warm up, and the consequent out-gassing from surfaces which had condensed out traces of air operates the vacuum monitor, which switches off the hydrogen compressor and so closes down the plant. The only serious fault which is not covered is a high pressure hydrogen burst in the liquefier room. But all the electrical equipment in that room is flameproof, so even if the compressor continued running until the gasholder was empty the local concentration of hydrogen in the atmosphere would cause no harm.

Tests have been carried out to discover the reasons for shut-downs, and the chief trouble appears to be due to impurities in the hydrogen gas supply, particularly nitrogen. At first sight it would appear that the hydrogen in the closed circuit should become more pure as time goes on, impurities being removed by the two charcoal traps at 77° K and 20° K in the liquefier. But it appears that these low charcoal traps do not remove the impurities completely, but only delay their progress round the circuit. Nitrogen is first of all absorbed at the beginning of a charcoal trap; after a time it is carried through to the end of the trap, where it is evolved into the gas stream again. The nitrogen particles are carried round the loop in liquid hydrogen, and are deposited where the hydrogen boils. The loop usually blocks with solid nitrogen at the point where most of the hydrogen boils, that is inside the moderator cooling coil, and not in the liquefier where the pipes are much smaller in bore. Longer runs should be obtained when a new more efficient charcoal cleaner is installed outside the liquefier.

### 5. MEASUREMENT OF COLD NEUTRON INTENSITY

To observe the gain in cold neutron flux when using the liquid hydrogen source, the neutron spectrum was measured with and without liquid hydrogen present. The neutron beam from the beryllium and bismuth filters was passed through a curved slot chopper. The neutrons transmitted by the chopper spinning at a given speed are roughly monochromatic and are counted by a BF<sub>3</sub>detector immediately behind it. By varying the rotor speed the wavelength range from 4 to 10Å was covered; at longer wavelengths the neutron flux without the liquid hydrogen source was too small to be counted easily.

The gains observed are shown in Fig. 4. The lower curve (full circles) was obtained with the chamber full of normal hydrogen (75% ortho-hydrogen), the upper curve (open circles) using hydrogen with its para-hydrogen content enriched. This was prepared by passing normal hydrogen over ferric hydroxide catalyst at 20° K; its composition was not measured, but it would probably contain a few per cent ortho-hydrogen.



Gain in cold neutron flux.

The liquid hydrogen source raises the flux of  $4\text{\AA}$  neutrons by a factor 4, the flux of  $10\text{\AA}$  neutrons by a factor of 7.5 with normal hydrogen, or 8.4 with enriched para-hydrogen.

## 6. COMPARISON WITH EL3 AND BEPO

The gains in cold neutron flux at various wavelengths in Dido are compared with Bepo and EL3 [5] in the following table.

### TABLE I

## GAIN IN COLD NEUTRONS

	5Å	7. 5Å	10Å
Dido (n-H <sub>2</sub> )	5.2	7.3	7.5
(p-H <sub>2</sub> )	5.4	7.9	8.4
Веро	7	20	25
EL3 (H <sub>2</sub> )	6.6	(19)	
(2/3H <sub>2</sub> , 1/3D <sub>2</sub> )	8.1	(16)	

From these figures Dido cold neutron source appears less efficient than either of the others. There are several reasons for this and the following factors which effect moderation may be noted.

(i) Bepo graphite temperature was  $400^{\circ}$  K; Dido heavy water temperature is  $335^{\circ}$  K. If the cold neutron beam emerging from both cold moderators has the same mean temperature, the gain in Bepo will appear to be 1.4 times the gain observed in Dido.

(ii) The cold moderator in EL3 is in a hole 6 inches in diameter, while the holes in Bepo and Dido are only 4 inches in diameter. When space has been taken by a thick-walled vacuum case and the necessary gap for thermal insulation, the diameter of the moderator chamber in EL3 is 10.6 cm, while the diameters in Bepo and Dido are less than 8 cm. EL3 has therefore the advantage of size.

(iii) In Bepo the hydrogen moderator is in the centre of the core, surrounded by fuel elements, and in a nearly isotropic flux of thermal neutrons. Many of the neutrons emerging in the beam from the reactor will have been scattered from the surface of the liquid hydrogen and will have suffered only one or two collisions. (This is one good reason why moderation is far from complete although the dimensions of the chamber are many times greater than the neutron mean free path in liquid hydrogen). In Dido, however, and in EL3, the moderator chamber is outside the reactor core where there is a considerable neutron flux gradient. In the absence of the liquid hydrogen moderator the neutron beam comes from a point in the heavy water moderator of the reactor some 15 cm nearer to the reactor core than the point of origin when the chamber is full of liquid hydrogen. At the latter point the thermal neutron flux is perhaps only half its value inside the heavy water. Thus Dido cold moderator has to gain a factor two before the cold neutron flux is increased at all.

(iv) The ideal shape for a cold moderator would be a large sphere, immersed in an isotropic flux of thermal neutrons, with a relatively small hole from the centre from which a neutron beam may emerge. This would correspond to the geometry of a "black body" furnace. In practice the size of the sphere of cold moderator is limited by the dimensions of any hold available in a reactor, by the refrigeration capacity available, and by absorption of neutrons by the substance used as cold moderator. The size of the hole from which the neutron beam emerges is made as large as the moderator chamber (or larger) to obtain the most intense beam of neutrons (at the expense of angular resolution). So a "black body" geometry is not possible.

The design of moderator chamber in Dido is a compromise; the whole area of the chamber is viewed by the collimators, but the central part of the chamber is made concave so that it acts as a rudimentary "black body" source. Most of the neutrons emerging from the central portion of the surface will have travelled through several centimeters of liquid hydrogen, and will not simply have been scattered from the surface after one or two collisions. Thus moderation to the low temperature should be more complete. It is not possible to check the improvement effected by this design without replacing the chamber by one with convex surfaces.

(v) Absorption of neutrons by liquid hydrogen will tend to reduce the efficiency of the cold moderator, especially as cold neutrons are preferentially absorbed. It is difficult to measure this effect, as altering the absorption cross-section invariably entails altering other parameters. Experiments on the similar loop at Saclay with hydrogen-deuterium mixtures [5] have shown that the flux of 4.45Å neutrons is increased as hydrogen is diluted with deuterium, and reaches a maximum for about 60% deuterium. However at neutron wavelengths greater than 5.6Å the smaller absorption in deuterium is balanced by the smaller efficiency of deuterium as a moderator, and pure liquid hydrogen gives the highest cold neutron flux. Experiments were make at Harwell by varying the ortho and para-hydrogen content of our moderator. For thermal neutrons ortho and para-hydrogen have the same cross-section, but for cold neutrons the ortho-hydrogen cross-section rises to 100 b per molecule, the para-hydrogen cross-section falls to 4 b per molecule. Though the absorption cross-section is not altered, the amount of absorption in para-hydrogen will be less than in ortho-hydrogen as the neutron path length will be smaller because there are fewer collisions. This effect is shown by the two curves in Fig. 4. Hydrogen enriched in parahydrogen content gives a higher cold neutron flux than normal hydrogen, and the difference is greatest at long wavelengths where absorption has the greatest effect. Para-hydrogen may be a very good moderator for providing cold neutrons; thermal neutrons are scattered with a high cross section (and thus moderated to very low energies) but when they reach low energies the neutrons are no longer scattered appreciably and so can escape easily. Thermal neutrons will not be absorbed greatly nor will the cold neutrons, for they escape so quickly. In fact para-hydrogen should act more or less as a cold neutron filter, scattering (and moderating) thermal neutrons, but allowing cold neutrons to pass freely. Para-hydrogen has another good feature as a moderator, as the para to ortho transition which may occur when a neutron is scattered takes a large amount of energy from the neutron. The performance of such a moderator has not yet been investigated fully.

## 7. CONCLUSIONS

By using this liquid hydrogen loop in Dido we have increased the flux of 4Å neutrons by a factor 4, and the fluxes of longer wavelength neutrons by rather greater factors. The value of this increase [2] is that it not only increases the statistical accuracy of results of neutron scattering experiments, or reduces the length of experiments, but it increases the cold neutron flux without increasing the background of  $\gamma$ -rays and fast neutrons. This increase of the counts-to-background ratio is a great asset. For experiments with good resolution, long counting times are still necessary to achieve the necessary statistical accuracy, so it is a great advantage if the cold neutron source runs unchanged for long periods. The liquefier requires a day for regeneration and starting up, and the most convenient length of time for running the cold moderator is one month, so that it is closed down only when the reactor is not operating. At present the average run is only 5 d but with planned improvements it is hoped to extend this to a full reactor operating period of 24 d.

The gain in cold neutron flux is rather less than measured with the loop in Bepo, but this is largely due to the arrangement of the cold moderator relative to the core of the reactor. To obtain greater effeciency the Dido installation would require a larger hole in the reactor so that a more sophisticated shape of cold moderator could be employed, and the moderating material could be changed to one of lower moderating efficiency but with negligible absorption, such as liquid deuterium. An installation in a tangential hole in a reactor would be a considerable improvement; the thermal neutron flux gradient would be perpendicular to the axis of the moderator chamber, (instead of parallel to the axis). and also the background of  $\gamma$ -rays would be much smaller than in a radial hole.

However, the thermal neutron flux of Dido is  $4 \times 10^{13}$  n/cm<sup>2</sup> s at the end of the hole being used (which is, 20 times as great as that in Bepo), and with the liquid hydrogen moderator in operation a very intense source of cold neutrons is available for inelastic scattering experiments, with a relatively low background.

## ACKNOWLEDGEMENT

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## DISCUSSION

W. WHITTEMORE: Could you comment on the differences between the Saclay results and those you obtained yourself with the liquid-hydrogen, cold-neutron source?

J. WEBB: The collimation has been improved so that only the central portion of the chamber is now viewed and the gain in cold neutrons is therefore higher.

W. WHITTEMORE: How many hours, or days, do you run at a time?

J. WEBB: 200 h is the longest run so far. The average of the last few runs has been about 100 h. We would like to run for a complete reactor cycle of 24 d; most of our failures lately have been quite trivial, such as oil-leak-age from the compressor.

W. WHITTEMORE: Surely, after 200 h, all your liquid hydrogen would be in the para state so why do you speak of diluting it with para?

J. WEBB: The rate of conversion to para-hydrogen is so slow that even after 200 h an appreciable fraction of ortho-hydrogen would remain, perhaps 10 - 15%. The spectrum measurements on normal and para-hydrogen were carried out within a few hours, so no alteration of the ortho- and parahydrogen content would have occured.

W. WHITTEMORE: Is there any evidence that para-hydrogen is converted to ortho-hydrogen in the gamma-ray field or the neutron field? You would then get ortho-hydrogen at the end of a long run and the addition of para-hydrogen might make a significant difference.

J. WEBB: We have no evidence of this at all. I do not think the crosssections are large enough for that.

G. SQUIRES: In view of the larger scattering cross-section of orthohydrogen, would it not be advantageous to use 75% ortho-hydrogen in a smaller volume of moderator, rather than a larger volume of pure parahydrogen?

J. WEBB: Ortho-and para-hydrogen have comparable cross-sections for thermal neutrons, so there is some minimum volume which can be used to provide the first stage of moderation below reactor temperature. However, it may be true that a smaller volume of ortho-hydrogen would provide a greater over-all moderating efficiency than a larger volume of para-hydrogen. There are few experimental data on the subject, and no calculations have been made.

W. WHITTEMORE: Do you have any information to indicate whether your cold neutron spectrum is in equilibrium with the source? The results we presented two years ago\* indicated that a para-hydrogen container 6 inches in diameter does not give an equilibrium spectrum.

J. WEBB: Our measurements of the neutron spectrum from our Bepo liquid hydrogen source showed a peak corresponding to the reactor temperature, with a pronounced tail on the low energy side. This curve could not be analysed as the sum of two Maxwell distributions. Similarly, Van Dingenen's spectrum measurements on methane and liquid hydrogen at 20°K departed widely from Maxwell distributions. In no case has perfect thermal equilibrium at the moderator temperature been observed.

\* "Inelastic Scattering of Neutrons in Solids and Liquids", IAEA, Vienna (1961) 421.

N. W. TCHERNOPLEKOV: What is the energy release in the Dido moderator? I have a second question regarding the discrepancy between your results and those obtained with the French EL-3 reactor using normal hydrogen or a mixture of hydrogen and deuterium as moderator; could this discrepancy be due to the moderator volume being too small?

J. WEBB: The nuclear heating is of the order of 25 W in Dido. In answer to your second question, I think it would be true to say that at long wavelengths the moderating efficiency of the deuterium is too small, so that with this hydrogen/deuterium mixture the chamber is in, fact too small to provide the optimum flux of cold neutrons.

# A NEW APPARATUS FOR INELASTIC, QUASI-ELASTIC AND ELASTIC COLD NEUTRON MEASUREMENTS\*

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## Abstract — Résumé — Аннотация — Resumen

A NEW APPARATUS FOR INELASTIC, QUASI-ELASTIC AND ELASTIC COLD NEUTRON MEASUREMENTS A new chopper apparatus for use at the Brookhaven High Flux Beam Reactor is now under construction. It is a three-element phased rotor system. The rotors are 80 cm in diameter, run at a maximum speed of 15000 rev/min, and are designed to give three neutron bursts of monochromatic neutrons per revolution. Two rotors spin about a horizontal axis whereas the third operates vertically. The system can be operated with either one, two or three of the chopper elements, depending on the type of measurement that is completed. For inelastic measurements where the neutron gains energy, a double rotor system will be most useful. For this configuration the burst time and wave length spread (full widths at 1/2 maximum) will be 16 µs and 0.16 Å for 4 Å incident neutrons, and the intensity at the sample ( $4 \times 1.6$  cm) will be  $2 \times 10^6$  n/s. For quasi-elastic and elastic neutron measurements the three-rotor configuration will be best suited. The corresponding burst time and wave length spread can be as small as 8 µs and 0.04 Å giving an intensity of 10<sup>4</sup> n/s on a sample of ( $4 \times 0.8$  cm). The wave length and time resolution are adjustable between the above two limits in such a way as to obtain the maximum neutron intensity for a given experiment.

UN NOUVEAU APPAREIL POUR LES MESURES DE DIFFUSION INÉLASTIQUE, QUASI-ÉLASTIQUE ET ÉLASTIQUE DES NEUTRONS LENTS. Un nouveau sélecteur destiné au réacteur à haut flux de Brookhaven est actuellement en construction. Il s'agit d'un dispositif à trois rotors déphasables. Les rotors ont un diamètre de 80 cm, tournent à une vitesse maximum de 15000 tours par minute et sont conçus de manière à fournir trois bouffées de neutrons monochromatiques à chaque tour. Deux rotors tournent autour d'un axe horizontal, le troisième, autour d'un axe vertical. Le dispositif peut fonctionner avec un, deux ou trois éléments, selon le type de mesure que l'on se propose de faire. Pour les mesures de diffusion inélastique où les neutrons gagnent de l'énergie, un dispositif à deux rotors sera très utile. Pour cette configuration, la durée et la dispersion de la longueur d'onde (largeur totale à mi-hauteur) seront respectivement de 16 µs et 0,16 Å pour des neutrons incidents ayant une longueur d'onde de 4 Å; l'intensité de la bouffée sur l'échantillon (4 × 1, 6 cm) sera de  $2 \times 10^6$  n/s. Pour les mesures de diffusion quasi-élastique et élastique, la configuration à trois rotors conviendra parfaitement. La durée de la bouffée et la dispersion de longueur d'onde correspondante peuvent atteindre des valeurs aussi faibles que 8 µs et 0,04 Å, ce qui donne une intensité de  $10^4$  n/s sur un échantillon de  $4 \times 0,8$  cm. La longueur d'onde et la résolution en temps peuvent être ajustées entre les deux limites susimentionnées, de manière à obtenir l'intensité de flux maximum pour une experience déterminée.

НОВЫЙ ПРИБОР ДЛЯ ИЗМЕРЕНИЯ НЕУПРУГОГО, КВАЗИУПРУГОГО И УПРУГОГО РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРО-НОВ. В Брукхейвене на реакторе с пучком большой интенсивности строится новый прерыватель. Он представляет собой трехэлементную сфазированную роторную систему. Роторы диаметром 80 см вращаются с максимальной скоростью 15 000 оборотов в минуту. Они предназначены для получения трех вспышек монохроматических нейтронов за один оборот. Два ротора вращаются вокруг горизонтальных осей, третий действует в вертикальном направлении. Система может работать с одним, двумя или тремя элементами прерывателя, в зависимости от запланированных измерений. При измерении неупругого рассеяния, в котором нейтрон получает энергию, наиболее эффективна система двух роторов. При такой конструкции время вспышки и интервал длины волны (длина на половину высоты) будут равны 16 мксек и 0,16 Å для падающих нейтронов с длиной волны 4 Åи интенсивность на образце (4x1, 6 см) будет равна 2-10° нейтронов в секунду. Для измерения квазум ругого и упругого рассеяния нейтронов лучше всего подходит конструкция из трех роторов. Соответствующие время вспыжи и интервал длины вол-

<sup>\*</sup> Work supported by the United States Atomic Energy Commission.
ны могут быть уменьшены до величин 8 мксек и 0,04 Å, далодих интенсивность на образце (4x0,8 см), равную 10<sup>4</sup> нейтронов в секунду. Длина волны и разрешение времени отрегулированы между двумя упо-Мянутыми пределами таким образом, чтобы получить в данном опыте максимальную интенсивность нейтронов.

NUEVO APARATO PARA MEDICIONES INELÁSTICAS, CUASI ELÁSTICAS Y ELÁSTICAS DE NEUT RONES FRÍOS. Se está construyendo un nuevo selector mecánico destinado al reactor de flujo intenso de Brookhaven. El aparato es del tipo de tres elementos rotores en fase. Los rotores, de 80 cm de diámetro, giran a una velocidad máxima de 15000 rev/min y se han diseñado de modo que emitan tres ráfagas de neutrones monocromáticos por revolución. Dos de los rotores giran alrededor de un eje horizontal, mientras que el tercero lo hace verticalmente. El sistema puede funcionar con uno, dos o tres elementos selectores, según el tipo de medición que se quiera efectuar. Para las mediciones inelásticas en que los neutrones ganan energía, lo más indicado es utilizar un sistema de dos rotores. En este sistema, la duración de las ráfagas será de 16  $\mu$ s y el ensanchamiento de longitudes de onda (amplitud plena a la mitad del valor máximo) de 0, 16 Å para neutrones incidentes de 4 Å; la intensidad en la muestra (4 × 1,6 cm) será de 2 × 10<sup>6</sup> n/s. Para las mediciones cuasi elásticas y elásticas resultará más apropiado el sistema de tres rotores. La duración de las ráfagas y el ensanchamiento de longitudes de onda pueden llegar a un mínimo de 8  $\mu$ s y 0,04 Å, respectivamente, lo que representa una intensidad de 10<sup>4</sup> n/s en una muestra de 4 × 0,8 cm. La longitud de onda y la resolución en tiempo pueden graduarse entre los dos lúmites citados, de modo que se obtenga la intensidad neutrónica máxima para un experimento determinado.

## 1. INTRODUCTION

A new time-of-flight neutron spectrometer for research in the solid and liquid state physics is under construction for use at the Brookhaven High Flux Beam Reactor. The system consists of three rotors spinning at a maximum speed of 15 000 rpm with a constant phase angle relative to each other, and produces bursts of monochromatic neutrons at the sample. The scattered spectrum is analysed by the time-of-flight method using a multichannel time analyser.

In order to obtain optimum neutron intensity and resolution for a given experiment, it is important to be able independently to change the burst time  $\Delta t$  and wavelength spread  $\Delta \lambda$  of the neutrons falling on the sample. For processes in which the incoming neutron gains energy and results in a large change in neutron velocity, a small uncertainty in the burst time,  $\Delta t$ , is more important than a small wavelength uncertainty.  $\Delta \lambda$ . (This is the principle underlying various cold neutron apparatuses using a nitrogencooled beryllium filter as a rough monochrometer, followed by a simple slow chopper time-of-flight spectrometer). The opposite is true for measurements where the neutrons lose energy. In an experiment where the scattering is elastic or quasi-elastic, the wavelength resolution  $\Delta \lambda / \lambda_0$ , and the time resolution  $\Delta t/t_0$  should be equal to obtain maximum resolution and intensity simultaneously.  $\lambda_0$  is the most probable wavelength in the neutron burst incident on the sample, and  $t_0$  is the time it takes those neutrons to travel the distance between the sample and the detector.

The spectrometer under construction will be used for elastic or quasielastic and inelastic scattering measurements. It was found necessary to adopt a three-rotor system in order to obtain the versatility required for the planned experiments. One, two or three-rotor configurations can be used depending upon the intensity and resolution requirements of the measurement.A one-rotor system will be most useful for experiments requiring maximum intensity. The two-rotor system is most useful for energy gain

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inelastic scattering measurements, whereas for quasi-elastic and elastic scattering the three-rotor configuration is the best one. The rotor system will give bursts of monochromatic neutrons with  $\lambda_0 = 3.5$  Å and longer, depending upon the speed of rotation of the rotors.

# 2. GENERAL CONSIDERATIONS OF MULTI-ROTOR SYSTEMS

The qualitative understanding of the operation of a multi-rotor system is straightforward. The steady flux of reactor neutrons is chopped by the first rotor into a periodic burst of neutrons having a broad energy spectrum. This burst then travels some distance to a second rotor, which has a fixed phase relation to the first. When it opens, the second rotor passes only a band of energies, related to the time-of-flight of the neutrons between the two rotors, the relative phase of the two rotors, and the open time.

The transmission of neutrons through a rotor system which can consist of one more rotors, is a function of the angular position,  $\gamma$ , of the slit of one of the rotors relative to the direction of the incoming beam of neutrons and their wavelength,  $\lambda$ . Let us call this function T ( $\gamma$ , $\lambda$ ). As a rotor system generally is constructed to give a maximum transmission for neutrons with a finite wavelength  $\lambda_0$ , the transmission of a wavelength  $\lambda$  can be given as a function of  $\lambda - \lambda_0$  and is called T ( $\gamma$ ,  $\lambda - \lambda_0$ ). By evaluting the integral  $\int T (\gamma, \lambda - \lambda_0) d\gamma$  with its proper limits one gets a function T ( $\lambda - \lambda_0$ ). This function is called the chopper function and gives the wave-length distribution of neutrons in the outgoing pulse. The time distribution of the outgoing neutrons at a particular point in the rotor system is achieved by performing the integrations of T( $\gamma$ ,  $\lambda - \lambda_0$ ) over  $\lambda - \lambda_0$  and putting  $\gamma = \omega \cdot t$  where  $\omega$  is the angular velocity of the rotors.



A. SAME DIRECTION OF ROTATION





Schematic representation of two-rotor systems.

The calculation of general analytical expressions for  $T(\lambda - \lambda_0)$  and T(t) is quite difficult. A great simplification is achieved, however, by considering only a set of neutrons travelling along paths parallel with the axis of the rotor system. This approach is meaningful because, in practice, the incident neutron beam is well collimated.  $T(\lambda - \lambda_0)$  and T(t) at the exit pupil of the rotor system, (at the point where the neutrons leave the last rotor) have been calculated for different rotor combinations. It is assumed that the dimensions of the incoming neutron beam and the slit in the rotors are equal.  $T(\lambda - \lambda_0)$  and T(t) are symmetric functions. Only one half of each has to be considered. The results are given below.

Fig. 1 shows a schematic representation of two-rotor systems. Each rotor has one slit which is fluted in such a way as to insure that the chopping of the beam will be performed by the smaller opening. The rotor system is thus equivalent to a system consisting of two moving slits placed a distance, 2 L, apart. Two different cases have to be considered: Case A - the rotors rotate in the same direction (the two chopping slits move in opposite directions); Case B - the rotors rotate in opposite directions (the two chopping slits move in the same direction).

In Case A the calculations show that the chopper function  $T(\lambda - \lambda_0)$  is described by two parabolas:

$$T (\lambda - \lambda_{0}) = \begin{cases} \frac{n \cdot d}{2\pi r} \left[ 1 - \frac{1}{2} \left( \frac{m\omega rL}{h \cdot d} \right)^{2} (\lambda - \lambda_{0})^{2} \right] & 0 \leq \lambda - \lambda_{0} \leq \frac{h \cdot d}{m\omega rL} \\ \frac{n \cdot d}{2\pi r} \left[ 2 - \frac{2m\omega rL}{h \cdot d} (\lambda - \lambda_{0}) + \frac{1}{2} \left( \frac{m\omega rL}{h \cdot d} \right)^{2} (\lambda - \lambda_{0})^{2} \right] \\ \frac{h \cdot d}{m\omega rL} \leq \lambda - \lambda_{0} \leq \frac{2 \cdot h \cdot d}{m\omega rL} \end{cases}$$
(1)

In Case B the chopper function is triangular in shape:

$$T (\lambda - \lambda_0) = \frac{n \cdot d}{\pi r} \left[ 1 - \frac{m \omega r L}{h \cdot d} \lambda - \lambda_0 \right] 0 \leq \lambda - \lambda_0 \leq \frac{h \cdot d}{m \omega r L} .$$
 (2)

The symbols used are:

2d = slit width,

- r = radius of the rotor,
- 2L = distance between the chopping points of the rotor system,
- $\omega$  = angular velocity of the rotors,
- m = mass of the neutron,
- h = Planck's constant,

n = number of neutron bursts per revolution.

The time distribution T(t) calculated at the last chopping point in the rotor system is the same for both cases and is given by

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$$T(t) = n \cdot h \cdot d/2\pi m \omega r L [1 - (r \omega/2d)t] .$$
(3)

 $T(\lambda - \lambda_0)$  and T(t) for the two cases A and B are shown in Fig. 2. They have been plotted in such a scale to make the area under the functions equal for a particular case. This is consistent with the requirement that the values



Fig.2

Calculated time and wavelength distributions of the output pulses for two-rotor systems. The time distribution refers to the last chopping point.

of the definite integrals f T(t) dt and  $f T(\lambda - \lambda_0) d(\lambda - \lambda_0)$  are the same. The full width at half maximum for T(t) and T( $\lambda - \lambda_0$ ) can easily be calculated from their analytical expressions. They are:

Case A  $\Delta \lambda = 2d \cdot h/m \omega r L$ ,  $\Delta t = 2d/\omega r$ . Case B  $\Delta \lambda = d \cdot h/m \omega r L$ , (4)  $\Delta t = 2d/\omega r$ .

As seen from these expressions,  $\Delta\lambda$  can be changed independent of  $\Delta t$  by changing the distance between the two chopping points in the system. In Case B,  $\Delta\lambda$  is one-half the value of  $\Delta\lambda$  in Case A. The total transmitted intensity, however, is the same in both cases because the peak transmission in Case B ( $T_{max} = d/\pi r$ ) is a factor of two greater than in Case A.

It should be mentioned that system A described above where the two rotors spin in the same direction and are separated by a distance 2L is equivalent to a system containing only one rotor with a diameter 2L, provided the peripheral speeds of the rotors are the same and that the angular velocity of the large rotor is a factor of L/r smaller than that of the small rotor. However, in order to obtain the same duty cycle for the two systems,

the large rotor would require more slits than the small rotor, the factor again being L/r. As the transmitted intensity for a given system and thermal flux is of special importance, it is necessary to take this into account when comparing different rotor configurations. When the incoming neutron spectrum is Maxwellian, the number of neutrons falling on the sample per s is,

$$I = \frac{2\varphi_0 \cdot \lambda_t^4}{\lambda_0^5} \exp \left(-\frac{\lambda_t}{\lambda_0}\right)^2 \cdot \frac{A^2}{4\pi\ell^2} \cdot T_{max} \cdot \Delta\lambda$$
 (5)

where

 $\varphi_0$  = thermal flux n/cm<sup>2</sup>s at the source,

 $\lambda_0$  = selected wavelength of the instrument,

 $\lambda_t$  = characteristic wavelength of the neutron spectrum,

A = area of the chopping slit of the rotors,

 $\ell$  = distance between the chopping point of the system,

 $T_{max}$  = transmission at the wavelength  $\lambda_0$ ,

 $\Delta \lambda$  = full width at half max of the wavelength distribution.

In deriving the formula above it is assumed that the angular dimension of the neutron source seen from the position of the last chopping point is always larger or equal to the angular dimensions of the first chopping point seen from the same position. This condition assures that the area of the source is large enough to "fill" the chopper system with neutrons.

Although the two-rotor systems discussed above transmit the same intensity in both cases when the distance between the slits is the same, the wavelength resolution of B is a factor of two greater than A. Therefore, in order to get the same  $\Delta\lambda$  and  $\Delta t$  for both Cases A and B, the distance between the chopping slits must be twice as large in Case A as in Case B. This will, however, decrease the intensity by a factor of eight, as seen from the formula above. The same improved wavelength resolution can also be achieved by decreasing the slit width by a factor of two and keeping the distance between the chopping points unaltered. In this case, the intensity will be only 1/16 of the original one. The time resolution will also be improved by a factor of two, and this explains the difference in intensity decrement for the two possible ways of changing  $\Delta\lambda$ .

In the discussions above concerning the intensity and resolution properties of a two-rotor system, it has been assumed that the rotor speed has been kept constant. It is obvious that the wavelength and time resolution, which can be improved by increasing the speed of the chopping slits, is by far the most superior method as far as intensity is concerned. Here the decrement in intensity varies linearly with the decrease of  $\Delta t$  and  $\Delta \lambda$ , as is easily seen from the intensity formula. In the foregoing examples the intensity decreased as the fourth power, when  $\Delta \lambda$  and  $\Delta t$  were changed by cutting down the slit width. This illustrates the well-known fact that the largest possible velocity of the moving slits gives the optimum performance for chopper systems.

One way of increasing the relative speed of the slits is to have a pair of adjacent slits moving in opposite directions. The calculation of  $T(\lambda - \lambda_0)$ and T(t) for this chopping system shows that the main improvement' is achieved when an extra slit is added at the second rotor of the two-rotor system, whereas very little is gained by adding a slit to the first one. A chopper

## PHASED ROTOR SYSTEM



Fig.3

Schematic representation of a three-rotor system and calculated time and wavelength distributions of the output pulse. Output pulse distributions for one-rotor and two-rotor systems are also shown. The time distributions refer to the last chopping point.

system consisting of three moving slits is equivalent to the rotor system in Case A, plus an extra slit at the last chopping point.

Fig.3 shows a schematic diagram of such a rotor system. The chopper function,  $T(\lambda - \lambda_0)$  and the time function, T(t) at the last chopping point are both triangular in shape and are,

$$T(\lambda - \lambda_0) = n \cdot d/2\pi r [1 - m\omega r L/h \cdot d_1(\lambda - \lambda_0)]$$

$$T(t) = n \cdot h \cdot d/2\pi m \omega r L [1 - (r \omega/d)t].$$

(6)

From these functions the expressions  $\Delta \lambda$ , and  $\Delta t$  are calculated to be,

$$\Delta \lambda = h \cdot d / m \omega r L,$$

$$\Delta t = d / \omega r .$$
(7)

The symbols used are the same as explained above. It is seen that the values of  $\Delta\lambda$  and  $\Delta t$ , as well as the intensity, have decreased by a factor of two with the addition of the extra moving slit at the last chopping point.

If this three-slit system is compared with a system consisting of two slits moving in the same direction (Case B), it is found that both systems are equivalent as time, wavelength and intensity are concerned. However, the geometrical dimensions (2d and 2L) of the three-slit system will be twice as large as the two-slit one.

# 3. THE BNL ROTOR SYSTEM

It is clear from the discussions above that optimum intensity and resolution are obtained with the highest possible speed of the slits. There is, however, an upper limit for the speed,  $(v_r = \omega r)$ , which can be obtained at the rim of the rotors. This limit is set by the strength of the rotor material used. As  $\omega$  and r can be chosen independently, a high v, can be achieved in two ways: either rotors with a large diameter and smaller angular velocity  $\omega$  or vice versa. Experience at Brookhaven in the design and construction of fast choppers has shown that as the rotor speed is increased, failure always occurs first at the periphery of the rotor. Since the stress at the periphery of a rotor is proportional to  $\omega^2 r$ , a rotor with a large diameter is best suited for obtaining the maximum velocity of the slits. Another advantage of large rotors (spinning perpendicular to the neutron path) is that for such rotors one can readily incorporate a large amount of material to stop unwanted neutrons. This is important, especially for fast neutrons, which cause a high background in the measurements. In the logical design of a large diameter chopper, the material with high stopping power for fast neutrons is placed in the centre of the rotors, because these materials have poor mechanical strength. The chopping action of the slow neutrons must be perfomed at the periphery, and fortunately the newly developed Mg/Cd alloy (10% Cd) with its high strength-to-weight ratio is quite suitable.

The system evolved at Brookhaven consists of three rotors, each having a diameter of 80 cm (Fig. 4), two rotors spinning on a horizontal axis and one on a vertical axis. The vertical rotor acts both as a chopping device and rotating collimator. It consists of an upper and lower disc machined from high strength Al forgings. The discs are bolted together with a ring 5-cm thick made of a Mg/Cd alloy (10% Cd) in between. Three equal slits spaced 120° apart are made in the ring with a height equal to the thickness of the ring. The paths of the neutrons are perpendicular to the rotor axis and travel trough its centre. Between the Mg/Cd ring and the centre are three identical pieces of a hydrogenous material. As these pieces are closer to the rotor axis their strength is sufficient to take up the forces.



Fig.4

Schematic representation of the proposed three-rotor system for the Brookhaven High Flux Beam Reactor.

With this type of rotor, a maximum and nearly constant amount of hydrogenous material is in the paths of the fast neutrons travelling through the rotor.

The horizontal rotors consist each of a disc made of the Mg/Cd alloy mentioned above. The slits, also spaced 120° apart, have the same dimension as the slits in the vertical rotor. The paths of neutrons through the "horizontal rotors" are parallel to their spinning axis. One of the horizontal rotors and the vertical rotor will be mounted in such a way that their slits are adjacent and move by each other in the opposite direction. The distance between the two horizontal rotors can be varied to change the wavelength resolution. Each rotor will be driven by a synchronous motor unit described below.

The analytical expressions for  $T(\lambda - \lambda_0)$  and T(t) for this system are given above. A factor of three enters in the numerator because the system gives three pulses per rotor revolution.  $T(\lambda - \lambda_0)$  and T(t) are plotted for three different rotor configurations in Fig. 3. The scale used is such to make the area of the two distributions equal for a particular configuration. The comparison is made for rotors with the same slit width. In the threerotor configuration, the distance between the two "horizontal rotors" is chosen to be twice the diameter of the vertical rotor. The expressions for the full width at half maximum for  $T(\lambda - \lambda_0)$  and T(t), the latter calculated with reference to the last chopping point, are shown in Table I, together with the expressions for the maximum value of  $T(\lambda - \lambda_0)$ , which corresponds to  $\lambda = \lambda_0$ .

#### TABLE I

# EXPRESSIONS FOR FULL WIDTH IN THREE-ROTOR CONFIGURATION

Rotor configuration	Δt	Δλ	T max
One rotor (II) (Vertical)	2d/rw	2d• h/mωr²	3•d/2πr
Two rotors (I + II)	d/rω	d∙h/mωr²	3•d/2πr
Three rotors (I + II + III)	d/rω	d∙h/mωrL	3•d/2πr

#### TABLE II

# COMPARISON OF CALCULATED NEUTRON INTENSITY FOR THREE DIFFERENT ROTOR CONFIGURATIONS

Rotor configuration	Δt ( μs )	Δλ <b>(Å</b> )	I(n/s )
One rotor (II) ( $\ell = 2r = 80 \text{ cm}$ )	25	0.25	8.10 <sup>6</sup>
Two rotors $(I + II)$ (l = 2r = 80  cm)	12.5	0.125	4.106
Three rotors (I + II + III) ( $\ell = 4r = 160 \text{ cm}$ )	12.5	0.063	5.105

Table II gives a comparison of the calculated neutron intensity on a sample ( $5 \times 1.25$  cm) for three different rotor configurations when the instrument is used at the Brookhaven High Flux Beam Reactor. These figures are based on a thermal flux of  $5 \times 10^{14}$  n/cm<sup>2</sup> s, the design flux at the bottom of the cold neutron beam hole. To estimate the flux of 4 Å neutrons a Maxwellian distribution was assumed. The angular frequency of the rotors is chosen to be 1250 s<sup>-1</sup>, which corresponds to a selected wavelength  $\lambda_0 = 4$ Å. Finally, the following values of the rotor parameters have been used:

2d =	1.25 cm ,	
'r =	40 cm ,	(8)
A =	1.25 X 5 cm.	

The formula (5) is used in the intensity calculations. For the configuration of the equipment at the Brookhaven High Flux Beam Reactor the angular dimensions of the neutron source seen from the position of the sample are always larger or equal to the angular dimensions of the entrance pupil seen from the same position for any rotor configuration and position. The transmitted intensity is then independent of the position of the rotors and depends only on the distance between the entrance and exit pupil of the instrument.

# APPARATUS FOR NEUTRON MEASUREMENT

The normal flight path using 4Å incident neutrons is 160 cm. Under these conditions no overlap can occur in the scattered spectrum from successive neutron bursts. With this flight path the flight time for 4Å neutrons will be ~1600 $\mu$ s. Using the values of  $\Delta t$  from Table II, the time resolution for the 160-cm flight path is 1-1.5%. The corresponding values of the wavelength resolution  $\Delta\lambda/\lambda_0$  is seen to be 1.5-6%, depending upon which rotor configuration is used. The value of  $\Delta t$  given in Table II is as mentioned above, and is calculated with reference to the last chopping point. In practice, the sample has to be placed a certain distance behind the last rotor. It is clear that the separation should be a minimum because the burst time at the sample will be larger than the values given in Table II, due to the spread in wavelength,  $\Delta\lambda$ , of the neutrons in the burst. For the Brookhaven apparatus, this effect will increase our burst time at the sample by about 10%. There will also be a spread in time because of contributions from the finite channel widths in the time analyser and finite thickness of the neutron detector. For the analyser and detectors planned, these time uncertainties are less than 1%.

#### 4. THE DRIVING SYSTEM

The driving system has been designed in cooperation with the Bogue Electric Manufacturing Company of New Jersey. Each rotor drive unit consists of two electric motors mounted in tandem. A wound two-pole induction motor driven from the mains brings the rotor up to 3600 rpm. At this speed, the induction motor is uncoupled by an electromagnetic clutch, and a synchronous induction motor will take over the driving. The speed of this motor can be set anywhere between 3600 - 15000 rpm.

Power to the synchronous induction motors will be provided by generators - one for each motor - mounted on a common shaft directly driven by a DC motor, which receives power from a 50 kW AC-DC motor generator set. A manual phase alignment can be perfomed by adjusting the stator of the generator with a micrometer screw. The final adjustment will be made by means of an eddy current brake, which is constructed as an integral part of the high speed motor. The brake will be modulated by a feedback system that will sense the relative position of the rotors and maintain relative phase swing between the rotors less than  $\pm 0.3^{\circ}$ .

The controls for the driving system allow for completely automatic start-up, speed control and automatic shut-down of the system.

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# DISCUSSION

W. KLEY: What energy range is covered by your phase rotor system? K. OTNES: The rotor system will be used for incoming neutrons in the wavelength range of  $3.5 \text{ \AA} < \lambda < \infty$ , which corresponds to energies lower than about 6.5 mV.

# A COLD NEUTRON MONOCHROMATOR AND SCATTERING APPARATUS

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#### Abstract — Résumé — Аннотация — Resumen

A COLD NEUTRON MONOCHROMATOR AND SCATTERING APPARATUS. A narrow band of neutron wavelengths (4 Å and greater) is selected from a collimated neutron beam obtained from the Dido reactor at Harwell. These neutrons are scattered by various samples and the energy transfer of the scattered neutrons measured using time-of-flight techniques.

The neutrons, moderated by a liquid hydrogen source in the reactor pass through first a liquid nitrogencooled filter, then a single crystal of bismuth and finally they are "chopped" by a magnesium-cadmium highspeed curved slot rotor. In this apparatus the wavelength spread of 0.3 Å at 4.1 Å is determined primarily by the Be-Bi filter, while the time spread (8  $\mu$ s) is determined by the rotor.

The monochromated neutron bursts from this rotor are scattered by a sample and detected in one of two counter arrays. When studying liquid or polycrystalline samples an array of six BF<sub>3</sub> counter assemblies (each 2 inches × 24 inches in area) are used covering scatter angles from 20° to 90°. This array is placed below the neutron beam. Above the line of the neutron beam is a second array consisting of three scintillators 2 inches in diameter, which is used for the study of single crystal samples.

The output of each counter is fed into a tape recording system which has 500 time channels available for each counter. This apparatus has been used to study neutron scattering from several gaseous, liquid and crystalline samples and the most recent measurements are presented in other papers in these proceedings.

MONOCHROMATEUR ET APPAREILLAGE POUR LA DIFFUSION DE NEUTRONS LENTS. Les auteurs extraient une bande étroite de neutrons (4 Å et plus) d'un faisceau collimaté de neutrons produits par le réacteur Dido de Harwell. On fait diffuser ces neutrons au moyen de divers échantillons et on mesure le transfert d'énergie des neutrons diffusés par la méthode du temps de vol.

Les neutrons ralentis par de l'hydrogène liquide placé dans le réacteur passent d'abord dans un filtre refroidi à l'azote liquide, puis dans un monocristal de bismuth. Finalement, un rotor à rainures courbes en magnésium et cadmium, ayant une vitesse de rotation élevée, les laisse passer par bouffées. Dans cet appareil, le filtre Be-Bi sert à déterminer la dispersion de la longueur d'onde (comprise entre 0, 3 Å et 4, 1 A) et le rotor, la dispersion en fonction du temps (8 µs).

Les bouffées de neutrons monochromatiques provenant du rotor sont diffusées par un échantillon et détectées dans l'une de deux séries de compteurs. Lorsqu'on étudie des échantillons liquides ou polycristallins, on emploie une série de compteurs  $BF_8$  (dimensions:  $2 \times 24$  pouces) couvrant des angles de diffusion variant de 20 à 90°. Cette série est placée en-dessous du faisceau de neutrons. Au-dessus de l'axe du faisceau neutronique se trouve la deuxième série comprenant trois scintillateurs (diamêtre 2 pouces) pour étudier des échantillons de monocristaux.

Chaque compteur agit sur un système d'enregistrement à bande magnétique qui comporte 500 canaux utilisables pour chacun des compteurs. Les auteurs se sont servis de cet appareil pour étudier la diffusion des neutrons dans plusieurs échantillons gazeux, liquides et cristallins. Dans d'autres mémoires présentés au Colloque ils donnent les résultats des demières mesures faites.

МОНОХРОМАТОР ДЛЯ "ХОЛОДНЫХ" НЕЙТРОНОВ И ПРИБОР ДЛЯ РАССЕЯНИЯ. Узкая полоска нейтронных водн (4Åи более) отбирается из коллимированного пучка нейтронов, получаемого в реакторе "ДИДО" в Харуэлле.

Эти нейтроны рассеиваются различными образцами, а отдача энергии рассеянных нейтронов измеряется с помощью отбора частиц методом времени пролета.

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Нейтроны, замедленные с помощью жидкого водородного источника в реакторе, проходят через первый фильтр из жидкого азотного охладителя, затем через монокристаллический висмут, и, наконец, они "прерываются" с помощью изогнутого паза из магния и кадмия в роторе, работающем на большой скорости. В этом приборе длины волны от 0,3 до 4,1 Å определяются в первую очередь с помощью фильтра Be-Bi, тогда как время распространения (8 мксек) определяется ротором.

Монохромированные вспышки нейтронов рассеиваются образцами и детектируются в одной из двух систем счетчиков. При изучении жидких или поликристаллических образцов используется система счетчиков 6 БF<sub>3</sub> (площадь 5 x 60 см), охватывающая интервал углов рассеяния 20-90°. Она помещается под нейтронным пучком. Над нейтронным пучком находится вторая система счетчиков, состоящая из трех сцинтилляторов диаметром 5 см, которая используется для изучения монокристаллических образцов.

Выход каждого счетчика подключен к ленте записывающей системы, которая имеет для каждого счетчика 500 хронирующих каналов. Этот аппарат применялся при изучении нейтронного рассеяния в целом ряде газообразных, жидких и кристаллических образцов.

'MONOCROMADOR Y APARATO DE DISPERSIÓN PARA NEUTRONES FRÍOS. De un haz colimado de neutrones, emitido por el reactor Dido de Harwell, se selecciona una estrecha banda de longitudes de onda neutrónicas (4 Å y mayores). Estos neutrones son dispersados por varias muestras y la energía por ellos cedida se mide según el método del tiempo de vuelo.

Los neutrones, moderados por una fuente de hidrógeno líquido situada en el reactor, atraviesan primero un filtro refrigerado por nitrógeno líquido, seguidamente un monocristal de bismuto, siendo, por último "interceptados" por un rotor de ranura curva, de magnesio-cadmio animado de gran velocidad. En este aparato el ensanchamiento de longitud de onda  $(0, 3 \text{ \AA a } 4, 1 \text{ \AA})$  queda principalmente determinado por el filtro de Be-Bi, y el de tiempo (8 µs), por el rotor.

Las ráfagas de neutrones monocromáticos provenientes del rotor son dispersadas por una muestra y detectadas en uno de dos dispositivos de recuento. Cuando se estudian muestras líquidas o policristalinas, se utiliza un dispositivo de seis contadores (de BF<sub>3</sub> de superficie unitaria) de 2 pulgadas por 24 pulgadas para ángulos de dispersión comprendidos entre 20° y 90°. Este dispositivo se coloca debajo del haz neutrónico. Por encima del eje del haz, se instala otro dispositivo integrado por tres centelleadores de 2 pulgadas de diámetro, que se utiliza para estudiar muestras monocristalinas.

Las señales emitidas por cada contador se transmiten a un grabador de cinta que dispone de 500 canales de tiempo para cada contador. El aparato se ha utilizado para estudiar la dispersión de neutrones por varias muestras gaseosas, líquidas y cristalinas. Las mediciones más recientes se exponen en otras memorias presentadas al Simposio.

### 1. INTRODUCTION

Cold neutron scattering experiments are now used frequently in studies of the solid and liquid state, because cold neutrons possess certain important properties of value in this field of research. First, the energy transferred in an interaction is often of the same order of magnitude or greater than the incident cold neutron energy and thus small energy transfer measurements are easy to make. Further, neutrons of sufficiently long wavelengths do not suffer Bragg reflections by crystals which may give rise to large backgrounds in some experiments. In this paper a machine is described with which the scattering from polycrystalline samples, liquids and single crystals have been studied.

To produce an intense beam of cold neutrons it is necessary to maintain a cold moderating source in the reactor. The results of using liquid hydrogen as the moderator have been known for some time [1] and with this information at hand a liquid hydrogen loop was designed and installed in the Dido reactor at Harwell. Neutrons from this source pass through a beryllium polycrystalline filter, which serves two purposes. First the fast neutron background in the beam is virtually eliminated and secondly the sharp "cutoff" at 3.94Å is used to improve the energy resolution of the neutron burst

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emerging from the rotor. The neutrons then pass through a single crystal of bismuth, which further reduces the fast neutron and  $\gamma$ -ray intensity of the beam. The neutrons then emerge from the reactor face and are "chopped" by a high speed curved slot rotor, giving a pulse of  $8\mu$ s duration (at 28300 rpm) and removing neutrons outside a given velocity band. These neutrons are scattered by the samples along a convenient flight path into the detectors. A signal derived from a magnetic pick-up [2], on the rotor drive system, is used to trigger a time analyser and hence the time-of-flight of the scattered neutrons is obtained. The analyser is of the multiple input type allowing simultaneous measurements to be made at six different angles by coupling to it the outputs of detectors spaced from 20° to 90° about the sample.

This machine came into full operation in 1961. Numerous experiments have been planned some of those completed are presented at this conference [3, 4, 5]. In this paper details of the construction and performance of the construction and performance of the apparatus are given followed by a section. on data presentation. Some possible improvements for the future are suggested.

# 2. DESCRIPTION OF THE APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1a. Fig. 1b is a photograph of the apparatus as seen from the reactor floor level. Details of the components of the apparatus are as follows.

#### 2a. The liquid hydrogen source

The thermal neutron spectrum in a reactor such as Dido has a Maxwell distribution of velocities corresponding to the moderator temperature, say 325° K, which means that only  $1\frac{1}{2}$ % of the total thermal neutron flux lies below 0.005 eV. This means that to achieve good statistical accuracy one must accept long counting times, and in a high resolution experiment the background due to fast neutrons and  $\gamma$ -rays tends to obscure the scattered moderator of the reactor (or part of it): if the thermal neutron flux could be brought into equilibrium at 30°K, the flux of neutrons of 0.005 eV energy would be increased by a factor 18. The liquid hydrogen loop in Bepo [1] showed that though one could not achieve such high increases with a cold moderator limited to dimensions of only 8 cm, the gain in cold neutron flux was still useful. The increases measured were a gain of a factor 7 for neutrons of 5 Å wavelength, rising to a factor 25 for neutrons of 10 Å wavelength.

The installation of a similar liquid hydrogen moderator in Dido was a much more complicated task, entailing building a closed circuit hydrogen refrigeration plant outside the reactor building, and conveying the liquid hydrogen to the reactor, along a vacuum-insulated pipeline some 60 ft long. More details of this apparatus are given in another paper [6]. The moderator chamber is a hemisphere 8 cm diameter, with a concave end; it holds 200 cm<sup>3</sup> of liquid hydrogen. The gain in cold neutron flux is shown in Fig. 2a, a factor of 4 at 4 Å, rising to a factor 8 at longer wavelengths.







# Fig.1b

# Photograph of apparatus.

- A ... Shielding around filter assembly.
- B ... Shielding around rotor vacuum chamber.
- C ... Tank containing detectors mounted at 90°.
- D ... Shielding tank around 6 BF, detectors.
- E ... Neutron beam stop.



Fig.2a

Graph of gain in flux versus neutron wavelength when liquid hydrogen is in pile.

#### 2b. The filters

Two filters are employed. The first a beryllium polycrystalline block of 12 inches in length scatters from the beam neutrons satisfying the Bragg Law (n  $\lambda$  = 2d sin  $\theta$ ), passing on only those neutrons of wavelength greater than twice the maximum plane spacing of the beryllium lattice. This beryllium "cut-off" occurs at 3.94 Å. The loss in intensity of neutrons of wavelength greater than this due to inelastic scattering is reduced by cooling the filter to liquid nitrogen temperatures. The second filter is a 4 in long single crystal of bismuth. As well as removing fast neutrons and  $\gamma$ -rays from the beam the bismuth also diffracts from the beam the neutrons which satisfy the Bragg condition from the plane spacing and particular orientation of the crystal. This leaves a "hole" in the spectrum which can be used to further reduce the neutron band with passed by the rotor. (See section on performance of apparatus).

A facility is built into the filter assembly so that the filters can be rotated out of the beam allowing an unfiltered beam to be used for alignment of single crystals for phonon frequency dispersion experiments.

2c. The rotor system

The rotors used in this apparatus are made from ZW6 magnesium alloy with 10% cadmium added. Curved slot rotors are used, the present slot shapes following a circular arc which is considered to be a sufficient approximation to the ideal curve (an Archimedes spiral). The radius of curvature is a function of the ratio of the neutron speed to the tip speed of the rotor NS/TS and the diameter of the rotor. Rotors of 10 in and 8 in diam. are used. Three different rotors have been used on this apparatus. The high resolution rotor has 12 slots of width 0.1 in and operates at 37 500 rpm. This rotor is found to distort after prolonged use and it was estimated that the lifetime of the rotor would be about 2000 h. A rotor of slightly lower resolution but same slot dimension was made which operates at 30 000 rpm, thus considerably reducing stresses set up in the rotor and prolonging the lifetime indefinitely. A low resolution rotor has also been used which has 3 slots of  $\frac{1}{4}$  in width and operates at 18 700 rpm.

The driving system employed is one which has been well tried and tested. It has been described fully by EGELSTAFF et al. [7]. Briefly it consists of a 40 W 3 phase hysteresis motor driving a main shaft, the rotor being suspended below this by a 3/32 in diam. wire 6 inches in length. The main shaft is suspended in a magnetic field and located in gas journal bearings, and the rotor is hung inside an evacuated steel tank. A vacuum seal is made along the length of the 3/32 in diam. wire.

A crystal oscillator followed by a 200 W power amplifier and a phase splitting circuit is used to supply the 3 phase power to the motor. The performance of this type of rotor system regarding stability, etc. is more than is required in a single rotor system but the reliability experienced in the running of other machines [8] justified the selection. The present cold neutron rotor system has been operating continuously for seven months at the time of writing this paper, the only stoppages being to change the rotor when different neutron burst characteristics have been required.

### 2d. The detectors and time analysing equipment

One arrangement of detectors consists of 6 groups of BF<sub>3</sub> counters mounted to detect neutrons scattered into angles of 20°, 30°, 45°, 60°, 75° and 90°. The detectors are mounted below the neutron beam and situated in a tank of boron and polythene shielding so that the flight path of the scattered neutrons along cadmum lined collimators is 1.28 m. The detectors covering the three smaller angles each consist of 2 BF<sub>3</sub> counters 1 in diam. and 12 inches in length mounted side by side so that the detector area is  $12 \text{ in} \times 2 \text{ in}$ . The larger angles of scatter use 4 BF<sub>3</sub> counters making the detector area 24 in  $\times$  2 in without worsening the angular resolution of the detectors which is  $\pm$  1°. This assembly is used to study the neutron scattering from polycrystals, liquids and gases.

The second arrangement consists of three neutron scintillation counters of 2 in diam. mounted above and at 83°, 85° and 90° to the neutron beam centre line. They are enclosed by a tank of water with a cadmium-lined centre collimating hole. These detectors are lithium fluoride zinc sulphide and boron plastic zinc sulphide scintillators of the type described by STEDMAN [9] and HARRIS [10] using pulse shape discriminators as described by WRAIGHT [11]. These counters provide high angular resolution and due to the high efficiency for small thickness of this type of detector (50% at thermal energy) plus an extended flight path of 2.2 m, the time-offlight resolution is high. This arrangement is used for studying phonon frequency dispersion relations in single crystals.

The output of each detector is fed into one of the 31 inputs of a time analysing magnetic tape recording machine of the type described by HALL [12] and manufactured by EMI. Each input of the analyser has 512 time channels associated with it which can be varied from  $2 \mu s$  to  $16 \mu s$ . Since only seven inputs are used (six for scattered detectors and one for the monitors), the recorder is coded so that the remaining inputs are used to record the information from other samples mounted on a 4 position sample changer.

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The time analyser receives its 'start' pulse from a magnetic pick-up mounted at the top of the main rotor drive shaft. A stop pulse is similarly derived which resets the time analyser  $25\mu$ s. before the start pulse arrives. If a neutron event is detected between the 'start'and 'stop' pulse times, it will also reset the time analyser. The number of time channels used in practice is dependent on the rotor period since all the 'start' to 'stop' pulse time is analysed. Usually from 300-500 timing channels are employed. The paralysis time of the recorder is 10 ms, thus two neutrons cannot be analysed from one burst through the rotor. In practice the total scattered count rates never exceed 1 count per 20 revs of the rotor.

Each neutron therefore has associated with it a detector number and a time channel number. This information is coded and recorded onto 16 track magnetic tape of 1 in in width. Reels of tape can record continuously for 48 h and the required data obtained by "playing back" on an analysing machine of 1024 channels. 'Playback' time is approximately 20 min for each pair of inputs. The data is then transferred to punch paper tape (2 min) which can be fed directly into a Feranti Mercury computer.

#### 2e. Sample mounting

Samples are fixed in the beam about 10 in from the rotor tip. Plain samples are inclined at 45° to the beam and cover the beam area 2 in width  $\times$  1 in high, scattering approximately 15% of the beam. A sample changer can be used for room temperature samples so that four samples can be studied together. The samples (cycled 4 times per h) usually include one empty sample container and one calibration sample.

Individual samples are mounted in vacuum furnaces to operate at temperatures up to 1000°C. Cryostats are also used to study cold samples. For single crystal phonon dispersion measurements the crystals are mounted in a goniometer.

# 3. PERFORMANCE OF THE APPARATUS

As shown in Fig. 2 (a) the 4 Å flux is increased by a factor of 4 when the liquid hydrogen is used. The effect of this increase in cold neutron flux is well illustrated by the results given in Fig. 2 (b), which gives the spectrum of neutrons scattered through 75° by hydrogen gas at room temperature. The dotted peak A represents the spectrum of incident neutrons, the horizontal dashed line the background of fast neutrons and  $\gamma$ -rays. In a 4 h run without the aid of the liquid hydrogen source the open circles were obtained; they are barely above the background level. In a 4 h run with the liquid hydrogen source in operation the full circles were obtained; the peak B of neutrons scattered inelastically is clearly seen. Thus the use of a liquid hydrogen cold neutron source can not only improve the counting rate in an experiment, the data is also greatly improved by the increase in counts-tobackground ratio.

By calculation it can be shown that the amount of inelastic scattering of neutrons wavelength 4 Å can be reduced by a factor of 4 if the beryllium filter is cooled to liquid nitrogen temperatures. Measurement of the 4.1 Å



Fig.2b

Scattering of neutrons from a sample with and without liquid hydrogen in pile.

flux through the rotor with filter at room temperature and when cooled, show that this has been achieved.

The theoretical burst width at the rotor centre for a parallel beam falling on the NS/TS = 3 rotor is  $\pm 4\mu$ s (half width at half height). In this apparatus the beam divergence is normally  $\pm 0.8^{\circ}$  and this increases the pulse width to  $\pm 8'\mu$ s. At monitor 1, which is 22 cm from the rotor centre, the pulse length is  $\pm 10\mu$ s and at the sample which is normally 20 cm from monitor the pulse is  $\pm 12\mu$ s. At the 1.3 m detectors the pulse width for elastically-scattered neutrons is  $\pm 50\mu$ s or  $\pm 39\mu$ s/m. Since the mean timeof-flight is  $1040\mu$ s/m the resolution of the incident beam is  $\Delta \tau/\tau = \pm 3.7\%$ . On the other hand the beryllium edge is defined (see Fig.3) to  $\pm 0.8\%$  using the 1.3 m detectors and  $\pm 0.5\%$  using the 2.2 m detectors.

A comparison of the neutron pulse lengths measured at monitor 1 for the three choppers is given below.

The NS/TS = 2 1/2 rotor gives a longer pulse than the NS/TS = 3 rotor because it cannot be run at a speed high enough to use the beryllium-bismuth filter spectrum properly. This rotor is mainly useful for studies at longer wavelengths of 5 to 6Å, and here the pulse length is  $\pm 20 \,\mu$ s because there is no reduction in width due to the beryllium and bismuth filters.

Curves of the neutron energy transmission measured on the second monitor, for two rotors (NS/TS = 3 and 4) are given in Fig. 3. The curve for the low resolution rotor clearly shows how the proper use of a hole produced in the spectrum by a single crystal (in this case bismuth) can improve the resolution of a rotor.

Distance errors in the scattered flight path arise from the finite sample and detector size. The maximum error due to  $BF_3$  detector thickness is 2%. When considering sample size the maximum error for neutrons scattered elastically through the sample is zero at zero angle of scatter rising to 4% at 90° of scatter. Averaged over the whole beam the errors are less than the maximum of course. As previously mentioned for phonon dispersion



Fig.3

Curves of transmission of two rotors.

Rotor NS/TS	Operating speed	Time spread of neutron burst	Flux of 4.1 Å neutrons at sample without hydrogen source			
$2\frac{1}{2}$	37 500 rpm	± 12 μs	5 x 10 <sup>5</sup> neutrons/min			
3	28 300 rpm	± 10 µs	6 x 10⁵ " "			
4	18700 rpm	± 19 μs	1.1 × 10 <sup>6</sup> " "			
	1	1	}			

measurements scintillation detectors are used of 1 mm thickness and in this arrangement the distance error is entirely due to the sample size.

The neutron flux of 4.1 Å incident on the sample is  $6 \times 10^5$  neutrons/min for the NS/TS = 3 rotor (see Table I). With liquid hydrogen in the pile this becomes 2.4 × 10<sup>6</sup> neutrons/min. For samples scattering 10% of the beam isotropically the neutron flux scattered into each counter of area 48 in is 400 neutrons/min. A typical experimental count rate for one such detector is 100 cpm. The flux of neutrons of wavelength 8 Å incident on the sample is about  $4 \times 10^5$  neutrons/min using the hydrogen source. D. HARRIS et al.

Background measurements made with blank samples and cadmium inserted in the beam showed that there was no time dependent background except that due to scattering from the sample container and this almost entirely in the region of the elastic peak. In many experiments the background is taken as that level observed in time channels in the region corresponding to very large energy gain (0.5 eV).

Fig. 2b shows the scattering obtained from a gaseous sample. Even in this case where a broad spectrum results the counts/background ratio is good. Figs.4a and 4b show the scattering spectrum from vanadium and methyl alcohol in which elastic peaks are clearly separable from the inelastic region and background.





Scattering from vanadium on detector at 45°.



Fig.4b Scattering from methyl alcohol on detector at 45°.

# 4. DATA ANALYSIS AND PRESENTATION

The method of simultaneous measurement of the scattered neutrons at several scatter angles has obvious advantages. To make full use of these advantages, a careful inter-calibration of the various detector efficiencies is required. The incoherent elastic scattering of vanadium metal has been employed for this purpose. For the present low neutron energies the Debye-Waller factor for room temperature vanadium deviates by only  $\sim 2\%$  (for 90° scatter) from unity. Hence the near isotropic elastic scattering provides a simple method for comparison of the detector efficiencies.

The standard 1 in diam. 70 cm hydrogen pressure-enriched  $B^{10} F_3$  filled proportional counters have stable and consistent efficiencies and the variation of the efficiency with neutron energy has been calculated from their known filling and geometry.

The incident time-of-flight and spectrum shape is conveniently obtained using the two monitors in the incident beam. The second is placed at the same distance from this sample as the detectors and so gives a clear picture of the time distribution of the incident neutrons as it would appear at the detectors. The first monitor is also used to measure the incident beamintegrated flux. Assuming the scattering cross-section of vanadium the results for other scatters may be evaluated as absolute differential cross--section.

Experimental results as counts per channel <u>versus</u> channel number are normally converted by the computer programme to units more useful for analysis. For example counts corrected for background, can scatter and detect efficiency variation or the cross-section for a given process. In the case of single crystal work the computer will find the position of the phonon peaks and evaluate errors.

# 5. CONCLUSIONS

An instrument has been described which provides information on the scattering of neutrons of long wavelength over a wide range of scattering angles. Certain experiments using neutrons of wavelength greater than 6 Å are made possible by the increase in flux available using a liquid hydrogen source. The out-of-pile apparatus has proved very reliable; servicing and routine maintainance being confined entirely to reactor shut-down periods allowing continuous operation of the machine at other times.

Certain improvements are planned. The design and manufacture of a rotor with slots cut to an Archimedes spiral is under way. A rotor tank is seen to be installed which will allow the sample to rotor tip distance to be reduced to less than 3 in. Both these modifications will improve the resolution of the machine. The addition of several more detectors is also planned.

# ACKNOWLEDGEMENTS

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# DISCUSSION

- D.W. CONNOR: I have two questions:
- (a) What is the length of your bismuth single-crystal filter?
- (b) Have you any transmission data for this filter?

S.J. COCKING: Our bismuth filter is 4 in long. I have the results of transmission measurements made at various selected neutron energies and will let you have them privately.

# УСТАНОВКА ДЛЯ ИЗУЧЕНИЯ РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ

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#### CCCP

#### Abstract — Résumé — Аннотация — Resumen

INSTALLATION FOR STUDYING THE SCATTERING OF COLD NEUTRONS. Using the pulsed fast reactor in the joint Institute ior Nuclear Research, an installation was set up to investigate the spectrometry of cold neutrons. The moderator, adjoining the reactor reflector, and the beryllium filter were at the temperature of liquid nitrogen. The scatterer, located at a distance of about 0.6 m from the moderator, was irradiated by flashes of cold neutrons, whose duration was determined by the lifetime of the neutrons in the moderator and the dispersion of the times-of-flight over a distance of 0.6 m. The frequency of the flashes was 8/s. The steep beryllium edge of the spectrum, lying around 200  $\mu$ s, was used for spectrometry in the quasi-elastic range. The energy of the scattered neutrons was determined by the time-of-flight over the distance between scatterer and detector, which was about 10 - 40 m.

 $ZnS + B_{10}^{10} O_{3}$  scintillation detectors with surfaces of 300 and 2000 cm<sup>2</sup> were used and the efficiency, for fast neutrons, was about 60%.

INSTALLATION POUR L'ÉTUDE DE LA DIFFUSION DES NEUTRONS THERMIQUES. A l'aide du réacteur à flux pulsé de neutrons rapides de l'Institut unifié de recherches nucléaires, les auteurs ont mis au point une installation pour la spectrométrie des neutrons thermiques. Le ralentisseur contigu au réflecteur du réacteur et le filtre de béryllium sont maintenus à la température de l'azote liquide. Le diffuseur, placé à environ 60 cm du ralentisseur, est irradié par une bouffée de neutrons thermiques dont la durée est déterminéé par la vie moyenne des neutrons dans le ralentisseur et par l'étalement des temps de vol nécessaires pour parcourir la distance de 60 cm. La fréquence des bouffées est de 8/s. Pour la spectrométrie dans la région quasi-élastique, on utilise la bande en bordure du spectre qui correspond au béryllium et s'étale sur environ 200  $\mu$ s. L'énergie des neutrons diffusés est déterminée par la durée du parcours entre le diffuseur et le détecteur. Les auteurs ont utilisé des détecteurs à scintillation à ZnS +  ${}^{10}B_2O_3$  ayant des surfaces de 300 et 2000 cm<sup>2</sup> et dont l'efficacité à l'égard des neutrons thermiques est d'environ 60%.

УСТАНОВКА ДЛЯ ИЗУЧЕНИЯ РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ. На базе импульсного быстрого реактора Объединенного института ядерных исследований создана установка для спектрометрии холодных нейтронов. Замедлитель, примыкающий к отражатель реактора, и бериллиевый фильтр находятся при температуре жидкого азота. Рассеиватель, помещенный на расстоянии около 0,6 м от замедлителя, обдучается вспышкой холодных нейтронов, длительность которой определяется временем жизни нейтронов в замедлителе и разбросом времен пролета расстояния 0,6 м. Частота вспышек - 8 раз в сек. Для спектрометрии в квазиупругой области используется крутой бериллиевый край спектра, занимающий около 200 мксек. Энергия рассеянных нейтронов определяется по времени пролета расстояния рассеиватель - детектор, составляющего 10 - 40 м. Используются сцинтиляционные детекторы на основе ZnS + B<sup>10</sup>0<sub>3</sub> площадью 300 и 2000 см<sup>2</sup> и эффективностью к тепловым нейтронам около 60<sup>4</sup>.

INSTALACIÓN PARA ESTUDIAR LA DISPERSIÓN DE NEUTRONES FRÍOS. En el reactor rápido pulsante del Instituto Central de Investigaciones Nucleares se instaló un espectrómetro para neutrones fríos. El moderador, contiguo al reflector del reactor, y el filtro de berilio se mantienen a la temperatura del nitrógeno líquido. El difusor, situado a unos 0, 6 m del moderador, se irradia con ráfagas de neutrones fríos, cuya duración se determina en función de la vida de los neutrones en el moderador y de la dispersión de los tiempos de vuelo en una distancia de 0, 6 m. La frecuencia de las ráfagas es de 8 por segundo. Para la espectrometría en la región cuasielástica, se utiliza la variación brusca del espectro del berilio, que es de unos 200  $\mu$ s. La energía de los neutrones dispersados se determina por el tiempo de vuelo en la distancia que media entre el difusor y el detector, a saber, 10 a 40 m. Los autores utilizan detectores de centelleo a base de ZnS +  ${}^{10}B_2O_3$ , de una superfície comprendida entre 300 y 2000 cm<sup>2</sup>, y cuya eficacia respecto de los neutrones térmicos, es del orden de 60%. В настоящее время исследования нейтронных спектров, возникающих при рассеянии холодных нейтронов, ведутся, как правило, на обычных реакторах непрерывного действия. Основная трудность таких экспериментов заключается в малой интенсивности рассеянного пучка холодных нейтронов. В настоящем сообщении описывается установка для измерений с холодными нейтронами, использующая импульсный реактор на быстрых нейтронах (ИБР)Лаборатории нейтронной физики объединенного Института ядерных исследований.

Эта установка позволяет получать поток холодных нейтронов, обеспечивающий интенсивность рассеянного пучка во много раз большую, чем на реакторах непрерывного действия с селекторами.

Реактор ИБР установлен в центре зала размерами  $10 \times 10$  м,стены и потолок которого служат защитой реактора. Активная зона реактора вместе с отражателем и органами регулирования имеет размеры примерно  $25 \times 25$  см. Реактор генерирует нейтроны периодическими импульсами с полушириной около 36 мксек при частоте повторения 8,3 раза в секунду. Средняя тепловая мощность реактора равна 1 квт; соответствующий средний выход нейтронов  $4,5 \times 10^{13}$  1/сек. Малая активная зона ИБРа дает возможность значительно более эффективно использовать нейтроны, рождающиеся в реакторе, чем это доступно на обычных реакторах на тепловых нейтронах. Импульсное выделение мощности приводит к малой величине фона в окружающих помещениях во время измерений.

Для вывода нейтронных пучков в защите имеется несколько каналов, три из которых в настоящее время заняты установкой для опытов с холодными нейтронами.



Pиc.1

Схема установки для измерений с холодными нейтронами

Схема установки приведена на рис.1. Быстрые нейтроны из реактора попадают на замедлитель, имеющий размеры 30×30×5 см<sup>3</sup> и установленный на расстоянии 5 см от отражателя реактора.

В качестве замедлителя использовался парафин или этиловый спирт. Вплотную за замедлителем помещен блок поликристаллического бериллия размером 24×12×12 см<sup>3</sup>, являющийся фильтром колодных нейтронов. Расположение бериллия вплотную к замедлителю увеличивает поток холодных нейтронов в несколько раз по сравнению со случаем, когда бериллий находится вдали от замедлителя. Выигрыш в интенсивности связан с тем, что бериллий играет роль отражателя тепловых и быстрых нейтронов. Холодные нейтроны, для которых бериллий прозрачен, выводятся из глубины замедляющего блока. "замедлитель-бериллий", где плотность тепловых, а значит и холодных нейтронов, существенно выше, чем на краю голого замедлителя при отодвинутом бериллии. Расположение фильтра вплотную к замедлителю повышает примесь тепловых нейтронов, и с этой точки зрения оно невыгодно. Эту трудность можно в принципе обойти, оставив около замедлителя слой бериллия толщиной в несколько сантиметров и поместив остальную часть фильтра посредине между замедлителем и образцом.

Как бериллий так и замедлитель находятся в пенопластовом криостате, заливка которого жидким азотом производится дистанционно из экспериментального зала. Охлаждение замедлителя и бериллия до температуры жидкого азота увеличивает в 10 раз интенсивность холодных нейтронов. Заметим, что при использовании в качестве замедлителя этилового спирта интенсивность холодных нейтронов возрастает примерно на 30% по сравнению с замедлителем из парафина.

За криостатом на оси пучка на расстоянии 60 см от замедлителя и 35 см от конца бериллиевого фильтра находится платформа, на которой расположены образцы. Дистанционно можно вводить в пучок холодных нейтронов один из двух образцов и кадмиевую заслонку. Последняя прекрывает пучок холодных нейтронов перед образцом с целью измерения фона, идущего на детектор.

Криостат и образцы со всех сторон окружены защитой из кадмия и карбида бора толщиной 3 см.

Со стороны активной зоны криостат закрыт парафиновой стенкой для уменьшения фона быстрых нейтронов, идущих на образец. В защите криостата имеются три окна, позволяющие пропускать нейтроны, рассеянные на углы 75 и 30°, и выводить в экспериментальный зал прямой пучок нейтронов, прошедших через бериллиевый фильтр. Нейтроны, рассеянные на образце на угол 75°, проходят по коллимационной трубе, окруженной карбидом бора и кадмием и вакуумированной до ~ 1 мм рт.ст., через защитную стену зала реактора в экспериментальный зал, где расположен детектор. Пролетная база от образца до детектора 10 - 45 м. Для защиты детектора от прямого пучка нейтронов и  $\gamma$ -лучей в зале реактора помещены свинец и парафин с бором.

Для регистрации нейтронов используется сцинтилляционный детектор на основе смеси ZnS (Ag) +  $B_2O_3$  (сцинтиллятор T-1).

Сцинтиллирующий порошок обладает наибольшей эффективностью для регистрации тепловых нейтронов при размере зерен 300 - 500 мк. Плоский слой такого порошка толщиной 0,7 мм (поверхностная плотность ~ 80 мг/см<sup>2</sup>) имеет эффективность к тепловым нейтронам 20% при эффективности к <sub>Y</sub>-лучам Со<sup>60</sup> ~ 10<sup>-4</sup>%. Благодаря большому световому выходу сцинтиллятора все захваченные бором нейтроны регистрируются - интегральная характеристика детектора имеет плато. Чтобы получить большую эффективность, вместо естественного бора был использован бор, обогащенный изотопом В<sup>10</sup> до 90%. Эффективность этого детектора к тепловым нейтронам 50%.

В настоящее время на установке используются два детектора с ZnS (Ag) +  $B_2^{10}O_3$ . При работе на длине пролета рассеянных нейтронов ~ 10 м используется детектор площадью 300 см<sup>2</sup>, собранный на одном фотоумножителе с диаметром фотокатода 200 мм (рис.2 а). При больших пролетных базах используется детектор площадью 2000 см<sup>2</sup> (рис.2 б), в котором при наличии воздушного световода четыре фотоумножителя включены в схему отбора совпадений.







- a) Схема детектора площадыю 300 см<sup>2</sup>
- б) Блок-схема детектора площадью 2000 см<sup>2</sup>:
- 1 сцинтиллятор;
- 2 фотоумножитель;
- 3 катодный повторитель;
- 4 двухканальный сумматор и усилитель;
- 5 дискриминатор;
- 6 временной анализатор;
- 7 блок высокого напряжения;
- 8 схема совпадений;
- 9 световод и отражатель света.

Схема совпадений уменьшает чувствительность детектора к ү-лучам, вызывающим сцинтиляции непосредственно в фотоумножителях, а также к шумам ФЭУ. Эффективность этого детектора к тепловым нейтронам всего лишь на 10% хуже, чем у детектора, в котором ФЭУ работают в непосредственном контакте со сцинтиллятором.

Одним из первых предварительных опытов на установке явилось изучение энергетического распределения пучка нейтронов, прошедшего фильтр.



Рис.3

Спектр нейтронов после бериллия, измеренный на расстоянии ~ 16 м от криостата. Нижняя кривая - фон.

На рис.З представлен спектр нейтронов после бериллия, измеренный на расстоянии 16 м от криостата при помощи 256-канального временного анализатора. Как видно из рисунка, отношение эффекта к фону в области холодных нейтронов составляет 100 : 1, хорошо разрешены кристаллографические плоскости (100), (100) и (002).

Видно также существование довольно большой компоненты тепловых нейтронов ( около 20% от холодных нейтронов). Ввиду большого просачивания тепловых нейтронов, описываемая установка в ее нынешнем виде мало пригодна для изучения неупругого рассеяния холодных нейтронов и используется в настоящее время для изучения квазиупругого рассеяния на жидкостях.

Для определения основных характеристик установки использовался сбразец ванадия толщиной 6 мм и рабочей площадью 70 см<sup>2</sup>. На рис.4 представлен спектр нейтронов, упруго рассеянных на ванадии на угол 75°, снятый при помощи детектора площадыю 2000 см<sup>2</sup> и 256-канального временного анализатора с шириной канала 64 мк/ож. Расстояние от образца до детектора 45 м. В максимуме пика холодных нейтронов мы имели ~ 4 отсчета/мин 64 мксек. Отношение эффекта к фону 3:4.

Временная полуширина наклона бериллиевой границы достигает 100 мксек, т.е. разрешающая способность установки в области энер-





Спектр нейтронов, упруго рассеянный на ванадии.

Расстояние от образца до детектора ~ 45 м.Ширина канала временного анализатора 64 мксек. Провал на кривой, отмеченной стрелкой, связан с наличием образца алюминия торщиной 6 мм на пути пучка.

гии 0,005 эв равна 0,5%. Наблюдаемый наклон бериллиевой границы в основном обусловлен временем жизни тепловых нейтронов в замедлителе.

Как видно из приведенных результатов, ИБР является перспективной установкой для исследований с холодными нейтронами. Поток рассеянных нейтронов, полученный на описываемой установке, примерно в 10 раз больше при разрешающей способности в области холодных нейтронов в 5-10 раз лучшей по сравнению с другими аналогичными установками, работающими на реакторах с постоянной мощьностью.

#### DISCUSSION

B.W. BROCKHOUSE: What is the 0.5% resolution you quote? Is this in wavelength ?

J.JANIK: Yes. It comes from the width of the beryllium cut-off, as measured with vanadium.

W. WHITTEMORE: What were the specifications of the moderator and what is its length in the beam direction?

J. JANIK: The dimensions are given in the paper:  $30 \text{ cm} \times 30 \text{ cm} \times 5 \text{ cm}$ . The length in the beam direction is 5 cm. We used paraffin, but experiments were also done with solid CH<sub>3</sub>OH and as a matter of fact we think there is some increase in intensity with methyl alcohol.

W. WHITTEMORE: What is the pulse length of the filtered beam for thermal neutrons?

J. JANIK: It is about 120  $\mu$ s - about five times longer than the fast-neutron pulse.

# УСТАНОВКА ДЛЯ ИЗУЧЕНИЯ РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ 125

H. PALEVSKY: I don't understand why you say the resolution is five times better than for a cold-neutron facility. Your burst time is 120  $\mu$ s, as compared to 20  $\mu$ s for chopper systems, but your flight path is 45 m and with choppers it is 5 m. Neglecting detector uncertainty you should, therefore, have a factor of  $(20/120) \times (45/5) = 1.5$  times better than chopper systems.

B.W. BROCKHOUSE: If the 0.5% wavelength resolution quoted by Dr. Janik is correct, then he is also correct in saying the improvement is by a factor of five because typical filter-chopper resolutions are about 3%.

H. PALEVSKY: Well, 3% is what you get when you use a thick  $BF_3$  counter because the resolution is all in the time-of-flight of the neutrons over the detector; using a scintillation counter the resolution is down to about 1%.

J. JANIK: Perhaps the factor of five is over-estimated; however, the very thin scintillation detectors we used give some improvement as compared with "conventional" apparatus.

W. KLEY: Might I suggest that the rather large thermal contamination you have with such a device could be avoided by using better collimation and a thermal neutron rotor phased with the reactor pulse?

J. JANIK: We are planning to do just that.

# ДВОЙНОЙ СПЕКТРОМЕТР МЕДЛЕННЫХ НЕЙТРОНОВ НА РЕАКТОРЕ ИБР

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# ФЭИ, МОСКВА, СССР

#### Abstract — Résumé — Аннотация — Resumen

A DOUBLE SLOW NEUTRON SPECTROMETER. The neutron spectrometer described in the paper is intended for measurements of the angular and energy distribution of monochromatic slow neutrons, inelastically scattered by liquid and solid bodies. Experiments of this type permit detailed information to be obtained concerning the dynamics of the atoms in various aggregate states of a substance.

The spectrometer is based on the time-of-flight method. The pulse source of neutrons is the IBR (1) reactor. A mechanical interrupter, rotating synchronously with the disc of the IBR and having a prescribed phase shift, serves as the monochromator. A special phasing system ensures a phase stability better than  $0.5^\circ$ . The neutrons scattered by the sample are recorded by a scintillation detector set at a given angle to the neutron beam. The resolving power of the spectrometer is - 15  $\mu$ s/m.

The paper gives a detailed description of the construction of the spectroscope and its characteristics.

SPECTROMÈTRE DOUBLE POUR NEUTRONS LENTS. Le spectromètre neutronique décrit dans le mémoire est destiné à mesurer la distribution en énergie, la distribution angulaire et la diffusion inélastique des neutrons lents monochromatiques dans des liquides et des solides. Les expériences de ce genre permettent d'obtenir des renseignements détaillés sur la dynamique des atomes dans de divers états de la matière.

Le spectromètre est fondé sur la mesure du temps de vol. Comme source pulsée de neutrons on a utilisé le réacteur IBR-1. Le système monochromateur était constitué par un interrupteur mécanique en rotation synchronisée avec celle du disque du réacteur IBR, avec un déphasage déterminé. Un dispositif spécial de déphasage assure la stabilité de la phase à 0,5° près. La diffusion des neutrons par l'échantillon est enregistrée à l'aide d'un détecteur à scintillations disposé sous un angle déterminé par rapport au faisceau de neutrons. Le pouvoir de résolution du spectromètre est d'environ 15 µs/m.

Les auteurs décrivent en détail la construction du spectromètre et donnent des indications précises sur ses caractéristiques.

ДВОЙНОЙ СПЕКТРОМЕТР МЕДЛЕННЫХ НЕЙТРОНОВ. Описываемый в докладе нейтронный спектрометр предназначен для измерений энергетических и угловых распределений монохроматических медленных нейтронов, неупруго рассеянных жидкими и твердыми телами. Эксперименты такого рода позволяют получить детальную информацию о динамике атомов в различных агрегатных состояниях вещества.

Спектрометр основан на методе времени пролета. Импульсным источником нейтронов является реактор ИБР[1]. Монохроматором служит механический прерыватель, вращающийся синхронно с диском реактора с заданным сдвигом фазы. Специальная система фазировки обеспечивает стабильность фазы, лучшую 0,5°. Нейтроны, рассеянные образцом, регистрируются сцинтилляционным детектором, располагаемым под заданным углом к пучку нейтронов. Разрешающая способность спектрометра составляет ~15 мксек/м.

В докладе дано подробное описание конструкции спектрометра и его характеристик.

ESPECTRÓMETRO DOBLE PARA NEUTRONES LENTOS. Los autores describen un espectrómetro neutrónico destinado a la medición de las distribuciones energéticas y angulares de neutrones monocromáticos lentos, dispersados inelásticamente en líquidos y sólidos. Los experimentos de esa índole permiten obtener información detallada sobre la dinámica de los átomos en distintos estados de agregación de la materia.

El espectrómetro se basa en la medida del tiempo de vuelo. Como fuente pulsante de neutrones se emplea el reactor IBR-1. Actúa como monocromador un interruptor mecánico, que gira sincrónicamente con el disco del reactor IBR con un defasaje prefijado. Mediante un sistema especial de regulación se obtiene una estabilidad de fase superior a 0,5°. Los neutrones dispersados por la probeta se registran con un detector de centelleo colocado en un ángulo determinado con relación al haz neutrónico. El poder de resolución del espectrómetro es del orden de los 15 µs/m.

Los autores describen en detalle la construcción del espectrómetro y proporcionan indicaciones precisas sobre sus características.

#### ВВЕЛЕНИЕ

Изучение угловой и энергетической зависимости медленных нейтронов, неупруго рассеянных жидкими и твердыми телами позволяет получить детальную информацию о динамике атомов в жидких и твердых телах [2,3]. Проведение экспериментов по определению дважды <u>d<sup>2</sup>σ</u> сопряжено с большими

дифференциальных сечений рассеяния

трудностями, связанными с необходимостью получения интенсивного импульсного пучка монохроматических нейтронов. Измерение указанной величины стало возможным только в последние годы, когда развитие техники спектрометрии медленных нейтронов по времени пролета достигло такого уровня, который позволил создать т.н. "двойные спектрометры", позволяющие осуществить анализ (по времени пролета) энергии нейтронов как падающих на образец, так и рассеянных им под данным углом.

В настоящее время уже созданы первые установки такого типа [2,3]. Они рассчитаны на работу на пучках нейтронов, выходящих из реакторов постоянной мощности. Для получения импульсного пучка нейтронов в этих установках служат специальные прерыватели (вращающийся кристалл, механический прерыватель). Эти устройства на 2-3 порядка снижают интенсивность нейтронного пучка.

Описываемый ниже двойной спектрометр расчитан для работы на импульсном источнике нейтронов. В нашем случае таким источником является импульсный реактор на быстрых нейтронах (ИБР). Он позволяет создать сравнительно простой по конструкции прибор, обладающий высокой светосилой и хорошим разрешением при малом уровне Последнее обстоятельство обусловлено тем, что во время фона. регистрации нейтронов мощность реактора равна нулю.

Анализ энергии нейтронов, падающих на образец, производится по времени пролета от замедлителя (расположенного у активной зоны реактора), до механического прерывателя. Анализ энергии нейтронов, рассеянных на образце, осуществляется по времени пролета от образца до детектора, расположенного под заданным углом.

#### **II. ОПИСАНИЕ УСТАНОВКИ**

Схема описываемой установки представлена на рис.1.

В активной зоне реактора (1) генерируются короткие импульсы быстрых нейтронов. Эти нейтроны замедляются в слое парафина (11). Вышедшие из парафина медленные нейтроны, проходя через коллимирующие устройства (2), (3) и (4), попадают на ротор (5) механического прерывателя, который может/быть установлен на расстоянии 8,5 - 14 м от светящейся поверхности ИБРа. В зависимости от заданного сдвига по отношению к моменту импульса мощности реактора,





#### Общая схема установки:

 реактор ИБР; 2 и 3 — коллиматоры; 4 — конусные коллиматоры; 5 — ротор мех.прерывателя; 6 — образец;7 — ловушка; 8 — детектор; 9 — бетонный домик; 10 — 256-канальный анализатор; 11 — парафиновая кассета.

ротор пропускает только нейтроны определенной энергии  $E_0 \pm \Delta E_0$ .Эти монохроматические нейтроны рассеиваются на образце (6), установленном за ротором на расстоянии 25 см от его центра, и регистрируются под определенном углом  $\theta$  детектором (8). Энергия рассеянных нейтронов определяется по времени пролета при помощи 256-канального временного анализатора (10).

Детектор может быть расположен на расстоянии 3-10 м от образца под углом 10 - 155° к направлению нейтронного пучка.

## Импульсный источник нейтронов

Реактор ИБР может генерировать нейтронные импульсы либо при каждом прохождении подвижной части активной зоны через неподвижную часть, либо при каждом десятом прохождении. Спектрометр рассчитан на работу в последнем режиме. При этом частота следования импульсов ~ 500 имп/мин. Длительность импульса — 36 мксек (полуширина). Форма импульса приведена в работе [1]. Средняя интенсивность нейтронов при мощности 1 квт, на которой обычно работает реактор, составляет  $4,5 \cdot 10^{13}$  нейтр/сек. Размер активной зоны  $40 \times 45$  см<sup>2</sup>.Парафиновая кассета, используемая в качестве замедлителя, имеет толщину 5 см. Форма нейтронного импульса после замедления приведена ниже.

#### Механический прерыватель

Механический прерыватель представляет собой систему из двух конусных коллиматоров, ротора с двигателем постоянного тока и фазирующего устройства. Ротор механического прерывателя имеет вертикальную подвеску и вращается синхронно с основным диском ИБРа с определенным сдвигом фазы. Частота вращения ротора может быть равной, либо кратной (n= 1,2,4) частоте следования импульсов мощности реактора, т.е. ротор может вращаться со скоростями 500, 1000, и 2000 об/мин. Вращение осуществляется двигателем постоянного тока типа 4 МИ-12С (p = 1,35 вт, n = 5300 об/мин, U<sub>R</sub> = 1106, I<sub>R</sub> = 16а, U<sub>возб</sub> = 26 в), питаемым от двух селеновых выпрямителей типа ВСА-111А. Схема питания предусматривает длительную работу двигателя. Скорость вращения ротора может меняться путем изменения напряжения, подаваемого на обмотку якоря.

В настоящее время работы ведутся в интервале энергий монохроматических нейтронов 0,02 - 0,3 эв. Для работы в этой области энергий используется ротор № 1 с параметрами, приведенными в табл.1. Щели ротора сдвинуты по отношению к его оси так, что за один оборот ротор пропускает только одну пачку нейтронов. Функция пропускания ротора, рассчитанная по формулам из работы [4], представлена на рис.2.



Функция пропускания ротора при n = 1000 об/мин.

Для проведения исследований с монохроматическими нейтронами, лежащими вне указанного выше интервала энергий, будут использоваться роторы другой конструкции.

Параметры этих роторов также приведены в табл.1. Ротор №2 предназначен для работы с нейтронами, имеющими энергии в области 0,001 — 0,02 эв, ротор №3 — для работы в области выше 0,3 эв.

Конструкция механического прерывателя предусматривает быструю взаимозаменяемость роторов.

Таблица 1

№ ро- Диам тора м		аметр, Ширина мм щели, мм мм	К-во щелей	Форма щели	Радиус кривиз- ны, м	Размер пакета, <sub>ММ</sub> 2	Материал	Коллиматор	
	Диаметр, мм							Консу- ность щели	Мате- риал
í	200	1,5	31	Прямо- угольная	-	100 × 100	Гетинакс	<b>4</b> 6′	Никель
2	200	1,5	31	Изогнутая по радиусу	3	100 × 100	Гетинакс	46′	Никель
3	200	0,5	65	Прямоуголь- ная	-	100 × 100	Гетинакс	46′	Никель

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двойной спектрометр медленных нейтронов

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### Система фазировки

Важной характеристикой спектрометра является точность поддержания заданной разности фаз между роторами прерывателя и импульсами мощности реактора. В описываемом спектрометре синхронизация вращения ротора и его фазировка осуществлялась с помощью специальной системы стабилизации оборотов и фазировки.

Для стабилизации оборотов питание двигателя осуществлялось через электромашинный усилитель ЭМУ-12А. Напряжение на обмотку возбуждения электромашинного усилителя подается с тахогенератора, укрепленного на одной оси с ротором прерывателя. В качестве тахогенератора используется сельсин СЛ-221. Осуществленная таким образом обратная связь обеспечивает достаточную стабильность оборотов ротора.

Дальнейшая стабилизация оборотов и фазирование ротора производится с помощью следующей системы. На одном валу с ротором установлен текстолитовый диск диаметром 200 мм, по окружности которого расположены 32 равномерно отстоящих друг от друга усеченных пермаллоевых сектора. Длина каждого сектора составляет 30 мм, угол 3,6°. Угловое расстояние между центрами роторов - 11,25°. 4 электромагнита, расположенные под 90° друг по отношению к другу, установлены таким образом, что пермаллоевые сектора при вращении диска поочередно проходят между полюсами этих магнитов. На обмотки электромагнитов подаются импульсы тока с частотой, в 32•n-раза (n = 1,2,4) превышающей частоту повторения импульсов мощности реактора. Длительность импульсов тока выбрана таким образом, что при вращении ротора с заданной кратностью относительно частоты следования импульсов мощности, она равна времени прохождения пермаллоевого сектора между полюсами электромагнита. Если ротор вращается с такой скоростью и фазой, что пермаллоевые сектора проходят через полюса магнитов как раз в момент подачи импульса тока, то система практически не влияет на скорость вращения ротора. Если же ротор начинает отставать по фазе, пермаллоевые сектора в момент импульса тока не будут находилься точно между полюсами магнитов. Вследствие этого в момент импульса тока на ротор будет воздействовать дополнительный крутящий момент. Под действием этого момента разность фаз между прохождением пермаллоевых секторов через полюса электромагнитов и моментами подачи импульсов тока будет уменьшаться и в конце концов обратится в нуль. То же будет происходить и при опережении фазы. Таким образом описанная система в принципе обладает свойством автофазировки.

Можно показать, что путем соответствующего подбора параметров системы может быть обеспечен устойчивый режим автофазировки, при котором любой сдвиг фазы, не превышающий некоторую заданную величину, автоматически сводится к нулю затухающими колобаниями фазы вокруг нулевого значения. Ясно, что предельная величина сдвига фазы не может превышать половины углового расстояния между центрами секторов (в нашем случае 5.62°). В нашем случае предел автоматической регулировки фазы определялся именно этой величиной.

Для того, чтобы можно было осуществить фазирование ротора по отношению к импульсам мощности реактора, на одном валу с основным диском ИБРа устанавливался дюралюминиевый диск, на поверхности которого было нанесено 128 равномерно отстоящих друг от друга магнитных рисок. Рядом с диском устанавливался магнитный датчик, импульсы с которого, после соответствующего пересчета, подавались через блок задержки и усилитель мощности на электромагниты системы фазировки.

Блок задержки позволяет осуществлять сдвиг фазы ротора относительно импульсов мошности реактора до 4 мсек с шагом 32 мксек. Большие времена задержки осуществляются с помощью перехода от одного пермаллоевого сектора к другому.

Используемая система автофазировки позволяет корректировать фазу 32 раза за один оборот ротора, что позволяет обеспечить высокую стабильность фазы. Точность фазировки при использовании данной системы определяется точностью изготовления диска и установки электромагнитов. Принципиальным в описанной выше системе фазировки являются многократная коррекция фазы за один оборот ротора ("умножение") и прямая импульсная электрическая связь вала ИБРа с валом ротора.

### Детектор

В выполненных к настоящему времени методических измерениях использовался детектор состоящий из 36 борных счетчиков типа СНМО-5, расположенных в два ряда. Счетчики были разбиты на группы по 4 штуки в каждой. С помощью несложной радиосхемы емкости отдельных групп счетчиков были разделены. Применение этой схемы включения значительно улучшило характеристики детектора по сравнению с обычным параллельным соединением счетчиков. Площадь детектора 1600 см<sup>2</sup>. Эффективность к нейтронам с энергией 0,03 эв ~ 25%. В дальнейшем спектрометр будет работать со сцинтилляционным детектором [5].

#### Защита

Для снижения фона нейтронов, рассеянных от стен помещения и окружающих предметов, ротор и образец окружены защитой из кадмия и смеси парафина с карбидом бора. Детектор помещен в специальную бетонную защиту, а в непосредственной близости счетчики с 4-х сторон закрыты кадмием и экраном из борного парафина. Стенки канала в бетонной защите, ведущего к детектору, выложены изнутри кассетами из борного парафина.

### З. ХАРАКТЕРИСТИКИ СПЕКТРОМЕТРА

В приближении треугольной формы импульса быстрых нейтронов проведен расчет формы импульса тепловых нейтронов. Результаты





Форма импульса тепловых нейтронов реактора ИБР (расчетная кривая).

расчета представлены на рис.3. Ширина импульса тепловых нейтронов на половине высоты составляет 135 мксек.

Измерение характеристик спектрометра проведено на пролетной базе от источника тепловых нейтронов до прерывателя 11 м. Пролетная база от ротора до детектора равнялась 5,3 м.

На рис.4 приводится форма спектральной линии, спектрометра при скорости вращения ротора механического прерывателя n = 500об/мин. Длительность нейтронного импульса ротора равна 150 мксек на половине высоты. Ширина канала анализатора 80 мксек. Сдвиг фазы выбран так, что энергия монохроматических нейтронов  $E_0 = 0,03$  эв.

Для сравнения на этом же рисунке представлена расчетная форма спектральной линии. При расчете не учтены настабильность фазы, расходимость пучка нейтронов и конечные размеры детектора. Ширина на половине высоты расчетной кривой составляет 290 мксек, что находится в удовлетворительном согласии с экспериментальным значением 330 мксек. Уширение спектральной линии обусловлено в основном нестабильностью фазы.



Рис.4

Экспериментальная и теоретическая формы спектральной линии.

На рис.5 приведены спектральные линии для оборотов ротора n = 1000 об/мин и n = 2000 об/мин.

Характеристикой работы системы фазировки являются приведенные на рис.6 кривые W = W(t.t.)для оборотов ротора n = 500 об/мин и n = 2000 об/мин. (W — вероятность регистрации фазы  $\phi(t)$ ; t время между стартовыми импульсами ИБРа и ротора).

Ассиметрия кривых вызвана тем. что система фазировки создает на валу кроме фазирующего момента сил постоянный ускоряющий или тормозящий момент сил (из-за несовершенства системы синхронизации).

Расчетная интенсивность монохроматических нейтронов, падарщих на образец, равная ~ 10<sup>5</sup>нейтр/сек хорошо согласуется с экспепериментальными значениями, приведеными ниже.

В табл.2 приведены экспериментальные характеристики спектрометра, пересчитанные для случая, когда пролетные расстояния на 1-м и 2-м плечах спектрометра равны 10 м.



### выводы

Исследование характеристик спектрометра показало, что он дает хорошие возможности для изучения динамики атомов в различных агрегатных состояниях вещества. На спектрометре намечено осуществить программу по изучению физики твердого тела и жидкостей.

Для улучшения характеристик спектрометра проводится работа по увеличению интенсивности монохроматических нейтронов, снижению фона, совершенствованию системы регистрации и дальнейшему улучшению фазировки.

В заключение авторы выражают благодарность А.И. Лейпунскому и Ф.Л. Шапиро за внимание к работе и ценные советы; П.С. Клемышеву, спроектировавшему механическую часть прибора.и Н.П. Карлову — за разработку системы стабилизации оборотов.

Таблица 2

n	∆t <sub>o</sub>	Δt	Δφ	$\mathcal{I}_{M}$	τ
об/мин	мксек/м	мксек/м	град	нейтр/сек	мксек
500	30	17	0,2	~ 4·10 <sup>5</sup>	80
1000	20	9	0,27	~ 2·10 <sup>5</sup>	32
2000	14	4,6	0,3	~ 10 <sup>5</sup>	16

n - число оборотов в минуту;

∆t<sub>о</sub> - полуширина спектральной линии, формируемой ротором на І-й пролётной базе (монохроматизация нейтронов, падающих на образец);

∆t - полуширина функции разрешения на 2-й пролётной базе;

Δφ - полуширина функции фазировки;

 J<sub>M</sub> - интенсивность монохроматических нейтронов на образце для наиболее вероятной скорости спектра замедления;
 τ - ширина канала анализатора.

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# THE TRANSMISSION OF THERMAL NEUTRONS THROUGH A LARGE SINGLE CRYSTAL OF BISMUTH AT LIQUID NITROGEN TEMPERATURE

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### Abstract — Résumé — Аннотация — Resumen

THE TRANSMISSION OF THERMAL NEUTRONS THROUGH A LARGE SINGLE CRYSTAL OF BISMUTH AT LIQUID NITROGEN TEMPERATURE. The transmission of a bismuth filter, at the temperature of liquid nitrogen, was measured using a slow chopper and a flight path of 5.4 m. The filter is made of two "single crystals", each 20 cm long and 5 cm in diameter. According to specification of the manufacturer each "single crystals" consists of maximum three of four columns of single crystals. In the energy range from 25 - 10 meV, the transmitted intensity is about 30% of the expected value. In the range from 5 meV to lower energies, the transmission is of the order of 60 - 70%.

A cadmium ratio of 5000 was measured. The actual cadmium ratio may still be higher since the measurement was not made with a really fast neutron collimator. In spite of many coherent dips in the transmission curve, the performance of the filter is rather satisfactory for the production of a thermal neutron beam that is predominantly free from fast neutrons and  $\gamma$ -rays. Possible applications of a filtered neutron beam are discussed.

TRANSPARENCE AUX NEUTRONS THERMIOUES D'UN GRAND MONOCRISTAL DE BISMUTH A LA TEM-PÉRATURE DE L'AZOTE LIQUIDE. On a mesuré la transparence d'un filtre de bismuth, à la température de l'azote liquide, en utilisant un sélecteur lent et une base de vol de 5,4 m. Le filtre était composé de deux « monocristaux » chacun avant une longueur de 20 cm et un diamètre de 5 cm. D'après les indications du fabricant, chacun des « monocristaux » comporte au maximum trois ou quatre colonnes de monocristaux. Dans la gamme d'énergie de 25 à 10 meV. l'intensité transmise représente environ 30% de la valeur prévue. Dans la gamme d'énergie inférieure à 5 meV, la transparence est de l'ordre de 60 à 70%.

On a mesuré un rapport cadmium de 5000. Il se peut que le véritable rapport cadmium soit encore plus élevé, du fait qu'il n'a pas encore été mesuré au moyen d'un collimateur spécialement conçu pour les neutrons rapides. Malgré un grand nombre d'inflexions cohérentes dans la courbe de transparence, le rendement du filtre est assez satisfaisant pour la production d'un faisceau de neutrons thermiques qui soit pratiquement libre de neutrons rapides et de rayons gamma. Le mémoire examine les applications possibles d'un faisceau de neutrons filtrés.

ПРОПУСКАНИЕ ТЕПЛОВЫХ НЕЙТРОНОВ ЧЕРЕЗ КРУПНЫЙ МОНОКРИСТАЛЛ ВИСМУТА ПРИ ТЕМПЕРАТУРЕ ЖИДКОГО АЗОТА. Пропускная способность висмутового фильтра изучалась с помощье селектора медленных нейтронов с траекторией полета 5,4 м при температуре жидкого азота. Фильтр изготовлен из двух "одиночных кристаллов" длиной 20 и диаметром 5 см каждый. Согласно описание изготовителя, каждый "одиночный кристалл" состоит максимум из трех или четырех столбиков одиночных кристаллов. В диапазоне энергий от 25 до 10 Мэв интенсивность пропущенного излучения составляет около 30% ожидаемой величины. В пределах 5 Мэв и ниже величина пропускания составляет 60 - 70%.

Измеренное кадмиевое отношение - 5 000. Действительное кадмиевое отношение может быть выше, поскольку измерение производилось без коллиматора быстрых нейтронов. Несмотря на наличие когерентных провалов в кривой пропускания, характеристика фильтра удовлетворяет требованиям получения пучка тепловых нейтронов, почти свободного от быстрых нейтронов и у-лучей. Обсуждаются возможности применения отфильтрованного нейтронного пучка.

TRANSMISIÓN DE NEUTRONES TÉRMICOS A TRAVÉS DE UN MONOCRISTAL DE BISMUTO DE GRAN TAMAÑO A LA TEMPERATURA DEL HIDROGENO LIQUIDO. Se midió la transmisión por un filtro de bismuto, a la temperatura del nitrógeno líquido, utilizando un periódico lento y una trayectoria de 5,4 m. El filtro

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consistió en dos "monocristales", de 20 cm de longitud y 5 cm de diámetro. Según las especificaciones del fabricante, cada "monocristal" estaba formado por un máximo de tres a cuatro columnas de monocristales. En el intervalo de energías comprendido entre 25 y 10 meV, la intensidad transmitida es de alrededor del 30% del valor esperado. Entre 5 meV y energías mas bajas, la transmisión es del orden del 60 - 70%.

Se midió una razón de cadmio de 5000. La razón de cadmio efectiva puede ser aún más elevada, ya que las mediciones no se han efectuado con un verdadero colimador de neutrones rápidos. A pesar de muchas inflexiones coherentes en la curva de transmisión, el rendimiento del filtro es bastante satisfactorio para la producción de un haz de neutrones térmicos prácticamente libre de neutrones rápidos y de rayos gamma. En la memoria se examinan las posibles aplicaciones de un haz de neutrones filtrados.

### I. INTRODUCTION

In the last four years a new type of filter consisting of large single crystals has been used by BROCKHOUSE [1] and LOWDE [2]. These filters are operated at low temperature and they pass preferentially low energy neutrons, so a thermal neutron beam is produced which is comparatively free from fast neutrons. An attenuation of resonance and fast neutrons down to  $10^{-4}$  was reported. Thus, this type of filter ought to be considered since it would help to suppress background which surely facilitates many beam hole experiments.

For the understanding of the function of these filters, we have to consider all the effects that lead to an attenuation of the thermal neutron beam by passing through a single crystal. The diverse cross-sections are:

- (1) Neutron capture,
- (2) Incoherent scattering,
- (3) Paramagnetic scattering,
- (4) Imperfections in the crystal which give rise to incoherent scattering,
- (5) Laue-Bragg scattering,
- (6) Thermal diffuse scattering.

From this list it is clear that one has to choose a material which does not capture the neutrons nor gives rise to incoherent scattering. For a few materials there are rather good single crystals available which also do not show any considerable paramagnetic scattering. We therefore have to consider in the discussion only the last two cross-sections, namely the Laue-Bragg and the thermal diffuse scattering. Since only a few Laue-Bragg peaks should show up in a large single crystal (which may consist of a few single crystals), the neutron spectrum should not be obstructed too badly. They take out a few narrow bands which can be neglected for all practical purposes.

A great part of the loss of intensity arises from the inelastic coherent and incoherent scattering which covers a large energy range and therefore has an important effect on the shape of the spectrum. These cross-sections depend very strongly on temperature and this effect can be used to generate high transmission through a crystal.

The thermal diffuse scattering cross-section can be estimated by :

 $\delta \frac{\text{diffuse}}{\text{th}} = \delta \frac{\text{total}}{\text{scattering}} - \left\{ \delta \frac{\text{elastic}}{\text{coherent}} + \delta \frac{\text{elastic}}{\text{incoherent}} \right\}$ (1)

At short wave length the total elastic scattering can be approximated by:

$$\delta \frac{\text{elastic}}{\text{coherent}} + \delta \frac{\text{elastic}}{\text{incoherent}} = \delta \frac{\text{total}}{\text{scattering}/4 \text{ K}^2 \text{W} [1 - e^{-4 \text{ K}^2 \text{W}}]}$$
(2)

with W = 
$$(3 h^2/4 \pi^2 m_A k \theta) [\theta(x)/x + 1/4]$$

and  $\phi(\mathbf{x}) = 1/\mathbf{x} \int_{0}^{\mathbf{x}} \xi \, \mathrm{d}\xi/\mathrm{e} - 1$ .

With (1) and (2) we find the following approximation for the thermal diffuse scattering cross-section:

 $\delta \frac{\text{diffuse}}{\text{th}} \approx 2 \text{ K}^2 \text{ W } \delta \frac{\text{total}}{\text{scattering}} = 8 \pi^2 \text{W} / \lambda^2 \delta \frac{\text{total}}{\text{scattering}}$ 

In Table I we have listed all the important figures for a comparison of the various filter materials being in use now :

### TABLE I

COMPARISON OF VARIOUS FILTER MATERIALS

Materiel	δ <sub>abs</sub>	$\overline{\delta}_{scattering}$	W(295° K)	W(77° K)	W(295°)	δ <sub>thd</sub> (77° K)
	(mb)	(b)	[cm <sup>2</sup> ]	[cm²]	w(11)	(b)
Bi	34	9	1.48 x 10 <sup>18</sup>	0.416 x 10 <sup>18</sup>	3. 57	2.97/ $\lambda^2$
Be	10	7	0.49 x 10 <sup>18</sup>	$0.348 \times 10^{18}$	1. 41	1. 92/ $\lambda^2$
Si02	160	10	1.08 x 10 <sup>18</sup>	0.443 x 10 <sup>18</sup>	2.42	3.5/ $\lambda$ <sup>2</sup>
	¢ (cm)	T <sup>neutron</sup> thermal	neutron Tresonance	T <sup>γ-rays</sup> ~2 meV	T <sup>neutrons</sup> ~2 meV	
Bi	40	0.35	4.5 × 10 <sup>-5</sup>	3.8 × 10 <sup>-8</sup>	2.2 × 10 <sup>-4</sup>	
Be	14.2	0.35 🔍	4.8 × 10 <sup>-6</sup>	0,356	1.25x 10 <sup>-2</sup>	
Si0 <sub>2</sub>	36	0.35	7 × 10 <sup>-5</sup>	8.6 × 10 <sup>-3</sup>	1.2 × 10 <sup>-3</sup>	

In the above table the length of the different filters was chosen in such a way that the transmission of thermal neutrons is 35% for all filters.

From the data of Table I it is obvious that beryllium is the best material for the attenuation of resonance neutrons, while for stopping  $\gamma$ -rays, bismuth is, of course, much more effective. Therefore, the best beam hole filter will be a composition of bismuth and beryllium as it was actually used by Lowde and his co-workers. The most difficult part is to obtain relative large single crystals of beryllium. Quartz is a good filter for resonance neutrons, but does not attenuate sufficiently the  $\gamma$ -beam that is emerging from the beam hole. On the other hand, the absorption is not negligible for low energy neutrons.

The present study of the transmission of single crystals of bismuth was performed to check the applicability of such a filter for a double chopper facility at Ispra, which is designed for the energy region of 100 MeV to subthermal neutrons. Apart from this, an attempt is being made to discover

whether the filter can be used for the measurement of very small absorption cross-sections by detecting the capture of  $\gamma$ -rays. At present, the filter is used for a parity experiment using the reaction Be<sup>7</sup>(n,  $\alpha$ ) $\alpha$ . It is also proposed to use the bismuth-filtered beam for routine work to determine the graphite content in uranium-graphite pellets.

# II. MEASUREMENTS AND EXPERIMENTAL RESULTS

The transmission experiments were carried out using a straight slit chopper and a flight path of 5.4 m. The layout of the experimental conditions is shown in Fig.1. The chopper is made out of a stack of aluminium and boron plastic plates. This compact rotor guarantees a low background of fast neutrons. The neutrons from the reactor were pre-collimated by a "water-shutter". A block of 10 cm of lead was placed in the beam to reduce fast neutrons and  $\gamma$ -rays that have a serious influence on the plateau of the BF<sub>3</sub> counters in an "open beam" run (without a bismuth filter in the neutron beam). The bismuth was packed in aluminium and cylindrical pieces of sintered boron carbide (1-cm thick and 10-cm long). For the transmission experiments we used two pieces of bismuth, 20-cm long and 5-cm diam.each. According to specifications given by Metals Research (England), each piece consisted of maximum 3 or 4 columns of single crystals of bismuth. This specification showed a promising aspect : that the coherent peaks should not obstruct the neutron spectrum too much.

In Fig.2 the measured time-of-flight spectra are given for the following conditions:

(a) Open beam (bismuth filter not in the neutron beam).

(b) 40 cm of bismuth at room temperature.

(c) 40 cm of bismuth at the temperature of liquid nitrogen.

In Fig. 3 the expected and measured transmission of a 40-cm long bismuth filter is given. From the data it is obvious that the transmission is relatively far from what one would expect of a real single crystal without imperfections. The coherent dips give a considerable reduction in intensity. The transmitted intensity is only about 30% of the theoretical value in the energy range from 25 - 10 meV. The total intensity of the filtered beam increased by a factor of 4, cooling it to the temperature of liquid nitrogen.

In Figs. 4 and 5 the equivalent data are given for a single piece of 20 cm of bismuth. This crystal was chosen for a separate measurement since it showed a transmission that was higher by a factor of 2 compared with the other one. The transmission is about 40% of the expected one. This crystal can be considered as having a rather good performance. Below 5 meV, the transmission is of the order of 60-70%.

The measurements mentioned above were carried out under an angle of collimation of 1°. Since the influence of the coherent dips in the spectrum is dependent on the collimation a measurement was carried out with  $1/3^{\circ}$  collimation. For this measurement the lead was withdrawn from the reactor channel and replaced by a collimator of 20 cm in length, made out of an array of  $15 \times 15$  channels, each of 1 mm<sup>2</sup> area. The result of this measurement is given in Fig. 6.



### Fig.1

Layout of the bismuth filter experiment. The boron-paraffin mixture is 25% boron + 75% paraffin.



Neutron spectra measured with a chopper facility as indicated in the insert. In the figure are represented:

- (1) The spectra obtained with bismuth-filter at room temperature (warm filter o) (40 cm long)
- (2) The spectra obtained with liquid nitrogen-cooled filter (cooled filter x)
- (3) The spectra obtained without Bi-filter (open beam o)



Transmission of 40 cm bismuth at liquid nitrogen temperature. The heavy line is the expected behaviour; the points are the experimental values.



but with a different length of the filter (20 cm).







Transmission of 20 cm bismuth at liquid nitrogen. The collimator was 0.3°.

The cadmium ratio of the 40-cm long bismuth filter was also measured under this condition. The cadmium ratio was as high as 5000. The real value for the cadmium ratio is most probably still higher since for the measurement no real fast neutron collimator was used.

Having the cadmium in mind, one can state that the bismuth filter shows a rather satisfactory performance in spite of the coherent dips that show up in the thermal energy region.

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## DISCUSSION

P. EGELSTAFF: I would like to make an historical comment on the subject of this paper. As reported in J. nucl. Engng 1 (1954) 57, a quasi-single-crystal filter was used with the Harwell slow chopper for exactly the same reasons as described in this paper. This filter was made by slow-cooling a melt of bismuth so that crystals of 1 to 3 cm in length were formed. (No special precautions are necessary to get crystals-of this size to grow in bismuth.) The extinction observed in a (quasi-single-crystal) block of this cast bismuth is very large as shown by the cross-section we published in J. sci. Inst. (1954), and this simple material seems to be somewhat more effective than the samples reported on today.

# НЕКОТОРЫЕ ВОПРОСЫ МОНОХРОМАТИЗАЦИИ МЕДЛЕННЫХ НЕЙТРОНОВ

# В.П. ВЕРТЕБНЫЙ, В.В. КОЛОТЫЙ и А.Н. МАЙСТРЕНКО СССР

### Abstract — Résumé — Аннотация — Resumen

PROBLEMS ASSOCIATED WITH THE MONOCHROMATIZATION OF SLOW NEUTRONS. The paper sets out the result of calculations to determine the shape of the spectral line of twin-rotor, pulsing, slow-neutron monochromators, as a function of the shifts in the phases between the rotors. Consideration is also given to the possibility of using certain light elements as slow-neutron filters.

QUELQUES ASPECTS DE LA MONOCHROMATISATION DES NEUTRONS THERMIQUES. Les auteurs exposent les résultats de leurs calculs relatifs à la forme du spectre des monochromateurs à impulsions et à deux rotors pour neutrons thermiques en fonction de la distance et du déphasage entre les rotors. Ils examinent également la possibilité d'autiliser certains éléments légers comme filtres à neutrons lents.

НЕКОТОРИЕ ВОПРОСЫ МОНОХРОМАТИЗАЦИИ МЕДЛЕННЫХ НЕЙТРОНОВ. Приведены результаты расчета формы спектральной линии двукроторных пульсирующих монохроматоров медленных нейтронов в зависимости от расстояния и сдвига фаз между роторами. Рассмотрена также возможность использования некоторых легких элементов в качестве фильтров медленных нейтронов.

ALGUNOS PROBLEMAS DE LA MONOCROMATIZACIÓN DE NEUTRONES LENTOS. Los autores exponen los resultados de sus cálculos relativos a la forma de la línea espectral de los monocromadores pulsantes de dos rotores para neutrones lentos en función de la distancia y del desfasamiento de los rotores. Examinan asimismo la posibilidad de utilizar algunos elementos ligeros como filtros de neutrones lentos.

### ВВЕДЕНИЕ

Структура веществ, а также вопросы термализации нейтронов в настоящее время широко исследуются с помощью изучения рассеяния монохроматических медленных нейтронов. В этих исследованиях применяются разные типы монохроматоров, а именно: кристаллические монохроматоры, пульсирующие однороторные и многороторные механические селекторы, механические монохроматоры с квазинепрерывным пучком, фильтры медленных нейтронов.

Для большинства упомянутых выше монохроматоров в литературе имеются довольно полные характеристики. В этой работе будут рассмотрены лишь некоторые вопросы, связанные с монохроматизацией нейтронов, по нашему мнению, недостаточно освещенные в литературе. найдена форма спектрального распределения нейтронов и форма нейтронной вспышки пульсирующего двухроторного прерывателя нейтронов; описано одно из видоизменений монохроматора с осью вращения, параллельной нейтронному пучку; приведены соображения по поводу возможных фильтров медленных нейтронов. I. ФОРМА НЕЙТРОННОЙ ВСПЫШКИ И ФОРМА СПЕКТРАЛЬНОГО РАСПРЕДЕЛЕНИЯ НЕЙТРОНОВ ПРЕРЫВАТЕЛЯ (МОНОХРОМАТОРА) НЕЙТРОНОВ, СОСТОЯЩЕГО ИЗ ДВУХ РОТОРОВ С ПЛОСКИМИ ЩЕЛЯМИ

В последнее время в ряде работ были описаны механические прерыватели нейтронов, состоящие из двух и нескольких роторов [1, 2, 3]. В этих работах изложены лишь качественные преимущества многороторных систем. Ниже приводится расчет функции пропускания и нейтронной вспышки для двухроторного прерывателя с плоскими щелями. Хотя эта система является самой простой, описанный ниже метод можно распространить без особого труда и на двухроторные прерывателя с профилированными щелями.

1. Расчет нейтронной вспышки и функции пропускания для одного ротора

Эта задача была уже рассмотрена в ряде работ и впервые успешно решена в работе В.И. Мостового и др.[4]. Здесь мы ее рассматриваем лишь для того, чтобы проиллюстрировать метод расчета на простом примере и чтобы использовать некоторые результаты решения для двух роторов.

Для простоты рассмотрим ротор с одной щелью, вращающейся по часовой стрелке относительно оси О, перпендикулярной к плоскости чертежа (рис.1). Система координат u, w неподвижна, система у, х



Рис.1

Системы координат, которые используются при расчете нейтронной вспышки и функции пропускания однороторного прерывателя (ширина щели S<sub>1</sub> = 2<sub>S</sub>).

жестко связана с ротором. Назовем ее вращающейся. Момент входа нейтрона в щель обозначен через  $t_0$ . Ординаты u ( $t_0$ ) и b назовем параметрами входа. С помощью преобразования координат (y,x)-(u,w) находим, при условии  $\omega t_0 \ll 1$  ( $\omega$  - угловая скорость ротора),

$$u = R\phi_0 + b.$$
 (1)

В дальнейшем условимся все координаты измерять в единицах радиуса

ротора. Тогда (1) можно записать так:

U=

$$U = \varphi_0 + B, \qquad (1a)$$
$$\frac{u}{R} \quad \varkappa \quad B = \frac{b}{R}.$$

где

С помощью преобразования (U,W) → (У,X)можно доказать, что траекнейтрона во вращающейся системе координат (при wto << 1) тория парабола:

$$X = \frac{\omega \tau}{2} X^2 + \omega \left( t_0 + \frac{\tau}{2} \right) X + B + \omega t_0, \qquad (2)$$

где  $\tau = \frac{2R}{v}$ , v - скорость нейтрона.

Чтобы нейтрон прошел через щель, его траектория не должна пересекать стенки щели, т.е. - S < У < + S при-1 < X < + 1. Это условие и определяет совокупность параметров входа B(t<sub>0</sub>), а,следовательно, и U (t<sub>0</sub>), при которых нейтроны будут пропущены ротором (предполагается, что материал ротора абсолютно непрозрачен для нейтронов). Если обозначить наибольшее значение параметра

входа U ( $\textbf{t}_{0}$ ,  $\tau)$  через  $\textbf{U}_{B}^{I}$ , а наименьшее значение через  $\textbf{U}_{H}^{I}$ , то действующая ширина щели в момент to определится следующим образом:

$$\Delta U^{I}(t_{0},\tau) = U^{I}_{B}(t_{0},\tau) - U^{I}_{H}(t_{0},\tau).$$
 (3)

Можно видеть, что интенсивность нейтронов с данной скоростых пролорциональна

 $\int_{t_0}^{\infty} \Delta U^{I}(t_0,\tau) dt_0$ 

и, следовательно, функция пропускания ротора, описывающая относительную прозрачность ротора в зависимости от v,

> $\mathbf{f}^{\mathrm{I}} \left( \tau = \frac{2 R}{v} \right) \sim \int_{t_0 \text{ Min}}^{t_0 \text{ Max}} \Delta \mathbf{U}^{\mathrm{I}} \left( \mathbf{t}_0, \tau \right) d\mathbf{t}_0.$ (4)

Подчеркнем еще раз, что t<sub>0</sub> - момент входа нейтрона в щель. Входные параметры сведены в табл.1. При нахождении формы вспышки (действующей ширины щели) потребуем, чтобы

$$- U_{B}^{I} \ge U_{H}^{I}$$
 (5)

С помощью таблицы 1, уравнений (3) и (5) получаем следующие выражения для нейтронной вспышки:

ТАБЛИЦА 1

ЗНАЧЕНИЯ ВХОДНЫХ ПАРАМЕТРОВ ДЛЯ ОДНОГО РОТОРА

t <sub>o</sub>	U <sub>H</sub>	to	U <sub>B</sub> <sup>I</sup>
t <sub>0</sub> ≼ - <sup>3</sup> /2 <sup>τ</sup>	$U_{11} = -S - \omega \tau \left(1 + 2 \frac{t\delta}{\tau}\right) + \omega t_0$	t <sub>0</sub> ≼ - τ/2	$U_{11}^{1} = S + \omega t_{0}$
$-\frac{3}{2}\tau \ll t_0 \ll \frac{\tau}{2}$	$U_{12} = -S + \frac{\omega\tau}{2} \left(\frac{1}{2} - \frac{t_0}{\tau}\right)^2 + \omega t_0$		
τ <sub>2</sub> ≤ t <sub>0</sub>	$U_{13} = -S + \omega t_0$	t <sub>o</sub> > − ż	$U_{12} = S - \omega \tau \left(1 + 2 \frac{t_0}{\tau}\right) + \omega t_0$

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$$\begin{aligned} & -\frac{S}{\omega} - \frac{\tau}{2} \leq t_{0} \leq -\frac{3}{2}\tau, & \Delta U^{I} = 2S + \omega\tau \left(1 + 2\frac{t}{\tau}\right); \\ & -\frac{3}{2}\tau \leq t_{0} \leq -\frac{\tau}{2}, & \Delta U^{I} = 2S - \frac{\omega\tau}{2}\left(\frac{1}{2} - \frac{t}{\tau}\right)^{2}; & (6a) \\ & -\frac{\tau}{2} \leq t_{0} < \frac{\tau}{2}, & \Delta U^{I} = 2S - \omega\tau \left(1 + 2\frac{t}{\tau}\right) - \frac{\omega\tau}{2}\left(\frac{1}{2} - \frac{t}{\tau}\right)^{2} \\ & \frac{\tau}{2} \leq t_{0} < \frac{S}{\omega} - \frac{\tau}{2}, & \Delta U^{I} = 2S - \omega\tau \left(1 + 2\frac{t}{\tau}\right) - \frac{\omega\tau}{2}\left(\frac{1}{2} - \frac{t}{\tau}\right)^{2} \\ & \Delta U^{I} = 2S - \omega\tau \left(1 + 2\frac{t}{\tau}\right) - \frac{\omega\tau}{2}\left(\frac{1}{2} - \frac{t}{\tau}\right)^{2} \\ & S \leq \tau \leq \frac{4S}{\omega} \end{aligned}$$

$$\left(\frac{1}{2} - \sqrt{\frac{4S}{\omega\tau}}\right)^{\tau} \leq t_0 \leq -\frac{\tau}{2} , \qquad \Delta U^{I} = 2S - \frac{\omega\tau}{2} \left(\frac{1}{2} - \frac{t}{\tau}\right)^2; \qquad (6 \ \sigma)$$

$$\left(-\frac{\tau}{2} \leq t_0 \leq \left(\sqrt{\frac{4S}{\omega\tau}} - \frac{3}{2}\right)^{\tau} , \qquad \Delta U^{I} = 2S - \omega\tau \left(1 + 2\frac{t_0}{\tau}\right) - \frac{\omega\tau}{2} \left(\frac{1}{2} - \frac{t_0}{\tau}\right)^2.$$

Функции пропускания для этих двух случаев найдены с помощью формулы (4):

$$f(z) = \begin{cases} 1 - \frac{8}{3} z^4 & \text{при } 0 \le z \le \frac{1}{2} \\ \\ \frac{16}{3} z (1-z)^2 (1+\frac{z}{2}) & \text{при } \frac{1}{2} \le z \le 1, \\ \\ z = \sqrt{\frac{\omega \tau}{4S}} \sim \sqrt{\frac{1}{v}}. \end{cases}$$
(7)

где

### 2. Расчет нейтронной вспышки для случая двух роторов

Взаимное расположение роторов и их фаз при wt = 0 показано на рис.2. Для расчета действующей щели в случае двух роторов не-





Взаимное расположение роторов в двухроторном прерывателе нейтронов.

обходимо найти параметры входа для второго ротора

υ<sup>II</sup> U<sup>II</sup> B и

Если обозначить  $U_B^{Min}$  меньшее из двух значений  $U_B^I$  и  $U_B^{II}$ , а  $U_H^{Max}$ 

большее их двух значений  $U_{H}^{I}$  и  $U_{H}^{II}$ , то действующая ширина щели

$$\Delta U(t_0,\tau) = U_B^{Min} - U_H^{Max} , \qquad (8)$$

при условии, что

 $U_{B}^{\min} \ge U_{B}^{\max} .$  (9)

Функция пропускания

$$f(\tau) \sim \int \Delta U(t_0, \tau) dt_0. \qquad (10)$$

Параметры входа в ротор II в момент входа нейтрона во вторую щель, равный t, могут быть записаны в такой же форме, как и для первого ротора в момент t<sub>0</sub>, если

to Max

$$\mathbf{t}_{*} = \mathbf{t}_{0} + \frac{2\mathbf{R} + \lambda}{\mathbf{v}} - \mathbf{T} \equiv \mathbf{t}_{0} + \alpha \tau, \qquad (11)$$

где

$$\alpha = 1 + \frac{\lambda}{2R} - \frac{T}{\tau} . \qquad (11a)$$

Итак, при  $\mathbf{t} = \mathbf{t}_{1}$ ,  $\mathbf{U}^{\Pi}$   $(\mathbf{t}_{1}) = \mathbf{U}^{\mathbf{I}} (\mathbf{t}_{0} \rightarrow \mathbf{t}_{1})$ .

Найденные таким образом параметры входа для второго ротора сведены в табл.2.

Для сравнения входных параметров обоих роторов чрезвычайно удобны диаграммы, приведенные на рис.3 и 4. Результаты сравнения параметров с помощью этих диаграмм представлены на рис.5 и 6.

Используя данные рис.5 и 6 и уравнения(8 – 10), получим следующие выражения для ширины действующей щели (формы вспышки):

при 
$$\alpha \le -2$$
 и  $\tau \le -\frac{2S}{\omega \alpha}$ 

 $\Delta U = 2S + 2\omega t_0 + \omega \tau + 2\alpha \omega \tau;$ (12 a)

 $\tau \leq \frac{S}{10}$ 

$$-\frac{1+\alpha}{2}\tau \leqslant t_0 \leqslant \frac{s}{\omega} - \frac{\tau}{2}, \qquad \Delta U = 2S - \omega\tau - 2\omega t_0;$$

при −2 < α < 0 и

 $-\frac{S}{\omega}-\frac{\tau}{2}-\alpha\tau \leqslant t_0\leqslant -\frac{1+\alpha}{2}\tau,$ 

ТАБЛИЦА 2.

# ЗНАЧЕНИЯ ВХОДНЫХ ПАРАМЕТРОВ ДЛЯ ВТОРОГО РОТОРА

t <sub>o</sub>	U <sub>H</sub> <sup>II</sup>	to	UB
t <sub>0</sub> ≤ - <sup>3</sup> / <sub>2</sub> τ - ατ	$U_{21} = -S - \omega\tau \left(1 + 2 \frac{t_0 + \alpha\tau}{\tau}\right) + \omega \left(t_0 + \alpha\tau\right)$	t <sub>0</sub> < - <sup>τ</sup> <sub>2</sub> - ατ	$U_{21}^{1} = S + \omega (t_{0} + \alpha \tau)$
- <sup>3</sup> 2τ - ατ ≤ t <sub>0</sub> ≤	$U_{22} = -S + \frac{\omega\tau}{2} \left( \frac{1}{2} - \frac{t_0 + \alpha\tau}{\tau} \right)^2 +$		
≤ ½ - ατ	+ $\omega$ (t <sub>0</sub> + $\alpha\tau$ )		$(1 \circ t_0 + \alpha \tau)$
$\frac{\tau}{2} - \alpha \tau < t_0$	$U_{23} = -S + \omega (t_0 + \alpha \tau)$	$t_0 \ge -\frac{\tau}{2} - \alpha \tau$	$U_{22} = S - \omega \tau \left( I + 2 - \frac{\tau}{\tau} \right) + \omega \left( t_0 + \alpha \tau \right)$



Рис.3

Диаграммы для сравнения нижних параметров входа нейтронов. .



Рис.4

Диаграммы для сравнения верхних параметров входа нейтронов.

$$-\frac{S}{\omega} - \frac{\tau}{2} - \alpha \tau \leq t_0 \leq -\frac{3}{2}\tau - \alpha \tau, \qquad \Delta U = 2S + \omega \tau \left[ (1 + 2\alpha) + 2\frac{t_0}{\tau} \right].$$
$$-\frac{3}{2}\tau - \alpha \tau \leq t_0 \leq -\frac{1 + \alpha}{2}\tau, \qquad \Delta U = 2S - \frac{\omega \tau}{2} \left( \frac{1}{2} - \frac{t_0 + \alpha \tau}{\tau} \right)^2; \qquad (126)$$











Зависимость верхних параметров входа нейтронов от времени t<sub>0</sub>.

$-\frac{1+\alpha}{2}\tau < t_0 < \frac{\tau}{2} ,$	∆U= 2S-	$\frac{\omega \tau}{2} \left( \frac{1}{2} - \frac{t_0}{2} \right)^2 2\omega t_0 - \omega \tau;$
$\frac{\tau}{2} \leq t_0 \leq \frac{S}{\omega} - \frac{\tau}{2} ,$	$\Delta U = 2S$	-2 ωt <sub>0</sub> -ωτ;
при - 2 < α < 0	и <u>S</u> ≺ т ≼	$\frac{16}{\omega(2-\alpha)^2}$
$\left(\frac{1}{2} - \alpha - \sqrt{\frac{4S}{\omega\tau}}\right) \tau < t_0 < - \cdot$	$\frac{1+\alpha}{2}\tau,  \Delta U = 2S -$	$\frac{\omega\tau}{2}\left(\frac{1}{2}-\frac{t_{0}+\alpha\tau}{\tau}\right)^{2};$
$-\frac{1+\alpha}{2}\tau < t_0 < \tau \left(\sqrt{\frac{4S}{\omega\tau}} - \frac{3}{2}\right)$	$\frac{3}{2}$ , $\Delta U = 2S - \frac{\omega \tau}{2}$	$\frac{1}{2} - \frac{t}{\tau} \partial^2 - 2\omega t_0 - \omega \tau;$
при 0 ≼ α ≼ 2	и т < $\frac{\overline{S}}{\omega}$	
$-\frac{S}{\omega} - \frac{\tau}{2} < t_0 < -\frac{3}{2} \tau ,$	$\Delta U = 2S + \omega \tau (1 +$	$2\frac{t}{\tau}$ );
$-\frac{3}{2}\tau \leq t_0 \leq -\frac{\tau}{2}\left(1+\alpha\right),$	$\Delta U = 2S - \frac{\omega \tau}{2} \left(\frac{1}{2} - \frac{\omega \tau}{2}\right)$	$\left(\frac{t_0}{\tau}\right)^2$ (12 r)
$-\frac{\tau}{2}\left(1+\alpha\right) \leq t_0 \leq \frac{\tau}{2} - \alpha \tau,$	$\Delta U = 2S - \frac{\omega \tau}{2} \left( \frac{1}{2} - \frac{\omega \tau}{2} \right)$	$a - \frac{t_0}{\tau} \int_{-\infty}^{\infty} d\tau - 2a\omega\tau - 2\omega t_0$
$\frac{\tau}{2} - \alpha \tau \leq t_0 \leq \frac{s}{\omega} - \frac{\tau}{2},$	$\Delta U = 2S - \omega \tau - 2c$	ωτ -2ωt <sub>0</sub> .
при 0 < α < 2	$u \qquad \frac{S}{\omega} < \tau$	$\leq \frac{16 \text{ S}}{\omega(2 + \alpha)^2}$
$\tau\left(\frac{1}{2}-\sqrt{\frac{4S}{\omega\tau}}\right) < t_0 < -\frac{1}{2}$	$\Delta U = 2S$	$-\frac{\omega\tau}{2}\left(\frac{1}{2}-\frac{t_0}{\tau}\right)^2;$
$-\frac{\tau}{2}(1+\alpha) \leq t_{c} \leq \left(-\frac{3}{2}-\right)$	$\alpha + \sqrt{\frac{4S}{\omega \tau}} \tau$	(12д)
$\Delta U = 2S - \frac{\omega \tau}{2} \left( \frac{1}{2} \right)^{-1}$	$\alpha - \frac{t_0}{\tau} \Big)^2 - \omega \tau - 2\alpha \omega \tau$	- 2wt <sub>0</sub> .
при 2 ≼ α	И	$\tau \leq \frac{S}{2\alpha\omega}$
$-\frac{S}{\omega}-\frac{\tau}{2} \leq t_0 \leq -\frac{\tau}{2}\left(1+\alpha\right)$	), $\Delta U = 2$	$S + \omega \tau \left(1 + 2 \frac{t_0}{\tau}\right);$ (12 e)
$-\frac{\tau}{2}(1+\alpha) \leq t_0 \leq \frac{S}{\omega} - \frac{\tau}{2}$	- ατ, ΔU = 2S	$-2\omega t_0 - 2\alpha\omega t - \omega \tau;$

## 3. Функция пропускания для случая двух роторов

После интегрирования выражения (10) получены следующие выражения для функции пропускания:

при 
$$0 \le |\alpha| \le 2$$
 и  $0 \le z \le \frac{1}{2}$ 

$$f_{1}(z,\alpha) = 1 - \frac{8}{3}z^{4} - 4|\alpha|z^{2} + 8\left(\frac{|\alpha|}{2} + \frac{\alpha^{2}}{4} + \frac{|\alpha|^{3}}{24}\right)z^{4};$$
(13 a)

при

$$0 \le |\alpha| \le 2$$
  $\mu$   $\frac{1}{2} \le z \le 1 + \frac{1}{1 + \frac{|\alpha|}{2}}$ 

$$f_{2}(z,\alpha) = \frac{16}{3} \cdot \frac{1}{1 + \frac{|\alpha|}{2}} z^{1} \left(1 - z^{1}\right)^{2} \left(1 + \frac{z^{1}}{2}\right),$$

$$z^{1} = z \left(1 + \frac{|\alpha|}{2}\right);$$
(13 6)

при

где

 $\alpha \ge 2$   $\mu$   $z < \sqrt{\frac{1}{2|\alpha|}}$ 

 $f_3(z,\alpha) = (1 - 2|\alpha|z^2)^2.$  (13 B)

Для расчета и построения функций пропускания удобно классифицировать их не по параметру  $\alpha$  (z), а по параметрам  $\beta$  и  $\gamma$ ;  $\beta$  и  $\gamma$  - параметры, которые определяются из выражения:

$$\alpha = 1 + \frac{\lambda}{2R} - \frac{T}{\tau} \equiv \beta - \frac{Y}{Z^2},$$

$$\beta = 1 + \frac{\lambda}{2R} ; Y = \frac{\omega T}{4S} ; S = \frac{S}{2R}.$$
(14)

Нетрудно видеть, что у пропорционально отношению времени запаздывания второго ротора к длительности вспышки одиночного ротора. Указанная классификация легко производится, если исследовать неравенства для у и z, содержащиеся в (13). Получены следующие выражения:

$$f(z,\alpha) = f_3 \quad \text{при} \quad \gamma < \frac{\beta + 2}{4} \qquad \text{для} \quad \frac{\gamma - \frac{1}{2}}{\beta} < z^2 < \frac{\gamma}{\beta + 2};$$

$$f(z, \alpha) == f_{1} \begin{cases} npu \quad \gamma \leqslant \frac{\beta}{4} & n\pi\pi \frac{\gamma}{\beta+2} \leqslant z^{2} \leqslant \frac{\gamma}{\beta}; \\ npu \quad \frac{\beta}{4} \leqslant \gamma \leqslant \frac{\beta+2}{4} & n\pi\pi & \frac{\gamma}{\beta+2} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} \begin{cases} npu \quad \frac{\beta}{4} \leqslant \gamma \leqslant \frac{\beta+2}{4} & n\pi\pi & \frac{1}{4} \leqslant z^{2} \leqslant \frac{\gamma}{\beta}; \\ npu \quad \frac{\beta+2}{4} \leqslant \gamma \leqslant \beta & n\pi\pi & \frac{1-\sqrt{1-\gamma(2-\beta)}}{2-\beta} \leqslant z \leqslant \sqrt{\frac{\gamma}{\beta}}; \\ f(z, \alpha) = f_{1} & npu \quad \gamma \leqslant \frac{\beta}{4} & n\pi\pi & \frac{\gamma}{\beta} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{\beta}{4} & n\pi\pi & \frac{\gamma}{\beta} \leqslant z \leqslant \frac{1+\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{\beta-2}{4} & n\pi\pi & \frac{1}{2} \leqslant z \leqslant \frac{\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \\ f(z, \alpha) = f_{3} & npu \quad \gamma \leqslant \frac{\beta-2}{4} & n\pi\pi & \frac{\gamma}{\beta-2} \leqslant z^{2} \leqslant \frac{\gamma}{4}; \\ f(z, \alpha) = f_{3} & npu \quad \gamma \leqslant 1 & n\pi\pi & \frac{\gamma}{4} \leqslant z^{2} \leqslant \frac{1}{4}; \\ npu \quad \frac{1}{2} \leqslant \gamma \leqslant 1 n\pi\pi & \frac{\gamma}{4} \leqslant z^{2} \leqslant \frac{\gamma}{2}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\gamma}{4} \leqslant z^{2} \leqslant \frac{\gamma}{2}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{\gamma}{2}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{\gamma}{2}; \\ f(z, \alpha) = f_{1} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{\gamma}{2}; \\ f(z, \alpha) = f_{1} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{2} \leqslant z^{2} \leqslant \frac{1}{4}; \\ npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{1} & npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{2} \leqslant z^{2} \leqslant \frac{1}{4}; \\ npu \quad \gamma \leqslant \frac{1}{2} & n\pi\pi & \frac{\sqrt{2}}{4} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant 2 & n\pi\pi & \frac{\sqrt{2}}{2} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant 2 & n\pi\pi & \frac{\sqrt{2}}{\sqrt{2}} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{2} & npu \quad \gamma \leqslant 2 & n\pi\pi & \sqrt{\frac{1}{2}} \leqslant z^{2} \leqslant \frac{1}{4}; \\ f(z, \alpha) = f_{3} & npu \quad \gamma \leqslant 0 & n\pi\pi & \sqrt{\frac{2}{2}} \leqslant z^{2} \leqslant \frac{1}{4}; \end{cases}$$

$$f(z, \alpha) = f_{3} \quad \text{при } \gamma \leq \frac{\beta+2}{4} \quad \text{для } \frac{\gamma-\frac{1}{\beta}}{\beta} \leq z^{2} \leq \frac{\gamma}{\beta+2};$$

$$f(z, \alpha) = f_{1} \begin{cases} \text{при } \gamma \leq \frac{\beta}{4} & \text{для } \frac{\gamma}{\beta+2} \leq z^{2} \leq \frac{\gamma}{\beta}; \\ \text{при } \frac{\beta}{4} \leq \gamma \leq \frac{\beta+2}{4} & \text{для } \frac{1}{\beta+2} \leq z^{2} \leq \frac{1}{4}; \end{cases}$$

$$f(z, \alpha) = f_{2} \begin{cases} \text{при } \frac{\beta}{4} \leq \gamma \leq \frac{\beta+2}{4} & \text{для } \frac{1}{4} \leq z^{2} \leq \frac{\gamma}{\beta}; \\ \text{при } \frac{\beta+2}{4} \leq \gamma \leq \beta & \text{для } \frac{\sqrt{1+\gamma(\beta-2)-1}}{\beta-2} \leq z < \sqrt{\frac{\gamma}{\beta}}; \end{cases}$$

$$f(z, \alpha) = f_{1} \begin{cases} \text{при } 0 \leq \gamma \leq \frac{\beta-2}{4} & \text{для } \frac{\gamma}{\beta} \leq z^{2} \leq \frac{\gamma}{\beta+2}; \\ \text{при } \frac{\beta-2}{4} \leq \gamma \leq \frac{\beta}{4} & \text{для } \frac{\gamma}{\beta} \leq z^{2} < \frac{1}{4}; \end{cases}$$

$$f(z, \alpha) = f_{2} \begin{cases} \text{при } \frac{\beta-2}{4} \leq \gamma \leq \frac{\beta}{4} & \text{для } \frac{1}{2} \leq z \leq \frac{1+\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \\ \text{при } \frac{\beta-2}{4} \leq \gamma \leq \frac{\beta}{4} & \text{для } \frac{1}{2} \leq z \leq \frac{1+\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \end{cases};$$

$$f(z, \alpha) = f_{2} \begin{cases} \text{при } \frac{\beta-2}{4} \leq \gamma \leq \beta & \text{для } \sqrt{\frac{\gamma}{\beta}} \leq z \leq \frac{1+\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \\ \text{при } \frac{\beta}{4} \leq \gamma \leq \beta & \text{для } \sqrt{\frac{\gamma}{\beta}} \leq z \leq \frac{1+\sqrt{1+\gamma(\beta+2)}}{\beta+2}; \end{cases};$$

$$f(z, \alpha) = f_{3} \quad \text{при } \gamma \leq \frac{\beta-2}{4} & \text{для } \frac{\gamma}{\beta-2} \leq z^{2} \leq \frac{\gamma+\frac{1}{2}}{\beta}.$$

Графики для случаев  $\beta = 1, 2, 4, 10$  и разных у  $(0 \le \gamma \le \beta)$  представлены на рис. 7 - 10.

Как видно из этих рисунков, при у = О система двух роторов работает как механический прерыватель. Граничная скорость увеличивается (уменьшается z) с увеличением расстояния между роторами (большие в). По мере увеличения параметра у происходит все большее ограничение пропускаемых скоростей не только снизу, но и сверху. В случае относительно больших  $\beta$  и  $\gamma$  система двух роторов работает как монохроматор. Чем больше В, тем меньше ширина линии при данном у. Эта зависимость хорошо иллюстрируется на рис.11.

Из всего сказанного следует, что одним из достоинств двухроторного прерывателя является возможность изменения по желанию





Функция пропускания двухроторного прерывателя при β = 1. Кривая IV - функция пропускания для однороторного прерывателя (приведена для сравнения).



Рис.8

### Функция пропускания двухроторного прерывателя нейтронов при β = 2: Кривая V - функция пропускания однороторного прерывателя.

функции пропускания путем изменения фазового сдвига и изменения расстояния между роторами.

На рис.12 показаны функции пропускания, умноженные на  $\frac{S^{-}}{R}$  одиночных роторов с радиусами R = r, R = 2r и двухроторного пре-





Функция пропускания нейтронов при β = 4. Кривая VI функция пропускания однороторного прерывателя.





Функция пропускания двухроторного прерывателя при β = 10.
 Кривая VI - функция пропускания однороторного прерывателя нейтронов.

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рывателя с радиусами роторов  $R_1 = R_2 = r$  при одной и той же длительности вспышки. Именно произведение  $(\frac{5^2}{R} f(z))$ является величиной пропорциональной интенсивности пропускаемых нейтронов. Видно, что при примерно одних и тех же фоне и разрешении по времени интенсивность нейтронов больше в случае двухроторного прерывателя.







Рис.12

Функция пропускания ротора, умноженная на S<sup>2</sup>, (при одинаковой длительности нейтронного импульса):

кривая I для ротора с радиусом R = r; кривая II для ротора с радиусом R = 2r; кривая III для двухроторного прерывателя с радиусами роторов R<sub>1</sub> = R<sub>2</sub> = r.

Одной из важнейших трудностей двухроторной системы является поддержание постоянства фазового сдвига. Это очень хорошо иллюстрируется сильной зависимостью функции пропускания на рис.11.

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II. РАСЧЕТ МОНОХРОМАТОРА НЕЙТРОНОВ, СОСТОЯЩЕГО ИЗ НЕСКОЛЬКИХ ДИСКОВ, С ПРОДОЛЬНОЙ ОСЬЮ ВРАЩЕНИЯ

Первый монохроматор медленных нейтронов был построен еще Данингом и сотрудниками [5]. Монохроматор представлял собою два кадмиевых диска, которые были расположены друг от друга на некотором расстоянии и вращались на общем валу.

В дисках были прорезаны радиальные щели. Путем изменения относительного углового смещения дисков можно было пропускать нейтроны той или иной скорости. Однако такой монохроматор пропускал не только нейтроны с заданной скоростью, но и нейтроны с кратными скоростями. Для устранения этого недостатка начали изготовлять монохроматоры этого типа со сплошным ротором [6], [7]; при этом прорезали или плоские продольные щели под углом к образующей ротора, или винтообразные, по форме траектории нейтронов в системе координат, связанной с ротором. Чтобы получить более или менее удовлетворительное разрешение, ротор такого монохроматора должен иметь диаметр 200 - 400 мм, длину до 1000 мм, вращаться со скоростью 10 000 об/мин.

Мы проанализировали принцип работы монохроматора нейтронов такого типа и путем несложных геометрических расчетов показали, что не обязательно делать ротор сплошным. Как будет показано далее, общий вес ротора может быть уменьшен по сравнению со сплошным в несколько раз, а это позволяет уменьшить объем работы при изготовлении ротора. Из фотооттиска работы Холта /Норвегия/ нам известно, что один из рассмотренных нами вариантов монохроматора осуществлен (два диска на концах вала), но диски имеют небольшое количество щелей, что было в этом случае связано с требованиями эксперимента.

### 1. Уравнение траектории нейтронов

Рассмотрим уравнение траектории в системе отсчета, связанной с ротором (рис.13). Пусть ротор вращается по направлению часовой



Рис.13

Системы координат, которые использовались для нахождения траектории нейтрона.

стрелки с угловой скоростью  $\omega$  около продольной оси; нейтрон летит со скоростью v параллельно оси вращения на расстоянии R от нее. Тогда траектория нейтрона в системе отсчета, которая вращается вместе с ротором, есть винтовая линия. С помощью элементарных преобразований в большинстве практических случаев винтовую линию с достаточной точностью можно заменить на прямую с наклоном к образующей:

$$x = -R \frac{\omega}{v} z = -\alpha z, \qquad (2,1)$$
$$y = R.$$

Таким же образом можно получить еще два полезных соотношения:

1. Уравнение траектории для нейтронов, летящих под углом (θ,φ) к образующей:

$$\mathbf{x} = -\frac{\omega}{v} \mathbf{z} \left( \mathbf{R}_0 - \frac{\mathbf{v}}{\omega} \boldsymbol{\theta} \cos \boldsymbol{\phi} \right),$$

$$\mathbf{y} = \mathbf{R}_0,$$
(2,2)

для случая  $\varphi = 0$ ,  $x = z(-\alpha + \theta)$ .

2. Уравнение траектории нейтронов для случая, когда ось ротора повернута на угол с в плоскости (z,x<sup>1</sup>):

$$\mathbf{x} = \mathbf{z} \left( -\alpha + \theta_{1} + \mathbf{y} \right). \tag{2,3}$$

Из соотношений (2,1) - (2,3) следует, что

а) каждой скорости нейтрона соответствует определенный наклон прямой;

 б) угловая расходимость пучка нейтронов приводит к тому,
 что одинаковый наклон траекторий будут иметь нейтроны разных скоростей;

в) изменять скорость нейтронов, прсходящих через щель, можно либо путем изменения  $\omega$ , либо ү. Отсюда следует, что конечные размеры щели приводят к разбросу в величинах углов  $\alpha$ , т.е. разрешение по скоростям пропорционально  $\frac{\Delta \alpha}{2} \sim \frac{S^2}{2}$  гле L – длина ротора, 2S – ширина щели.

2. Максимально возможное количество щелей

Ротор, состоящий из двух дисков. Кинематическая картина, поясняющая этот случай, изображена на рис.14. Разрешение по скоростям в этом случае обусловлено общей длиной L лишь тогда, когда траектории с наклоном за пределами  $\Delta \alpha$  не проходят через соседние щели. Для этого, как видно из рисунка, не-



Рис.14

# Щели двухдискового монохроматора нейтронов и траектории нейтронов.

обходимо, чтобы  $\beta$  ( $l_1 + l_2$ )  $\leq 2s + 2a$ , где  $l_1$  – длина первого диска,  $l_2$  – расстояние между дисками, 2s – ширина щели, 2a – рас-

стояние между щелями. Так как  $\beta = \frac{2s}{l_1}$ , то

$$\frac{2a}{2s} > \frac{\ell_2}{\ell_1} . \tag{2,4}$$

Зная минимальное расстояние, можно определить максимальное количество щелей

$$\kappa \leq \frac{2\pi R}{2a + 2s}$$
 (2,5)

Ротор с тремя и четырьмя дисками. Сначала рассмотрим ротор из трех дисков (рис.15).

Разрешение будет обусловлено длиной ротора лишь в том случае, если траектории нейтронов 1 и 2 не проходят через соседние щели, т.е.

$$\beta_1 (l_1 + l_2) \leq 2s + 2a ,$$

$$\beta_2 (l_1 + l_2 + l_3 + l_4) \leq 2s + 2a.$$
(2,6)

T.K.  $\beta_1 = \frac{2s}{l_1}$ , a  $\beta_2 = \frac{2s}{l_1 + l_2 + l_3}$ , to ypabhenus (2,6) можно



Рис.15

Щели трехдискового монохроматора и траектории нейтронов.

привести к такому виду:

$$\frac{2a}{2s} > \frac{l_2}{l_1}; \qquad (2,7a)$$

$$\frac{2a}{2s} * \frac{l_4}{l_1 + l_2 + l_3} . \qquad (2,76)$$

Для определения максимального количества щелей необходимо использовать наиболее жесткое из этих условий. При этом получаем

$$\kappa \leqslant \frac{2\pi R}{2s+2a}.$$

Из соотношений (2,7) следует, что ширина щели равна промежутку (2 S = 2a) лишь тогда, когда  $l_2 = l_1$  и  $l_4 = l_1 + l_2 + l_3$ . Положив для примера  $l_2 = l_1 = l_3 = l_5 = l$ , получим, что общая длина ротора  $L_3 = l_1 + l_2 + l_3 + l_4 + l_5 = 7l$ .

Если на расстоянии  $l_6$  поместить четвертый диск длиной  $l_7$ , то, рассматривая систему дисков как комбинацию двух дисков с эффективной длиной  $L_3$  и  $l_7$ , получим, что 2s = 2a лишь при  $L_3 = l_8$ 

# (2,4).

Отсюда можно сделать вывод, что из четырех дисков длиной 41 можно построить монохроматор, разрешение которого определяется длиной  $L_4 = L_3 + \ell_6 + \ell_7 = 15 \ell$ , если  $\ell_7 = \ell$ . Безусловно, при= веденные варианты с несколькими дисками не являются единственно возможными.

Простейший монохроматор такого типа изготовлен в Институте физики АН УССР. Его параметры таковы: два диска диаметром 600 мм и толщиной 60 мм расположены на расстоянии 680 мм (между внешними поверхностями). Щели радиальные имеют ширину 2 мм, высоту 80 мм. Количество целей 48, скорость вращения до 3000 об/мин. Размеры пучка 40 х 80 мм. Коллиматор к монохроматору имеет 17 щелей и изготовлен из кадмиевых пластин. Диски изготовлены из

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текстолита; щели облицованы кадмием толщиной 0,35 мм. Выбор скорости нейтронов осуществляется путем задания угла оси вращения к падающему пучку и изменением скорости вращения.

### **111. ВОЗМОЖНЫЕ ФИЛЬТРЫ НЕЙТРОНОВ**

Применение поликристаллических веществ для фильтрации медленных нейтронов получило широкое распространение при исследовании неупругого рассеяния нейтронов. В качестве фильтров применялись C, Be, BeO, Pb, Bi и некоторые другие вещества. Если условно считать, что для фильтров подходят лишь те ядра, у которых сечение захвата меньше 200 миллибарн, то, по-видимому, для фильтрации нейтронов можно использовать такие элементы, как D, Be, C, O, F, Mg, Si, P, Zr, Pb, Bi. Не исключено использование и соединений этих элементов. У используемых в настоящее время фильтров граничная длина волны лежит в области от 4 до 7 А. Возможно, что среди названных элементов или их соединений в будущем будут найдены вещества позволяющие получить  $\lambda$  гр вплоть до 18 Å.

В качестве фильтра может быть использовано также нейтронное зеркало. Известно, что предельный угол отражения

$$\theta_{\rm np} = \lambda \sqrt{\frac{{\rm Na}}{\pi}} ,$$
(3,1)

где λ – длина волны; N – число ядер в кубическом сантиметре; а – амплитуда когерентного рассеяния нейтронов. Так как приблизительно выполняется условие

$$R_{\lambda}(\theta) = 1$$
 при  $\theta \leq \theta_{np}$ ;  
 $R_{\lambda}(\theta) = 0$  при  $\theta \geq \theta_{np}$ ,  
(3,2)

где  $R_{\lambda}$  ( $\theta$ ) - коэффициент отражения под углом  $\theta$ , то под данным

углом в отраженном спектре будет обрыв, соответствующий  $\lambda$  гр для данного угла. Резкость этого обрыва зависит от степени коллимации пучка нейтронов. Учитывая, что для 6 Å предельный угол отражения составляет несколько десятков минут, применение такого фильтра, по-видимому, возможно для  $\lambda > 6$  Å.

С помощью зеркал нетрудно осуществить пульсирующий фильтр и, таким образом, сделать возможным применение метода времени пролета. Схема такого пульсирующего устройства показана на рис. 16. Предположим, что коллимация пучка такова, что пучок может считаться параллельным, Пусть ширина источника нейтронов 2 S, а угол падения  $\theta$ . На расстоянии D от зеркала расположен коллиматор длиной  $\ell$  и шириной щели 2 S так, что в него попадают нейтроны, отраженные под углом  $\theta$ ; C - счетчик.


Схема пульсирующего фильтра нейтронов, основанного на принципе отражения нейтронов' от зеркальной поверхности.

Нетрудно видеть, что отраженный пучок ("нейтронный зайчик") будет скользить по щели с угловой скоростью 2 ш, если зеркало вращается со скоростью ш. Отсюда следует, что скорость счета в счетчике будет треугольной функцией времени:

I (t) = 0  
I (t) = 1 - 
$$\frac{|+|}{s/\omega(D+\ell)}$$
 AJA  $|t| \ge \frac{S}{\omega(D+\ell)}$   
(3,3)  
I (t) = 1 -  $\frac{|+|}{s/\omega(D+\ell)}$  AJA  $|t| \le \frac{S}{\omega(D+\ell)}$ .

С помощью формул (3,3) и (3,2) нетрудно найти спектральную отражательную способность в течение вспышки (рис.17):



Отражательная способность пульсирующего зеркального фильтра в зависимости от длины волны нейтрона.  $I (\lambda) = 0 \qquad \text{при} \qquad \lambda < \lambda_{1}; \qquad (3,4)$   $I (\lambda) = \frac{1}{2} \left( 1 - \frac{\lambda_{0} - \lambda}{\lambda_{0} - \lambda_{1}} \right)^{2} \qquad \text{при} \qquad \lambda_{1} < \lambda < \lambda_{0}; \qquad (3,4)$   $I (\lambda) = 1 - \frac{1}{2} \left( 1 - \frac{\lambda - \lambda_{0}}{\lambda_{2} - \lambda_{0}} \right)^{2} \qquad \text{при} \qquad \lambda_{0} < \lambda < \lambda_{2}; \qquad (3,4)$   $I (\lambda) = 1 \qquad \qquad \text{при} \qquad \lambda > \lambda_{2}.$   $\lambda_{1} = \theta_{1} \sqrt{\frac{\pi}{Na}} = \left( \theta - \frac{S}{D+\ell} \right) \sqrt{\frac{\pi}{Na}}; \qquad \lambda_{2} = \theta_{2} \sqrt{\frac{\pi}{Na}} = \left( \theta + \frac{S}{D+\ell} \right) \sqrt{\frac{\pi}{Na}}.$ 

Отсюда видно, что

$$\frac{\Delta\lambda}{t^{\lambda}} = \frac{S}{D+l} \cdot \frac{S}{\theta} . \qquad (3,5)$$

Однако в реальных условиях следует учитывать угловую расходимость падающего пучка. Общий вид зависимости отражательной способности от длины волны не изменится, но спад станет более пологим. Разрешение уже более не определяется формулой (3,5); при достаточно большой угловой расходимости

$$\frac{\Delta\lambda}{\lambda} \sim \frac{S}{\ell\theta_0}$$
 ,

т.е. не зависит от расстояния между зеркалом и приемной щелью. Для увеличения светосилы прибора следует применять многощелевые коллиматоры. По светосиле в области 6 - 10 Å,безусловно,пульсирующий зеркальный фильтр уступает многим известным приборам, однако пульсирующий фильтр не сложен для изготовления и поэтому в ряде случаев может найти применение.

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# SCINTILLATION COUNTERS FOR NEUTRON SCATTERING EXPERIMENTS

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### Abstract — Résumé — Аннотация — Resumen

SCINTILLATION COUNTERS FOR NEUTRON SCATTERING EXPERIMENTS. Scintillation counters discussed in this paper are of two types: (i) LiF or  $B_2O_3$  fixed with zinc sulphide in varving composition, (ii) Li containing glasses of varying composition.

The ideal composition of each type for neutron scattering experiments and their relative sensitivity to neutrons and  $\gamma$ -rays are considered. The ZnS type can be used with a  $\gamma$ -ray pulse shape discriminator and practical experience of its use in a multi-counter time-of-flight experiment is described. The Li glass has higher  $\gamma$ -background but also higher neutron efficiency. Performance figures of a scintillator containing 25% by wt. Li<sub>2</sub>O and 1 mm thick will be given.

COMPTEURS A SCINTILLATIONS POUR LES EXPERIÉNCES DE DIFFUSION NEUT RONIQUE. Les compteurs à scintillations étudiés sont de deux types: i) Li F ou  $B_2O_3$  fixé par du sulfure de zinc en composition variable, ii) verres contenant du lithium en composition variable.

Les auteurs examinent la composition idéale de chaque type de compteur pour les expériences de diffusion de neutrons, ainsi que leur sensibilité relative aux neutrons et aux rayons gamma. On peut utiliser le compteur à ZnS avec un discriminateur de forme pour rayons gamma; les auteurs décrivent l'expérience qu'ils ont de son emploi dans une expérience de temps de vol à plusieurs compteurs. Le compteur verre-Li a un mouvement propre plus élevé pour les rayons gamma mais une meilleure efficacité vis-à-vis des neutrons. Les auteurs donnent quelques chiffres concernant le fonctionnement d'un scintillateur contenant 25% en poids de Li<sub>2</sub>O et ayant une épaisseur de un millimètre.

СЦИНТИЛЛЯЦИОННЫЕ СЧЕТЧИКИ ДЛЯ ЭКСПЕРИМЕНТОВ С РАССЕЯНИЕМ НЕЙТРОНОВ. В докладе обсуждаются сцинтилляционные счетчики двух типов: а)счетчики, наполненные L1F или B<sub>2</sub>O<sub>3</sub>, с сульфидом цинка в различных пропорциях, и б)счетчики из стекла, содержащего L1 в различных пропорциях.

Рассматриваются идеальные пропорции для каждого типа в опытах с рассеянием нейтронов и относительная чувствительность счетчиков к нейтронам и у-дучам. Нейтронные счетчики типа Zns могут

быть использованы с импульсным дискриминатором у-дучей; описывается их применение в экспериментах по измерению времени продета нейтронов с использованием нескольких счетчиков. Счетчики из стекла с L1 обладают более высоким фоном у-излучения, но также и бодее высокой эффективностью по отношению к нейтронам. Будут приведены дакные, характеризующие сцинтиллятор толщиной 1 мм, содержащий 25 вес \$ Li<sub>2</sub> 0.

CONTADORES DE CENTELLEO PARA EXPERIMENTOS DE DISPERSIÓN NEUTRÓNICA. Los contadores de centelleo examinados en esta memoria son de dos tipos :

- a) de LiF o B<sub>2</sub>O<sub>2</sub> mezclado con sulfuro de cinc en proporciones variables;
- b) de vidrios litiados de diversas composiciones.

Los autores estudian la composición ideal de cada tipo para experimentos de dispersión neutrónica, así como su sensibilidad relativa a los neutrones y a los rayos gamma. El tipo de ZnS puede utilizarse con un discriminador de amplitud de impulsos para rayos gamma; los autores describen la experiencia adquirida con su empleo en un experimento de tiempo de vuelo realizado con varios contadores. El vidrio litiado pre-

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senta una actividad de fondo más elevada para los rayos gamma, pero también una mayor eficiencia en el registro de neutrones. En la memoria figuran cifras relativas al rendimiento de un centelleador de 1 mm de espesor, que contiene 25% en peso de litio.

# 1. INTRODUCTION

The choice of neutron detectors for a particular scattering experiment is not usually clear cut. This is because, in different experiments, different weight may be given to the various features of small thickness, attainable efficiency, shape of sensitive area, gamma sensitivity, overall size and shape, complexity of assembly and so on. One very important factor is the nature of the "background" radiation. For example, in the case where a substantial epithermal neutron background is present, increasing the thermal neutron efficiency above about 40% may involve increasing the epithermal efficiency by such a greater factor that the overall statistical error of a measurement may be increased through worsening the signal to background ratio. The useful neutron efficiency is defined as the efficiency when the detector is biased (or otherwise set up) so that the gamma efficiency has a suitably low value, and this in turn depends on the ambient gamma flux.

Also, some experiments require rectangular detectors which can be assembled adjacent to one another, giving a uniform geometry with varying scattering angle. In this, and some other situations, adequate shielding of detectors can be a problem.

It is the purpose of this paper to describe two types of scintillator which possess different advantages, and to assess the merits of these detectors in neutron scattering experiments. The two types are (i) scintillators based on ZnS (Ag) as the phosphor, and (ii) glass scintillators, with the emphasis on those containing lithium.

The first of these to be developed was the ZnS (Ag) type. ZnS (Ag) was chosen because of its low response to  $\gamma$ -radiation. The earliest version used ZnS (Ag) in fused B<sub>2</sub>O<sub>3</sub> glass [1]. This requires a high temperature to fuse the B<sub>2</sub>O<sub>3</sub> and resulted in damage to the ZnS (Ag) phosphor. SUN [2] used boron in the form of a low melting point organic borate polymer. Sun's plastic is difficult to prepare in a clear, colourless glass form, but new plastics [3] are satisfactory in this respect. However, this type of scintillator suffers from the disadvantage that it is relatively opaque, due to the high refractive index of the zinc sulphide, and the necessity to use small grain sizes of zinc sulphide. This limits the useful thickness to about 1/2 mm. For example, the light transmission of a typical scintillator is about 10%.

For the photomultiplier to "see" scintillation occurring on the far side of the scintillator, it would be advantageous to use lithium instead of boron, which has a higher disintegration energy (4.8 meV instead of 2.8 meV).

This should give more light in the actual scintillation resulting in a greater probability of detection by the photomultiplier. However, the cross-section of Li<sup>6</sup> is only a quarter of that of B<sup>10</sup>, so with a given thickness of scintillator, less neutrons are absorbed. In fact, lithium, owing to the strong electrovalent character of its bonds forms no stable organic compounds, and only inorganic compounds with high melting points. Therefore, zinc sulphide cannot be mixed into any glass-like lithium compound. This problem

nas, however, been overcome by STEDMAN [4] who has made pressed slabs of LiF, ZnS (Ag) with perspex as the transparent bonding material. Because of the lower cross-section of lithium, there is little to choose between the two types on the basis of efficiency.

The outstanding advantage of the zinc sulphide type of scintillator is that a very effective form of gamma discrimination may be employed [3, 5]in order to obtain good working neutron efficiency. Other features are the small thickness (1/2 mm) and the fact that manufacture in substantial areas and other than circular shapes is possible. For example, rectangular detectors are in use coupled to the photomultiplier by being spaced a few inches from the photocathode on a shaped can with a highly reflective surface. This simple method of mounting the sample is practicable because good pulse height resolution is not required, since the discrimination is on a pulse shape basis rather than an amplitude basis, and in any case because, owing to the opacity of the scintillator, the neutron pulses are already of widely varying amplitudes.

The glass type of scintillator can contain either lithium or boron, as both form suitable oxides. The basic difference from the zinc sulphide type is that the scintillators are clear, produce a peak in the amplitude distribution and, therefore, discrimination is on an amplitude selection basis. For the glasses tested so far there is insufficient pulse shape difference to utilize for shape discrimination. For this reason, care has usually to be taken in the use of these glasses to preserve good pulse height resolution. Also, because the glasses are clear and readily transmit the scintillation light, much greater thicknesses can be used than with ZnS types. The obtainable efficiency is therefore not intrinsically limited.

The choice between lithium and boron glasses depends upon the application: boron glass has a higher efficiency per unit length, but much lower pulse height than the lithium glass. These factors will be considered in detail later.

# 2. SCINTILLATORS CONTAINING ZINC SULPHIDE (SILVER-ACTIVATED)

# Pulse shape discrimination

The big advantage of the ZnS scintillator lies in the significant difference in pulse shape arising from  $\gamma$ -ray and  $\alpha$ -particle excitation. Photographs of the decay of the phosphor using a fast oscilloscope type 1239 (2 nS rise time) and a 56 AVP photomultiplier (Fig. 1a) showed the pulses due to gamma rays to the sharp pulses, width less than 20 nS and the neutron pulses long, ragged pulses decay time about 0.3  $\mu$ s. An efficient circuit which discriminates against narrow pulses has been developed by WRAIGHT [5]. This circuit has also been found to reduce other backgrounds due to gamma sensitivity of the photomultiplier, tube noise, etc. The bias curve with the discriminator is given in Fig.1b showing the superior  $\gamma$ -discrimination compared to the normal method of Fig.1c.

### Choice of lithium fluoride or boron plastic

Comparisons of the relative efficiencies of boron plastic and LiF scintillators have been made by STEDMAN [4] and HARRIS [7]. Stedman's com-





H.T. bias curve for LiF/ZnS scintillator using pulse shape discriminator.

**parison was made using a boron plastic type considerably inferior to that used in the comparison made by Harris. The latter reports LiF to be 25% more efficient to 0.03 eV neutrons than boron scintillators when pulse shape discriminators are not used. Tests have been made recently using the discriminator described by WRAIGHT <u>et al.</u> [3], and a neutron detection** 



Fib.1c

Bias curves for .020 in scintillator using two different bands of zinc sulphide grain size.

efficiency of 48% at 0.03 eV was obtained for a boron scintillator whilst the best efficiency achieved for a LiF type was 52%. Thus the pulse shape discriminator gives a bigger improvement to the boron than to the lithium type.

Each type has certain advantages. The composition of the boron type is such that more intimate contact exists between the absorber material and the zinc sulphide. This is because the zinc sulphide is embedded in the boron plastic, whereas in the other type both the zinc sulphide and the absorber are embedded in perspex.

The main advantage of the lithium type is that it is stable in the atmosphere, whereas atmospheric moisture decomposes the glass-like boron plastic. Although a straight forward method of manufacture has been developed for the boron type so that the scintillator is never exposed to the atmosphere [3], they still have to be handled carefully in use to preserve the sealing.

### Choice of ZnS particle size

The range of  $\alpha$ -particles in the boron plastic is 5  $\mu$ m approximately. Therefore the grain size of the ZnS should be of this order or smaller. When the grain size used becomes very small the optical transmission of the scintillator will be too low. SUN [2] and STEDMAN [4] have reported that varying the grain size in the range 5-15  $\mu$ m produced no attendant change in performance of their scintillators. Bias curves obtained for neutrons when two different bands of ZnS grain sizes are used with boron plastic are shown in Fig. 10. The samples available were coarse filtered with sizes from 5-10  $\mu$ m or finely filtered powder containing 5-15  $\mu$ m grain sizes. The graphs shown illustrate the superiority of the smaller grain size since the neutron detection efficiency for the same gamma ray efficiency (the working point) is 50% greater.

### Scintillator thickness

Since the scintillator consists of a mixture of materials differing markedly in refractive index the light is scattered many times before leaving the scintillator and hence the scintillator has a poor optical transmission. Thus neutrons absorbed at the front surface of a scintillator will give rise to smaller pulse heights than those absorbed nearer the photo-cathode. In the limit, increasing thickness leads to a lower neutron detection efficiency the front layer acting merely as neutron shielding.

WRAIGHT [3] has derived an equation showing that the amount of light (P) reaching the photo-cathode of a photo-multipher from a boron plastic scintillator varies as:

$$P = e^{-\mu d} - e^{-\nu d} / \nu - \mu$$

where

$$\mu = m(1 - f)\rho$$

- $\nu = [\mathrm{Kf} + 1(1 f)]\rho$
- m = const  $\times$  T(n $\alpha$ ),
- f = fraction by weight ZnS,
- $\rho$  = density of scintillator,
- K = light attenuation factor due to ZnS,
- 1 = light attenuation factor due to boron plastic.

The theoretical curve of relative light output as a function of thickness where f = 0.65 and neutron energy is 0.067 eV is shown in Fig. 2. Experimental points obtained by measuring the efficiency of three scintillators of various thickness are also shown. This graph shows that greatest thermal neutron detection efficiency is obtained with the boron plastic scintillators in the range 1/4 to 1/2-mm thickness.

Sun and Wraight have shown a ratio of ZnS: boron plastic of 2 to give the best relative light output and for all tests this has been used.

# Performance of the detector

The boron ZnS and LiF ZnS scintillator are in use on the Cold Neutron Scattering Apparatus at Harwell [17]. Discs of 2-in and 3-in diam. about 1/2-mm thickness have replaced a bank of BF<sub>3</sub> detectors in that part of the apparatus where a better definition of the scattered flight path was required. They give about the same neutron detection efficiency as 9 cm of B<sup>10</sup> F<sub>3</sub> at 70 cm H (~ 50% at 0.03 eV) and have a background only 0.6 times the background of a BF<sub>3</sub> bank having the same area exposed to the neutron beam which was previously used.

Thirty scintillators have been in use on the Scattering Law Apparatus [18] at Chalk River. This apparatus consists of a multi-rotor velocity selector producing bursts of monoenergetic neutrons which are scattered from a sample placed at  $45^{\circ}$  to the beam. The scattered neutrons are detected at various angles (from  $10^{\circ} - 160^{\circ}$ ) by scintillation detectors placed in an



Graph of relative light output versus scintillator thickness for neutrons of 0,067 eV.

arc 1.3 m from the sample. The neutron energies of interest in this experiment range from 0.004 eV to 0.4 eV and the number of neutrons scattered from the sample into a particular detector is small (~10-30 n/min). Therefore ideally a detector is required which has a low background and is almost 100% efficient over this range. In fact, for most measurements there is no point in striving for efficiencies greater than 60-70% at 0.025 eV (falling as 1/V to 20-25% at 0.4 eV) because this can only be won at the expense of a proportionately larger increase in the background due to fast neutrons which are always present in any such experiment. The background due to  $\gamma$ -rays in this apparatus is quite small (~0.25 mr/h at the detectors) and they can be biased off without any loss in efficiency.

Two sizes of scintillator have been used 4 3/4 in<sup>2</sup> on a 5-in photomultiplier EMI 9530B and 6 in  $\times$  3 in on a 2-in photomultiplier EMI 9514B, each coupled by means of a light guide. The scintillators are backed with 62%  $B_2O_3$  glass 1/2-in thick which absorbs both neutrons penetrating the scintillator and those incident from the rear of the detector. Hence elaborate shielding round the photomultiplier is not necessary. The square detectors are described in detail by STEDMAN [4] and the rectangular detectors by HARRIS [7] . The 6-in  $\times$  3-in detectors were a special design in which a poor light collection geometry was accepted in order to allow a close side by side packing of the detectors. This entailed a loss in the neutron detection efficiency; the average detector efficiency for this design is 30% at 0.025 eV. In the design of the 4 3/4 in<sup>2</sup> detector the major requirement was for the best • possible neutron detection efficiency. A graph of efficiency V energy for this detector is shown in Fig. 3. The efficiency was calculated by measuring the count rate when neutrons are scattered from a standard vanadium sample into the detector. This figure is compared with the number detected by a fission chamber of known efficiency versus energy placed in the beam prior



Efficiency versus time of flight for 43 square LiFZnS scintillators.

to the sample. This technique has been used previously by EGELSTAFF et al. [18].

All scintillators used in this apparatus are coupled to a pulse shape discriminator [5]. The most striking effect of using these circuits is the large reduction in non-neutron background achieved, in some cases from 50 to 3 counts/min.

The variation in neutron detector efficiency across the detectors was found to be good. For the oblong detectors the efficiency in the corners being 75% of that in the centre and for the square detectors this efficiency ratio was better than 90%. A comparison of the detection efficiencies of five different scintillators was made and the relative efficiency found to vary by only 5% if the same photomultiplier was used: when complete detectors are compared however variations of 30% in relative detection efficiency have been observed.

# 3. GLASS SCINTILLATORS

Ideally a scintillator would absorb all incident neutrons and give a large pulse height and good discrimination against background radiations. For a given application, in this case the detection of scattered neutrons with energies below 1 eV, the considerations affecting these properties, (for example whether to use lithium or boron as the absorber) must be individually reviewed. The first part of this section is devoted to this.

## (a) Lithium or boron

The main factor affecting the efficiency of a glass scintillator is the product of the cross-section of the capturing nucleus and its concentration • in the glass, i.e. a macroscopic absorption factor (subsequently denoted by A in Table I).

The cross-section of boron is four times that of lithium, the thermal cross-sections ( $\sigma$ ) being for boron 3840 b and for lithium 950 b. At present

# TABLE I

Glass type	$C \frac{\text{atoms} \times 10^{22}}{\text{g}}$	$A = \frac{C x_{\sigma}}{100}$	R	E, keV	e,%	P, keV
Boron glasses: G1 G5 Lithium glasses GS 20 HP 349	0.90 0.99 0.79 1.27	34.6 38.0 7.5 12.1	0.091 0.044 0.336 0.335	208 100 1610 1605	5 5 15 7	10.5 5.1 241 112

PROPERTIES OF GLASSES INVESTIGATED

greater concentration of lithium atoms can be obtained in glass, than of boron atoms; this is largely owing to the valency of lithium being unity against three for boron. Table I shows the absorber atom concentration, C, for some high-lithium and high-boron glasses, and the resulting absorption factor A.

Further, in favour of lithium glasses is the fact that larger pulses are obtained than with boron glasses. This is because the available energy in the disintegration is greater for lithium (4.79 meV against 2.31 meV), the fact that the ionizing particles have less specific ionization giving a greater pulse height for a given energy loss, and also because in general lithium glasses have a larger scintillation efficiency. These effects are also represented in Table I. R is the ratio of the pulse height E for neutron detection (measured in terms of the energy of an electron which would produce a pulse of the same amplitude) to the actual energy of the ionizing particles. "e" is nominally the efficiency of the glasses relative to NaI(T1) for electron excitation (values given are from [8, 14]; the experimental conditions for the measurement of this factor appear to have been similar) and "p" is the product of "e" and E giving a measure of the absolute amplitude of the pulses approximately equal to the equivalent electron energy in NaI(T1). An explanation of the glass numbers is given below Table II.

In practice the pulses from the best boron glasses are not far removed from noise, so if the required detection efficiency can be obtained without excessive glass thickness, lithium glasses would appear preferable.

A high concentration of absorber atoms is desirable so that thin sheets of glass may be used, so reducing the  $\gamma$ -ray efficiency relative to the neutron efficiency. For example E for lithium glasses has been stated as about 1600 keV, but an electron of this energy has a range of approximately 3 mm, and so might leave a piece of thin glass, e.g. 1-mm thick, before dissipating all its energy. In fact, the maximum energy imparted to an electron scattered at an angle  $\phi$  to the original photon direction is  $2\text{mc}^2 \cot^2 \phi(-\cot^2 \phi \text{meV})$ . For a 1-mm piece of glass,  $\gamma$ -radiation incident normal to the glass, and assuming roughly straight electron tracks, the maximum electron energy which can be dissipated in the glass by a primary Compton scattered electron is approximately 1 meV. With glasses of this thickness, since there is a high probability of Compton electrons of maximum energy leaving the glass,

# TABLE II

Glass	Molar Ratios					Li.O	e%
	Li <sub>2</sub> O	A1 203	MgO	SiO <sub>2</sub>	Ce <sub>2</sub> O <sub>3</sub>	% wt	C N
V4	3, 3	0.26		10.0	0.17	13.5	8
G8	3, 3	0,68		10.0	0.09	11,7	9
HP89	2.0		7.0	10.0	0,24	5,9	15
GS1	2.0	3,5	6.5	10.0	0,27	5.6	13
G6	1.3	1.0	5.2	10.0	0.10	· . 3 <b>.</b> 7	14
GS20(HP <b>346</b> )	5,9	1,9	0.97	10.0	0.13	16.8	15
HP349	10,3	1,9		10.0	0 <b>.</b> 12	27.0	7

### COMPOSITION OF VARIOUS GLASSES

the familiar Compton distribution is not observed, but rather a distribution falling smoothly from a high value at low amplitude to cut-off at a higher amplitude.

Thus, although BROOKS [10] reports lithium glass as having greater sensitivity to high energy  $\gamma$ -rays than boron glass, since his remarks were based on lithium glass 1.5 in thick they would not apply to the thin glass considered here. Although the ideal conditions of straight electron tracks and normal incidence of  $\gamma$ -radiation are not fully realised in practice, it is clear that, 1-mm thickness of lithium glass would have lower  $\gamma$ -sensitivity than a similar boron glass scintillator. Since as will be seen later the required neutron efficiency for slow neutron scattering experiments can be obtained with glasses of this thickness lithium is the automatic choice in this case.

# (b) Glass composition

The most satisfactory composition of the glass has been considered by several authors. The cerous ion has been reported as the only activator producing cathodoluminescence in glasses [9, 11]. GINTHER [8] and ANDERSON [14] have developed lithium-aluminium-magnesium silicate glass, while VOITOVETSKII [12] has found a lithium-calcium silicate glass successful.

The ideal glass would possess the greatest neutron capture efficiency and the greatest pulse height efficiency obtainable in one glass, and also be perfectly clear to its emitted light. To some extent these requirements are contradictory, for example the absorption and emission spectra overlap slightly, and VOITOVETSKII [12] has found it helpful to reduce the cerium molar concentration from 0.1 to 0.06 on increasing the glass thickness from 0.1 to 1.0 cm.

The greatest neutron capture efficiency is obtained by incorporating the maximum amount of  $Li^6$ , though with the glasses known at present, this

leads to a reduced pulse height. The present limit of lithium content (glass HP349, 27%  $\rm Li_2O)$  is set by the glass becoming cloudy.

The greatest pulse height efficiency for a given glass is obtained by increasing the cerium content, though beyond a certain value set by the conversion of some cerium to the quadravalent state, and possibly by concentration quenching, the efficiency falls again. In order to incorporate a high cerium loading without reaching this limiting value it is necessary to melt the glass under strongly reducing conditions [9, 11, 13].

The addition of aluminium and magnesium oxides appears to have several effects. One, which may be connected with producing a certain order in the glass facilitating energy transfer to the emitting centres, is an increased pulse height efficiency. This is supported by the fact that some of the more efficient glasses show a tendency to devitrify by crystallization; for example, crystals of forsterite,  $2MgOS:O_2$  tend to form in the pouring of glass of composition GS1. Also it appears possible to incorporate more cerium without reaching the limiting value [13, 14] and without preventing all the batch components from dissolving [15]. The former also leads to greater pulse height.

Table II shows for some of the best glasses made so far the composition in molar ratios with the % by weight of  $Li_2O$ , and the efficiency "e" of Table L The molar ratios are for convenience normalized to 10 mol SiO<sub>2</sub>. Glass numbers prefixed by G apply to the glasses of Ref. [8]. Those prefixed by GS are made by Levy West Laboratories Ltd. Those prefixed by HP are described in Ref. [14]. V4 is the glass of Ref. [12].

Examples of the neutron efficiencies obtained for 1-mm thickness are; for glass GS20, 82% at neutron energy 0.025 eV and for glass HP349E 35% at 1 eV. The letter "E" denotes the use of enriched lithium, 96% Li<sup>6</sup>, as is used for GS20.

(c) Tests on glass specimens (containing 96% enrichment in Li<sup>6</sup>)

Tests were made to demonstrate the variation of gamma-ray sensitivity of the glass with thickness. Samples were irradiated in a field of 5 mr/h of  $\gamma$ -rays from a Co<sup>60</sup> source and the number of pulses of amplitude equal to pulses due to neutron capture were recorded. The results were as follows:

Thickness of glass mm	1.5	3	6	9
Count rate due to Co <sup>60</sup> gamma rays counts/s	8	110	182	240

These tests, together with the theory discussed previously, indicate the superiority of glass in the range of 1-mm thickness.

Further tests were carried out in 4 different samples of lithium glass of thickness 1 to 11/2 mm. Each sample was coupled in turn directly onto the photo-cathode of a 2-in diam., 11 stage EMI photomultiplier (type CV2316). The assembled detector was then placed in the 0.067 eV diffracted beam of a neutron crystal spectrometer. A 3/4-in diam. collimator was placed immediately in front of the detector. The differential bias curve obtained



Fig.4

### TABLE III

Sample	% Li <sub>2</sub> O calculated from neutron transmission	Detection efficiency of $1\frac{1}{2}$ mm at 0.2 eV	Resolution of $\eta$ , a peak	
1½ mm HP89X	7%	30%	12%	
1½ mm 344E	15.9%	57%	18%	
1½ mm 346E	13.2%	· 50%	16%	
1 mm 349E	26.2%	75%	32%	

#### PERFORMANCE OF SCINTILLATING LITHIUM GLASS

for sample HP89X using a 100 channel pulse height analyser is shown in Fig. 4. The background was obtained by inserting a piece of cadmium in the beam immediately prior to the crystal.

The resolution of the  $\eta$ ,  $\alpha$  peak, given by the full width at half height divided by the peak pulse height, is 12% for sample HP89X. This was achieved without the use of a light guide or the special selection of a photomultiplier of particularly uniform photo-cathode response. The tests were repeated for three other samples and the results included in Table III.

It is seen that the resolution broadens as the lithium content is increased. This can probably be overcome by improved manufacture techniques since there is no obvious reason for the broadening depending on the lithium concentration. In fact the 349E sample had centres of cloudiness due to some constituent not being completely dissolved. A further point is that the percentage by weight of  $Li_2O$  in the glass is not always completely controlled by the manufacturing process. In the case of the 344 E glass a Li<sub>2</sub>O content of 17.8% was claimed by the maker, for 349 E 27% and for 346 E 16.9% was stated to be added in the melt but lower figures were deduced from neutron transmission measurements.

The HP89X sample has been compared with a BF<sub>3</sub> counter in a crystal spectrometer on the Bepo reactor at Harwell. In this apparatus where the gamma-ray flux is less than 0.25 mr/h inside the detector shield the glass was found to have a counts to background ratio of 65 compared to 32 for the BF<sub>3</sub> counter. The glass is therefore preferred to the BF<sub>2</sub> counter in this apparatus. On the cold neutron apparatus in Dido, however, the counts to background ratio of a 3-mm thick glass specimen was measured as 0.4: 1 compared to 14:1 for a BF<sub>3</sub> assembly. This is attributed to the high  $\gamma$ -background found in this apparatus (~1 mr/h) and because the resolution of this glass was poor (~25%).

# 4. CONCLUSIONS

Two types of scintillator have been discussed, particularly in relation to their use for slow neutron scattering measurement. They have different characteristics, and different criteria govern the choice of composition. However, for both types  $\text{Li}^6$  has been chosen in preference to  $\text{B}^{10}$ . In the case of the zinc sulphide type this is primarily because the lithium version is chemically inert and thus more rugged than the boron plastic version. For the glass scintillators, lithium is chosen because, (though it has alower cross-section than boron), scintillators of high efficiency may be made 1-mm thick, and for this thickness the greater neutron pulse height of lithium leads to a lower efficiency.

The important advantage of the zinc sulphide type is the low efficiency to  $\gamma$ -radiation which is obtained by the use of pulse shape discrimination. These scintillators automatically have low efficiency to fast neutrons because their thickness is limited by opacity to 10 mg/cm<sup>2</sup> Li<sup>6</sup> giving 52% efficiency at 0.03 eV, falling to 20% at 0.2 eV. In the measurement of these figures, a pulse shape discriminator was used so that 5 mr/h of Co<sup>60</sup>  $\gamma$ -rays registered less than 1 count/min.

The main features of the lithium glass scintillators are that thickness is not limited by opacity and thus larger thicknesses may be used, though at the expense of increased  $\gamma$ -ray efficiency. Also owing to the clarity of the glass, which gives a well resolved peak for neutron events, the detection efficiency may be simply measured since it is (very closely) equal to the transmission. The use of a high Li<sup>6</sup> content gives good efficiency, for example 1-mm thick scintillators of GS20 glass give 82% efficiency to 0.025 eV neutrons and of HP349E glass 35% at 1 eV. The former might typically count 100/min in a 5 mr/h field of Co<sup>60</sup>  $\gamma$ -radiation incident from the front compared to 1 count/min for the ZnS type.

Either of these types of scintillator are attractive, depending on the particular experimental conditions. Owing to their small volume it is easier to shield them from an isotropic fast neutron background than would be the case with  $BF_3$  counters, which would be quite thick for comparable efficiency.

Further development of the zinc sulphide type would best be directed towards improving the electronic aspects of the pulse shape discriminator; for example to use a faster photomultiplier than the "Venetian-blind" type normally used, and a correspondingly faster discriminator circuit. The glass would be improved if a composition containing more lithium can be developed (though there is only room for an improvement of about 1.5 here) and if compositions could be found giving usable pulse shape differences for neutron and gamma-ray excitation. The high lithium type would also be more attractive if their resolution could be improved; there does not seem any basic reason why this could not be done.

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### DISCUSSION

N.A. TCHERNOPLEKOV: What is used as the activator in the lithium glass scintillators to which you refer? Secondly, has material been published anywhere on the technology of manufacturing the boron scintillators and lithium glasses with a high percentual content of lithium to which you refer?

B. HAYWOOD: The activator used was cerium in the form of the cerium ion. Reports were published at a Stockholm conference in 1960 on the manufacture of glasses containing 6%  $Li_2O$ . Reports on glass with the highest content of lithium should shortly be published by Mr. D.G. Anderson of the British Scientific Instrument Research Association.

W. WHITTEMORE: At General Atomic we have been using plastic scintillators for a number of years to detect thermal neutrons, but we have had enormous difficulty with the  $\gamma$ -rays. Our problem here is that we get a prompt pulse of  $\gamma$ -rays from our linear electron accelerator, which saturates the crystal and electronics for as long as a thousand micro-seconds. Do you have any information on methods by which this effect may be reduced or the neutron/gamma response improved?

B. HAYWOOD: I am afraid I have not. One gets the best results from these scintillators if they are kept dark for about 10 or 12h immediately after being made. I should imagine you are getting the same sort of effect. You get a bright flash of light and this leaves the zinc sulphide activated.

H. PALEVSKY Do you find any difference in the position of the Compton edge for the cobalt line, or in the relative pulse heights of the neutrons and gamma rays as you change the concentration of lithium?

B. HAYWOOD: No. The lithium concentration has practically no effect on the  $\gamma$ -rays.

B. JACROT: There are two English firms making this scintillator glass. Have you compared these two products?

B. HAYWOOD: No. It all comes from the same source, actually.

B. JACROT: Why does one glass have higher content of lithium than the other?

B. HAYWOOD: There are two retail outlets.

W. CLAESER: Have you actually used these  $Li^6$ -glasses in scattering experiments? I am asking this because we have tried to use some lithium glasses we got from an English firm, and got a much larger background than with ZnS scintillators.

B. HAYWOOD: We have not used Li<sup>6</sup>-glass in scattering experiments because we would expect a high background from  $\gamma$ -rays. The advantage of the ZnS detectors in this respect is that by use of the pulse-length discriminators described, the  $\gamma$ -ray sensitivity can be reduced by several orders of magnitude.

H. PALEVSKY: I don't understand why - if the glass is as good as the data in your paper indicate.

B. HAYWOOD: Well, for most practical purposes the  $\gamma$ -ray flux is the thing. If one can reduce the  $\gamma$ -ray background by one order of magnitude, or even two or three orders of magnitude, this is much more advantageous than increasing the efficiency, and an efficiency of 60% for thermal neutrons is really about as high as you can go without becoming offensively efficient for fast neutrons, which are always present.

H. PALEVSKY: Was Mr. Glaeser thinking of the  $\gamma$ -ray background?

W. GLAESER: Yes. We have used the detector behind the crystal, where the  $\gamma$ -ray background is much lower than with a chopper, and there we have such a large background of  $\gamma$ -rays that we found scattering experiments out of the question.

P. EGELSTAFF: The  $\gamma$ -ray curve for lithium glass shown in this paper was obtained with a Co<sup>60</sup> source. In the case of the gamma field in the neighbourhood of a reactor the energy spectrum is such that a long "tail" of gamma pulses extends over the region of the neutron pulse. With sensitive neutron scattering experiments the neutron-to-gamma sensitivity of the detector should be  $10^4$  and this cannot at present be achieved with the lithium glass.

H. PALEVSKY: But that isn't exactly correct. The point is, if you're scattering  $\gamma$ -rays off a sample, they've lost energy.

P. EGELSTAFF: They are degraded  $\gamma$ -rays but they've originated from many different areas in the general gamma field, as it were, that the detector is placed in.

III

# LIQUIDS AND MOLECULES

# LIQUID DYNAMICS FROM NEUTRON SPECTROMETRY

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### Abstract — Résumé — Аннотация — Resumen

LIQUID DYNAMICS FROM NEUTRON SPECTROMETRY. Recent experiments carried out at Chalk River on the dynamics of liquids using neutron inelastic scattering are reviewed, including one by Sakamoto <u>et al</u>, in which the Van Hove self-correlation functions in water at 25°C and 75°C were determined, and another in which the correlation functions in liquid argon near its triple point were studied.

The possible occurrence of short wavelength phonons in classical liquids is discussed, in analogy with their existence in the quantum liquid  $He^4$ , and in connection with incomplete experiments on liquid tin.

DYNAMIQUE DES LIQUIDES PAR LA SPECTROMÈTRIE NEUTRONIQUE. Le mémoire décrit les expériences faites récemment à Chalk River sur la dynamique des liquides d'après la diffusion inélastique des neutrons, Il analyse notamment une expérience effectuée par Sakamoto et ses collaborateurs, au cours de laquelle ont été déterminées les fonctions d'autocorrélation de Van Hove dans l'eau à 25°C et à 75°C, ainsi qu'une expérience ayant pour objet d'étudier les fonctions de corrélation dans l'argon liquide aux environs de son point triple.

Les auteurs discutent l'existence éventuelle de phonons de courte longueur d'onde dans les liquides classiques, du fait de leur existence dans le liquide quantique <sup>4</sup>He et compte tenu des résultats d'expériences incomplètes avec l'étain liquide.

ГИДРОДИНАМИКА НА ОСНОВАНИИ НЕЙТРОННОЙ СПЕКТРОМЕТРИИ. Рассматриваются недавние эксперименты, выполненные в Чок Ривер, по динамике жидкостей с использованием неупругого рассеяния нейтронов, включая эксперимент Сакомото и др. В одном эксперименте были определены функции самокорреляции Вак Гофа в воде при температурах 25 С и 75°С, а в другом – изучались функции корреляции в жидком аргоне около его тройной точки.

Обсуждается вопрос о возможном наличии коротковолновых фононов в классических жидкостях по аналогии с их существованием в квантовом жидком He<sup>4</sup> и в связи с неполными экспериментами на жидком одове.

ESTUDIO DE LA DINÁMICA DE LÍQUIDOS POR ESPECTROMETRÍA NEUTRÓNICA. Se revisan los experimentos efectuados recientemente en Chalk River para estudiar la dinámica de líquidos por dispersión inelástica de neutrones; entre los experimentos figura uno de Sakamoto y colaboradores en el que se determinaron las funciones de autocorrelación de Van Hove en agua a 25° y 75°C, y otro en el que se estudiaron las funciones de correlación en argón líquido en las proximidades de su punto triple.

En relación con experimentos con estaño líquido aún sin terminar, se discute la posibilidad de que en los líquidos clásicos aparezcan fonones de onda corta, que existen en el líquido cuántico <sup>4</sup>He.

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# 1. INTRODUCTION

In this paper we present an experimental review of the more recent Chalk River work on the dynamics of liquids. The work has been inspired by the philosophy that one should attempt to deduce information directly from the experiments, as far as possible by inversion procedures rather than by comparison with calculations based on models which are almost certain to be much over-simplified.

At the time the paper was scheduled for the Symposium we hoped to be able to discuss the results of two new experiments: one an experiment to determine the pair correlation function in liquid argon, and the other, on liquid tin, to study the question of the existence of photons in liquids. Because of circumstances beyond our control, the experiments were not finished in time for the Symposium and we present here preliminary and incomplete results of the experiments.

We first briefly review the familiar notation and ideas of the VAN HOVE [1] formalism for discussing the dynamics of classical liquids. The fundamental variables are the momentum transfer or wave vector transfer Q = |Q| and the energy transfer  $\hbar \omega$ . The scattering function,  $S(Q, \omega)$ , the intermediate scattering function, I(Q, t), and the correlation functions,  $\overline{G_s}$  (r, t) (the self-correlation) or G(r, t) (the pair-correlation), are linked by the Fourier transformation equations

$$G(\mathbf{r}, \mathbf{t}) = 1/2\pi^{2} \int_{0}^{\infty} I(\mathbf{Q}, \mathbf{t}) (\sin \mathbf{Q}\mathbf{r}/\mathbf{Q}\mathbf{r}) \mathbf{Q}^{2} d\mathbf{Q},$$

$$I(\mathbf{Q}, \mathbf{t}) = \int_{-\infty}^{\infty} S(\mathbf{Q}, \omega) \cos \omega \mathbf{t} d\omega$$
(1)

and their inverses.

# 2. THE SELF-CORRELATION FUNCTION FOR THE PROTONS IN WATER

The first experiments were carried out on water, in which it was found that there exists a quasi-elastic component to the scattering which, however, is <u>only</u> quasi-elastic; there is an energy broadening, and this broadening is related to the diffusion of the atoms in the liquid [2]. Fig. 1 shows energy distributions obtained several years ago [3], with curves for water at 6° C and at room temperature, and for ice at  $-50^{\circ}$  C. The distribution for water at room temperature is broader than that for water at 6° C which, in turn, is broader than that for ice. The pattern for ice represents strictly elastic scattering broadened by the instrument resolution function, so that it is actually the resolution function for the other patterns. The width as a function of temperature varies somewhat as the experimental coefficient of self-diffusion for water, but is a little smaller, and a theoretical interpretation of these facts was given on the basis of the specific nature of the diffusive motions.

A little later it was proposed by other workers, first by HUGHES <u>et al</u>. [4] at Brookhaven, that in fact the quasi-elastic peak is not broadened but split. Now the statistics in Fig. 1 are not very good, and while it is not likely



Energy distributions from water at 6°C and 24.5°C and from ice at -50°C (open circles) [3].

that the broadening is in fact interpretable as a splitting of the line into three components, it is perhaps conceivable. However, the curves shown in Fig. 1 are Lorentzian functions broadened by Gaussian resolution, with a single parameter (the width of the Lorentzian) fitted to the distribution in each case. Thus the curves apparently have shapes close to the Lorentzian shape expected for a broadened line.

It was exceedingly difficult to understand how the components of the split line could simulate this behaviour in the two patterns of Fig. 1 as well as in several other patterns at different temperatures and Q's [3]. It was, in any case, difficult to understand why the splitting should have been observable in the Brookhaven experiments and not in the Chalk River experiments, in view of the facts that the resolutions in the two series of experiments were the same, about  $3 \times 10^{-4}$  eV, and that our experiments utilized a line method rather than the edge method employed at Brookhaven.

More recently, work has been carried out on water at 25°C and 75°C by SAKAMOTO et al. [5] using a resolution of about  $2 \times 10^{-4}$  eV. Fig. 2 shows a wavelength distribution, one of about 20 taken at 25°C (though not to the same statistical accuracy) using 4.06Å neutrons and the rotating crystal spectrometer [6]. The arrows on either side of the elastic position show the presumed positions of the two extra components of the quasi-elastic line. The other arrows indicate the positions of other sharp lines also reported [4]. No evidence for any of them was visible in the patterns.

From distributions such as that shown in Fig. 2, the scattering functions  $S(Q, \omega)$  for water at 25° C and at 75° C were constructed [5]. The parts of the functions involving small energy transfers are shown in Fig. 3. The broadening with increasing Q that is expected from diffusion and the strong increase in that broadening with increasing temperature, are both visible.

The Van Hove transformations were carried out on these data [7], and the self-correlation functions for the protons were obtained as shown in Fig. 4. There is not much that one can say directly from these curves, but it is perhaps pleasant to have a mapping of the motions of the atoms in this way.



Wavelength distribution of 4.06 Å neutrons scattered by room temperature water (SAKAMOTO et al. [5]). The resolution function, as measured by elastic scattering from vanadium, is shown as open circles.

From the curves of Fig. 4, the mean square distance in which the atom moves as a function of time can be computed. This is perhaps better carried out by means of a mathematical trick [5], using data further back in the transformation process, namely the intermediate scattering function. (The mathematical trick is of such a nature that a fairly accurate value for the mean square displacement is obtained.) In Fig. 5 the mean square distance which the atom has travelled from its position at the origin at time zero, is plotted as a function of time. On such a log-log plot calculations for various simple models appear as straight lines. Fig. 5 shows calculated lines for several models: for a gas of mass one atoms at room temperature, for a gas of mass 18 atoms at the two temperatures, and for atoms obeying the diffusion equation [1, 8] with coefficients of self-diffusion equal to those measured at the two temperatures by means of nuclear magnetic resonance [9]. For times greater than a few times  $10^{-12}$  s the experimental points agree with the calculations for simple diffusion. It is more informative, however, to look at the ordinate  $(displacement)^2$  scale. For both temperatures it appears that the diffusion equation is obeyed after the atoms have undergone mean square displacements of about 5Å<sup>2</sup>, roughly corresponding to Root Mean Square displacements of one intermolecular separation.



The scattering function  $S(Q, \omega)$  for water at 25°C and 75°C (SAKAMOTO et al. [5]). The resolution functions are shown as dashed curves.

# 3. THE SCATTERING FUNCTION FOR LIQUID ARGON

Wavelength distributions of 4.06Å neutrons scattered by liquid argon under its own vapour pressure (550 mm pressure, equivalent to a temperature of 84.5°K) have been measured for about twenty angles of scattering between 17° and 110° using the rotating crystal spectrometer [6]. Typical distributions at three angles are shown in Fig. 6, together with similar patterns taken with the specimen container empty. For both series, the fast neutron background was monitored at short intervals by inserting cadmium in the beam, and has been subtracted. The approximate magnitudes of the fast neutron backgrounds are indicated by the horizontal straight lines. The







The self-correlation function  $G_{s}(r, t)$  for water at 25°C and 75°C.

Mean square displacement of protons in water at 25°C and 75°C as a function of time (SAKAMOTO et al. [5]).

Fig.5



Energy distributions from liquid argon at three angles of scattering.

resolution at the incoming energy was approximately 2% in wavelength or  $2\times 10^{-4}\,\mathrm{eV}.$ 

Fig. 7 shows an idealized picture of the scattering function for liquid argon at 84.5° K, obtained from patterns similar to those of Fig. 6.

For convenience of the ordinate and abscissa scales, the data are presented as  $S(Q, \lambda')$  instead of  $S(Q, \omega)$ . Resolution functions are shown for Q=0 and Q=2Å<sup>-1</sup>.

We had considerable difficulty from more or less trivial causes in these experiments, and they have taken quite a lot of time. This was partly due to a mistake in the basic design which may be worth recounting. In all our experiments we have been very concerned with the influence of multiple



Scattering function  $S(Q, \dot{\lambda})$  for liquid argon.

scattering, and in this experiment we took good care that there was very little; in fact we estimate that multiple scattering amounts to only about 3% of the primary scattering at larger Q's. We achieved this low level by putting horizontal cadmium absorbers in the argon specimen chamber, as suggested to one of us by Dr. G. H. Vineyard [private communication], but in eliminating multiple scattering we also eliminated too much of the primary scattering. As a result the statistics are not as good as we would have wished, and the background subtractions are not as accurate. Not only this but the counting times were so long that difficulty was encountered in getting sufficiently compatible experimental results, due to equipment failures and changes. Nevertheless, we think that the results are sufficiently accurate that we will have errors of only 5%, or at worst 10%, in the transformed quantities in the regions of interest.

Fig. 8 (a) shows the full width at half maximum of the curves of Fig. 7, corrected for resolution, and plotted as a function of Q, with bars indicating estimated errors in W and resolution in Q.

Fig. 8 (b) shows the integrated intensity. At small Q the scattering comes largely from the incoherent component of the scattering cross-section. In this region the width has approximately the value  $2\hbar DQ^2$  expected [2] from diffusion, using the value of the coefficient of self-diffusion D=1.53×10<sup>-5</sup>



(a) Energy width of scattering function, corrected for resolution;(b) Integrated intensity as function of Q.

 $cm^2$  /s measured by CINI-CASTAGNOLI and RICCI [10]. (It should be pointed out, however, that other workers [11] have given values about 30% higher).

At larger values of Q, in the region of the first diffraction peak, the scattering is predominantly coherent, and the coherent narrowing of the energy distribution is visible. In the region of Q = 1.5Å<sup>-1</sup> the width makes a transition between the two types of behaviour as the scattering changes from predominantly incoherent at small Q, to coherent in the vicinity of the peak.

The narrowing of the distribution due to coherence, predicted by DE GENNES [12] and observed earlier in liquid lead [13], is striking. (This entire phenomenon, it should be noted, is outside the scope of the convolution approximation [8].)

We hope to complete these experiments by extending the range of Q, and to have in the near future, complete scattering and correlation functions for liquid argon near the melting temperature.

# 4. A SEARCH FOR PHONONS IN LIQUID TIN

Finally we discuss an experiment designed to study the question: "Is a liquid dynamically like a solid in any realistic and quantitative sense?" From the experiments of LARSSON <u>et al.[14]</u> in particular, it is known that the frequency distribution (in the sense of EGELSTAFF [15]) for the liquid, must be very similar to that for the solid. In our view, however, this fact does not provide an answer to the question posed; a liquid has roughly the same

volume as the corresponding solid, the potentials between the atoms in the liquid are the same as those in the solid, so the motions are necessarily constrained in much the same way and the Fourier components of the motion must be nearly the same for the two. The real question can be posed as: "Does there exist in a classical liquid something akin to the dispersion relation for the normal modes of a solid?" Since a liquid is isotropic the dispersion curve - if it exists - can depend only on the magnitudes of Q.

For the quantum liquid He<sup>\*</sup> it is known that such a dispersion relation exists. Experiments by PALEVSKY et al.[16] at Stockholm, YARNELL et al. [17] at Los Alamos, and HENSHAW et al.[18] at Chalk River, are in very good agreement as to the form of the curve. Fig. 9 shows the points of Yarnell et al. as crosses and of Henshaw and Woods, as closed circles. The integrated intensity (structure factor) of the liquid as measured by HENSHAW [19] is also shown, as open circles. The dispersion curve starts at small Q with the slope given by the measured velocity of sound, shows a maximum at the position of the first zone boundary<sup>\*</sup> in the liquid, falls rather symmetrically on the other side of the zone boundary to a minimum near the structure factor maximum, then rises again towards a possible second maximum near the structure factor minimum, all in rather close analogy to the behaviour of the dispersion curve in a crystal.



Fig.9

The dispersion curve and integrated intensity for liquid He<sup>4</sup>.

The question to be answered by the experiments is: "Can we see at least vestiges of such a dispersion curve in a classical liquid?" We know that longitudinal sound waves can be propagated in a liquid so we know that the initial part of the dispersion curve exists. We know that for at least some solids, at temperatures near the melting temperature, the phonons for wave vectors near the zone boundary are very much energy-broadened due to short life-

<sup>•</sup> The spherical zone is defined to contain one degree of freedom per atom. For liquid helium at 1. 15K this leads to a value 1.  $09\text{\AA}^{-1}$  for the zone boundary.

times for the phonons. In a liquid the lifetime of a phonon can hardly be longer than that for the corresponding phonon in the solid, so we expect any phonon groups near to, or beyond, the first zone boundary, to be very broad at best.

Liquid tin was selected as the subject for the experiments because it is a convenient material whose scattering is almost completely coherent, and especially becuase of the fact that one can reduce multiple scattering effects in liquid tin by dissolving cadmium in it without much altering other properties of the liquid. This is discussed in detail later.

Fig. 10 indicates the main facts known a priori about the "dispersion curve" in liquid tin. It must start off at small Q with the slope given by the velocity of sound in liquid tin,2464m/s, and at the "zone boundary",  $1.28\text{\AA}^{-1}$ , should have an energy certainly no greater than that corresponding to the Debye temperature of solid (white) tin,  $170^{\circ}$  K. If we accept a prescription of MOTT[20], the Debye temperature of the liquid would be expected to be  $110^{\circ}$  K corresponding to the quantum energy indicated in the figure. The dispersion curve would then be expected to bend over symmetrically about the zone boundary and take a small energy near the position,  $\sim 2.2 \text{\AA}^{-1}$ , of the main diffraction peak.





Information on "dispersion curve" in liquid tin and experimental constructions.

On the figure we have plotted several lines which correspond to the energies and wave vectors which would be observed in conventional experiments at energy loss for several outgoing energies, E', at a scattering angle of 10°, perhaps the minimum reasonable scattering angle one can use. (At smaller angles similar lines would occur to the left of those shown, at larger angles, to the right.) Even for E' = 36.2 meV we could not observe phonons on the linear part of the dispersion curve, although we could within the first zone.

The experiments are made difficult by the fact that we wish to study the region of Q before the first diffraction peak, the very region that one ordi-

narily considers to have almost zero primary intensity. Indeed under ordinary conditions most of the scattering observed in this region is multiple scattering, so to study phonons in liquids one must try to minimize the multiple scattering, and then make a reasonably accurate correction for what remains. In our experiments we used a thin specimen of tin (transmission  $\sim 87\%$ ) in which sufficient cadmium (0.78%) was dissolved to lower the transmission to about 50%. Cadmium dissolves in liquid tin to any amount, the two substances are both metals with approximately the same atomic weight, and we hope that the cadmium acts in liquid tin simply as another isotope but one that converts the tin to an isotopic form which has a large absorption and therefore for which the multiple scattering is reduced [21].

To take background we place a duplicate empty specimen container at the position of the specimen, and at the same time place in the beam a thin cadmium absorber with approximately the same transmission as the specimen. This is done automatically at each spectrometer position and background is subtracted directly from the signal point-by-point. By this means we obtain a background correction which takes accurate account in one operation of the fast neutron background and of container and air scattering.

Fig. 11 shows a preliminary set of results obtained at  $Q = 1.4 \text{\AA}^{-1}$  and 1.8Å<sup>-1</sup> (after background subtraction) using the constant Q method and the triple axis spectrometer [6]. The dashed curves represent multiple scattering computed in an approximation which assumed that two scatterings occurred, both at angles of scattering of 90°, and that the energy distribution for each scattering was that for a tin gas at 250°C. Even with this improved specimen, most of the scattering seems to be multiple scattering. If sharp phonons existed in the liquid we calculate that they should be seen with the



Energy distributions from liquid Sn at Q = 1.4 and 1.8  $Å^{-1}$ .

intensity and approximate shape indicated by the triangles. At Q = 1.8Å<sup>-1</sup> it is clear that there are no sharp phonons in the region of interest but, as discussed earlier, we do not expect sharp phonons anyway. At Q = 1.4Å<sup>-1</sup> there are no sharp phonons below about 10 meV which at any rate is above the Mott estimate. The statistics and accuracy of the experiments done so far do not allow more definite statements to be made. We have patterns with better statistics but the experiments were interrupted before the absolute normalization necessary could be carried out. We hope that the completed experiments will allow convincing evidence to be produced for what we think is the case; that there are no sharp phonon groups near the zone boundary, but rather a continuous distribution of intensity (with perhaps some slight structure). We think that the quasi-elastic scattering observed in Fig. 11 is probably just the result of an extremely broad phonon line, a line so broadened that there is little sense in calling it a phonon at all.

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### DISCUSSION

B. MOZER: What was the incoming neutron energy in your experiments?

B.N. BROCKHOUSE: About 5 mV.

K.E. LARSSON: Have you made any estimate of the damping necessary for complete disappearance of the phonon in your tin experiments?

B.N. BROCKHOUSE: I don't think that any of the theoretical estimates mean anything when you have that kind of damping. Perhaps Dr. Hahn might like to comment on that.

H. HAHN: My simple perturbation approach starting from a harmonic solid does not apply here.

B. MOZER: A theory that might give some of the answers for liquid metals might be to treat the metal as a two-component plasma: quantum electrons and classical ions. Then all the formalism developed by Landau and others on plasma oscillations will give estimates of the broadening of these oscillations ("phonons") from individual particle effects and will also yield the "phonon" dispersion relation. Bohm and Staver used this successfully to get a frequency spectrum of longitudinal modes in solids in reasonable agreement with experiment.

H. PALEVSKY: I think one has to be a little careful in making this type of comparison, saying that a liquid such as liquid helium represents real phonons and then comparing it to another system. In his oral presentation Brockhouse mentioned a zone boundary in helium and compared it with a solid, but this is really not quite right because, unlike what normally happens in solids, the origin of these excitations in liquid helium has nothing to do with order in space. I think this is well known.

B.N. BROCKHOUSE: I doubt that phonons in solids have very much to do with the order either. What does have to do with the order is the perfect repetition of the dispersion curve of the phonons. At the beginning a disordered system must show some tendency towards a dispersion curve and this is what we are looking for in the classical liquid.

P. EGELSTAFF: British theoreticans with whom I have spoken agree that you will get a dispersion curve in a disordered solid - say in something like a glass. In this connection it may be rather interesting to try to measure the dispersion curve for a glass by the technique you are suggesting, to find whether you can see these  $\tau = 0$  phonons in a disordered material.

B.N. BROCKHOUSE: Unfortunately this is even harder because for one thing the frequencies are higher. We have thought of this too.

# INTERPRETATION OF COHERENT NEUTRON SCATTERING BY LIQUIDS

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### Abstract — Résumé — Аннотация — Resumen

INTERPRETATION OF COHERENT NEUTRON SCATTERING BY LIQUIDS. The thermal motion in liquids differs from that in solids (collective modes only) and gases (single particle modes only) by having both collective and single particle modes of equal importance. Coherent neutron scattering offers a powerful tool for studying the properties of these modes, in particular the interactions between them, and such effects are shown to be important at low momentum and energy transfers. It is shown also how the damping of longitudinal sound waves is large for the frequencies excited by the neutron interaction and should be observable experimentally. Qualitative comparisons are made between the theoretical predictions and the experimental data on liquid lead and tin, which indicate profitable directions for future work.

INTERPRÉTATION DE LA DIFFUSION COHÉRENTE DE NEUTRONS PAR LES LIQUIDES. Le mouvement thermique intervenant dans les liquides diffère de celui qui se produit dans les solides (modes collectifs seulement) et les gaz (modes de particules simples seulement) du fait que l'on y observe des modes collectifs et des modes de particules simples d'importance égale. La diffusion cohérente des neutrons constitue un excellent moyen d'étude des propriétés de ces modes, notamment de leurs interactions réciproques. Le mémoire montre que ces effets sont importants pour de faibles transferts de quantité de mouvement et d'énergie. Il explique aussi pourquoi l'amortissement des ondes sonores longitudinales est intense pour les fréquences excitées par l'interaction des neutrons et devrait pouvoir être observé dans des expériences. Il contient des comparaisons qualitatives entre les prévisions théoriques et les données expérimentales relatives au plomb et à l'étain liquides, qui permettent de déterminer l'orientation des travaux futurs,

ОБЪЯСНЕНИЯ-КОГЕРЕНТНОГО РАССЕЛНИЯ НЕЙТРОНОВ В ЖИДКОСТЯХ. Тепловое движение в жидкостях отличается от такового в твердых телах (только коллективные формы) и в газах (только в форме отдельных частиц) тем, что при тепловом движении в жидкостях одинаково важную роль играют коллективные формы движения и формы движения отдельных частиц. Когерентное рассеяние нейтронов предоставляет мощное средство для изучения свойств этих форм движения, в частности взаимодействий между ными. Показано, что такие эффекты играют важную роль при низком моменте и переходах энергии. Такте показано, что затухание продольных звуковых воли является значительным для частот, возбужценных нейтронным взаимодействием, и его можно наблюдать экспериментально. Даются количественные сравнения между теоретическими предположениями и опытными данными на жидком свинце и жидком олове. Эти оравнения открывают перспективы для будущей работы.

INTERPRETACIÓN DE LA DISPERSIÓN NEUTRÓNICA COHERENTE EN LOS LIQUIDOS. La agitación térmica en los líquidos, a diferencia de la que se produce en los sólidos (modos colectivos únicamente) y en los gases (modos de partículas aisladas únicamente), se caracteriza por presentar modos colectivos y de partículas aisladas de igual importancia. La dispersión neutrónica coherente constituye un instrumento eficaz para estudiar las propiedades de dichos modos, en particular sus interacciones; se ha observado que esos efectos son importantes cuando la cantidad de movimiento y las transferencias de energía son bajos. Se ha demostrado también que el amortiguamiento de las ondas sonoras longitudinales es elevado para las frecuencias excitadas por interacciones neutrónicas y se estima que debería poder observarse experimentalmente. Se han efectuado comparaciones cualitativas entre los valores predichos por la teoría y los datos experimentales obtenidos en el caso del plomo y del estaño líquidos, lo que abre un camino interesante para trabajos futuros en esa esfera.

### 1. INTRODUCTION

The theory of liquids has suffered from the lack of a model which adequately represents the thermal motion of the atoms. One reason for this is
that macroscopic experiments average over many of the details of thermal motion and so the data obtained do not usually provide an exacting test of rival models. With the advent of cold neutron scattering techniques it is possible to study the thermal motions in liquids on a microscopic scale and, in principle, more exacting tests of models are possible. To make such a test it is necessary to relate specific features of the neutron scattering pattern to the behaviour of parameters in the model.

As an example consider the problem of finding a model to describe the basic modes of diffusion. Traditionally the models fall into two classes, first those based on the ideas of jump diffusion in solids and secondly those based on the ideas of Brownian motion. Macroscopic experiments are analysed in terms of a diffusion equation which is based on the assumption that the time-scale involved is sufficiently great that only an average over the thermal motion is needed. On the other hand microscopic experiments provide information on the interaction of atoms and hence on the length of time  $(t_0)$  over which the motion has to be averaged to justify the use of the diffusion equation. In a recent paper EGELSTAFF [1] analyses the experimental neutron data (viz. data on the half-width of the quasi-elastic peak) to derive this time,  $t_0$ , and shows how it is related to the two classes of models. Since the temperature dependence of  $t_0$  is opposite for the two cases, the basic type of model required can be deduced from measurements of  $t_0$ .

EGELSTAFF [1] concludes that the present experimental information favours a modified version of the Brownian motion model. In this model the liquid is imagined to be composed of an assembly of "spinning globules". Each globule consists of approximately 50 atoms in a disordered closepacked structure, and the motion of its centre of gravity is Brownian.

Another aspect of the model which can be studied by neutron scattering is how collective and single particle modes interact. In a liquid the collective modes are those associated with the transmission of acoustical waves while the single particle modes are those associated with diffusion. The interactions between these modes can be seen through the damping of the collective modes.

Qualitative predictions can be made for the various models. The globule model suggests strong damping for wavelengths of the order of a globule diameter, while crystal models suggest strong damping for frequencies of the order of the jump frequency. EGELSTAFF's [1] discussion shows that these effects are of similar magnitude near the melting point and that the method of distinguishing between them is through their temperature dependence.

Coherent neutron scattering is sensitive to the collective modes of the scattering system, and a qualitative discussion of this type of scattering is given in Section 2. This indicates the important regions of momentum and energy transfer, and that the relatively long time behaviour of the system only is observable in coherent scattering. New formulae are introduced in Section 4 to give methods of obtaining semi-quantitative information about the damping constants for longitudinal waves. Throughout this paper the predicted behaviour is compared to that observed in liquid lead and tin.

#### 2. GENERAL REMARKS ON COHERENT SCATTERING

Owing to the complex nature of coherent scattering phenomena, it is convenient to choose a representation suited to the problem in hand rather than use a general formulation. Two examples have been discussed in another paper at this conference (EGELSTAFF [2]). For the present discussion, which will be concerned with the large position (r) and time (t) behaviour of the Van Hove correlation function  $G_d(r, t)$ , the following method seems most useful.

The instantaneous pair correlation function g(r) is thought of as representing the distribution of density fluctuations seen from a given atom. The Van Hove function describes the damping of these fluctuations and may be written:

$$G_{d}(r,t) - g_{0} = (g(r) - g_{0})F(r,t)$$
 (1)

where, since isotropic systems are being considered, the distance "r" is a scalar and  $g_0$  is the average density. The damping has been specifically contained in the function F(r, t), defined at Eq. (1).

Eq. (1) may be Fourier-transformed with respect to "r" and "t" to give:

$$S_{d}(Q, \omega) = \int I_{d}^{0}(Q - Q') R(Q', \omega) dQ'$$
<sup>(2)</sup>

where  $I_d^0(Q) = \int S_d(Q, \omega) d\omega$ , (and hence  $\int R(Q, \omega) = \delta(Q)$ ), hQ and h $\omega$  are the momentum and energy transfer, and R is the double Fourier transform of F. Thus experimentally the function R will be observed with a "resolution" width given by the structure factor  $I_d^0$ . The most convenient point to study it would seem to be at the first maximum in  $I_d^0$ , which for many liquids is roughly Gaussian in shape and has a width  $\sim 0.5 \text{ Å}^{-1}$ .

The damping function F(r, t) may be separated qualitatively into two components, in the same manner as is usually done for Van Hove's "self" term. One part includes the short time motion which will affect F(r, t) principally at small "r" and thus give a contribution to R which is spread over a wide range of  $\omega$  and Q. In Eq. (2), therefore, the short time damping of the density fluctuations blurs out the fluctuations in  $I_d^0$  so giving a rather small contribution to the integral. In this region the experimental crosssections will be due almost entirely to the self term. This is in accord with the experimental observations of EGELSTAFF [2] and of COCKING and GUNER [3] which show that at energy transfers of about half the Debye temperature the peaks of Id cannot be observed and the cross-section is approximated by the self term. For this reason, at medium to high frequencies, it is possible to observe the frequency distribution only, rather than a dispersion law. This phenomenon is well known in the case of polycrystal scattering, where the momentum conservation condition  $Q + q \ge 2\pi\tau \ge Q - q$ allows the coherent cross-section to be averaged over a broad region of the structure factor. The form of Eq. (1) implies analogous behaviour for all systems.

The second component of F is a long time one associated with diffusion and expected to have a form similar to that obtained in self-diffusion. This component gives a term in R which is confined to a narrow range of Q and  $\omega$ . Consequently the peaks of  $I_d^0$  will be observed at low  $\omega$  over a range comparable to that of the self-diffusion function. This is in accordance with **experimental observations, particularly** those of BROCKHOUSE and POPE [4] and of TURBERFIELD [5] on liquid lead. These experiments were carried out at a peak in the function  $I_d^0$  and they show that energy broadening in coherent scattering is similar to that for self diffusion. A similar observation is possible at the minimum in  $I_d^0$  near Q = 0. At this point  $I_d^0$  is negative and the contribution from Eq. (2) will cancel the positive contribution from the self term. Thus the coherent, cross-section (which is the sum of S<sub>d</sub> and S<sub>s</sub>) should not show a "quasi-elastic" peak at low Q. The observations of COCKING and GUNER [3] on liquid tin show how these two terms cancel almost completely.

Thus Eqs. (1) and (2) are convenient for a qualitative discussion of the behaviour of the interference and coherent cross-sections. The improvement through the use of Eq. (2) rather than, for example VINEYARD's [6] approximation, lies in the convolution integral, which broadens the peaks in  $I_d^0$  when R is a broad function of Q. For a quantitative discussion it is necessary to define F(r, t) over a range of "r" and "t", and this is possible in principle for specific liquid models. However there is one component of F(r, t) which can be evaluated from classical theory. This is the damping of that part of the density fluctuations caused by longitudinal sound waves. It may be shown that for crystals where the damping is small the cross-section for this effect cannot be observed unless the neutron velocity is greater than the velocity of sound. However with the substantial damping that occurs in a liquid a significant cross-section is possible. This question will be considered in Section 4.

#### 3. GENERAL ANALOGUE OF THE DISPERSION LAW

In order to discuss the propagation of cooperative modes in a liquid it is desirable to define an experimentally-accessible quantity which can be thought of as a "dispersion law" and which reduces to the normal mode dispersion law in the case of a polycrystal. A convenient quantity in this respect is the width ( $\Delta Q$ ) of R(Q,  $\omega$ ) taken from a plot of this function against Q at fixed  $\omega$ . Since R(Q,  $\omega$ ) is observed experimentally as a convolution with  $I_d^0$ , it is only possible to measure its width at the peaks in  $I_d^0$ , in particular at the most prominent peak. This width ( $\Delta Q$  versus  $\omega$ ) has the character of a dispersion law and reduces to the normal mode one for a polycrystal as required above.

At the present time the range of experimental data is not sufficient to allow this quantity to be evaluated properly\*. However an attempt was made to evaluate the order of magnitude of the velocity of propagation of cooperative modes from existing data on liquid metals and this suggested that it was of the same order as the velocity of sound as expected.

<sup>\*</sup> New data on liquid argon (BROCKHOUSE et al.) and liquid sodium (RANDOLPH et al.) may reverse this situation.

#### 4. $\tau = 0$ CROSS-SECTIONS FOR A LIQUID

A convenient starting point is to consider the one phonon cross-section for inelastic scattering by a crystal associated with the origin (i.e.  $\tau = 0$ ) of reciprocal space. This cross-section is easily written down from the work of WEINSTOCK [7], for an energy transfer much less than the sample temperature, as:

$$\frac{d^2 \sigma}{d\Omega d\omega} = a^2 (k'/k) \cdot \exp(-2w) \cdot Z$$
  
where  $Z = T/2Mc^3 \delta(Q-q) \delta(\omega-cq)$  (3)

T is the temperature in energy units, "a" is the coherent scattering length, "k" and "k" are the incident and scattered neutron wave numbers, exp(-2w) is the Debye-Waller factor, "q" is the wave number of the phonon, M is the nuclear mass and "c" is the velocity of sound. The  $\delta$ -functions express conservation of momentum and energy and limit the scattering to the following condition:

$$Q/q > c/v \qquad (4)$$

where "v" is the neutron velocity (this follows from the standard rule that  $vQ > \omega$  for scattering to take place).

The interesting feature of this formula is the absence of an explicit dependence on momentum transfer, so that it does not vanish in the limit  $\mathbf{Q} \to 0$ . In this limit the integral of Z over  $\omega$  at constant Q gives the usual result of cross-section proportional to T times the compressibility. In the same limit it can be shown that the two phonon cross-section goes to zero as  $\mathbf{Q}^2$ , and for this reason it will not be considered here (however in order to preserve constant Q as  $\mathbf{Q} \to 0$  it is necessary to allow  $\mathbf{v} \to \infty$ , and this is very far from normal experimental conditions so that the two phonon term should be calculated properly in some practical cases).

The origin of reciprocal space ( $\tau = 0$ ) is a good scattering point for a liquid and the cross-sections will be given by the same expressions as for a solid. But unlike the solid the mean free path of longitudinal waves in a liquid is short and consequently the conservation of momentum and energy will not be given by the delta functions at Eq. (3). Scattering is allowed in this case over a range of Q and  $\omega$  and is possible even when the condition (4) is not satisfied. In principle both the energy and wave number of the phonon will be complex quantities but for simplicity it will be assumed that the wave number is real and the energy complex. This means that the second delta function of Eq. (3) must be replaced by a Lorentzian, i.e.:

$$Z = (T/2Mc^3) \cdot (1/\pi) \cdot s/[(\omega - cQ)^2 + s^2]$$
(5)

where "s" is the reciprocal of the phonon life-time. This formula is based upon the assumption that  $(\omega - cQ)$  varies much more rapidly (as a function of

Q for fixed  $\omega$ ) than either "s" or Q, so allowing these quantities to be taken as constants when integrating the Lorentzian. This assumption will be shown to be poor in practical cases, so that Eq. (5) has a qualitative significance only. The error in its use is probably  $\sim cQ/\omega$ .

In addition this formula is based on the simple (dispersion) law  $\omega = cq$ ; in practice a more complicated dispersion law holds which can lead to substantial changes in the magnitudes predicted by Eq. (5).

#### 5. EVALUATION OF THE LONGITUDINAL WAVE DAMPING CONSTANT

In considering the transmission of sound waves through a liquid metal it will be assumed that the thermal conductivity is sufficiently high that the system is isothermal and the damping is given entirely by the viscosity. Then the relation between frequency and wave-number of the waves is found to be:

$$q^2 = (\omega^3 \alpha + i\omega^2)/(\omega \alpha c_1^2 + ic_2^2)$$
(6)

where  $\alpha$  is Maxwell's relaxation time and  $c_1$  and  $c_2$  are the sound velocities at very high and very low frequencies respectively. Thus:

$$c_1^2 = [B + (4/3)G]/\rho; c_2^2 = B/\rho; \alpha = \eta/G;$$
 (7)

where B and G are the bulk and rigidity modulii respectively and  $\eta$  is the viscosity coefficient. This equation reduces to the ideal fluid results of STOKES [8] at low frequencies and the elastic continuum results of MAX-WELL [9] at high frequencies, and is derived [10] by arguments analogous to those used by FRENKEL [11]. It shows how the waves are transmitted in the region where both viscous and elastic effects are important.

For simplicity in discussing Eq. (6) it will be assumed that q is complex and  $\omega$  real. The square of the imaginary component of q is readily evaluated as:

$$(\text{Imag. } q)^2 = \frac{u(u+1)\beta}{2\alpha^2 c_1^2 (u+\beta)} \cdot \left[\sqrt{1 + \frac{u(1-\beta)^2}{(u+1)^2\beta}} - 1\right]$$
(8)

where 
$$u = \frac{\omega^2 \alpha^2}{\beta}$$
,  $\beta = \frac{c_2^2}{c_1^2} \leq 1$ . from (7).

Inspection of this equation shows that the imaginary part of "q" varies as  $\omega^2$  at low frequencies and is independent of  $\omega$  at high frequencies. The important factor is the ratio of the imaginary part of q to  $\omega$ , and this ratio is plotted in Fig. 1 for a value of  $\beta$  of 0.5. The peak will come near u = 1 for any value of  $\beta$  and shows that the absorption is high for periods of the order of the Maxwell relaxation time. In Table I the critical frequencies corresponding to u = 1 are given for lead and tin compared to typical values which can be obtained in neutron experiments (for the momentum transfer case a sound velocity of  $2 \times 10^5$  cm/s was assumed).

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Fig.1

Damping factor for longitudinal waves in a liquid plotted as a function of frequency. The value of the frequency is given in units of the critical value  $c_2/\alpha c_1$ .

It can be seen that neutrons can excite (or de-excite) sound waves in this critical region of large absorption, and for this reason Eq. (5) for the cross-section will be valid to order of magnitude only. However, the examination of this region with cold neutrons should be especially valuable in testing liquid models.

#### TABLE I

# CRITICAL FREQUENCIES FOR ABSORPTION OF LONGITUDINAL SOUND WAVES, COMPARED TO COLD NEUTRON FREQUENCIES

Case →	Lead 340°C	Tin 250°C	Neutron energy transfer 1 meV	Neutron momentum transfer 0.5Å <sup>-1</sup>
Frequency				
10 <sup>12</sup> c/sec	2	6	1.5	10

In the introduction it was pointed out that absorption at certain frequencies was predicted by the liquid diffusion models; in this section the same phenomenon has been derived from another point of view. Near the melting point the critical frequencies calculated from the diffusion models are of the same order as those given in Table I, but the temperature variation is different (this is discussed by FRENKEL [11]). However in one simple case good agreement is obtained for the critical damping predicted by both methods; this is the case of a compressed gas. For this example the peak in Fig. 1 comes at a wavelength ( $\lambda_c$ ) given by:

$$\lambda_k \simeq \eta / c\rho. \tag{9}$$

The spinning globule diffusion model predicts the globule diameter (2r) to be (where "d" is the diffusion constant):

$$2r = T/\eta d = (4\pi r^3 c^2 \rho^2)/3\eta^2 \text{ or } r \simeq \eta/\varphi$$
 (10)

since for a gas, the diffusion constant is equal to  $\eta/\rho$  and the squared velocity of sound is equal to  $T/\rho \times volume$ ). Thus  $\lambda_0$  and r are equivalent.

#### 6. COHERENT CROSS-SECTIONS OF LIQUID LEAD AND TIN

The coherent inelastic cross-section of lead over the temperature range from melting point to 520°C, has been measured for low momentum transfers by EGELSTAFF [12]. At the lowest scatter angle studied the crosssection was found to be nearly independent of temperature. This observation is unusual since cross-sections normally contain a temperature factor as at Eq. (5). However from Eq. (8) the width "s" is proportional to viscosity at low frequencies, and hence <u>decreases</u> as the temperature is raised. This effect will decrease the cross-section with temperature and offset the normal increase. Even a qualitative result is of some significance here, because in the high frequency region the damping varies as the reciprocal of viscosity which increases with temperature. Thus the qualitative nature of this result suggests that the experiment is being done in the region covered by the lower frequency side of Fig. 1 (this in turn means that the peak of Fig. 1 comes a little higher than the value given in Table I).





Comparison of liquid  $\tau = 0$  cross section with the experimental data [3] on liquid tin. The theoretical curves correspond to taking q real and  $\omega$  complex or the reverse, and the difference between them indicates the present theoretical uncertainty (this Fig. was kindly supplied by S.J. Cocking).

1.

COCKING and GUNER [3] have measured the inelastic cross-section of liquid tin at 240°C for low momentum and energy transfers. Assuming that the low frequency region of Eq. (8) is applicable to this case the width "s" required in Eq. (5) can be readily evaluated. Comparison of the tin data (6Åneutrons scattered through an angle of 20°) with the predictions of Eq. (5) is given in Fig. 2. The lowest momentum transfer data has been chosen since this should offer the best comparison with the theory. This figure shows that the theoretical cross-section has the right general shape but the absolute value is substantially less than the experimental one. Several deficiencies in the theory have been pointed out and these may account for this discrepancy. In particular this result could be taken as confirmation that the experiment is being conducted near the peak of Fig. 1, so requiring a special theory. Alternatively there may be other terms coming from the long time behaviour of F(r, t) - Eq. (1) - which are not completely cancelled by the self term at the values of momentum transfer employed in the experiment. Again this would require a detailed theoretical discussion.

#### 7. CONCLUSIONS

The discussion of Section 2 showed that significant contributions to the interference term in neutron scattering are to be expected at low momentum and energy transfers. In this region the scattering should be analysed in terms of the long time motion of the atoms in the liquid. Two types of motion were emphasized, one the "single particle" diffusive modes and another the "collective" longitudinal modes. In the scattering pattern these two effects have different widths, the damping of the longitudinal modes by interaction with the diffusive modes produces a width one or two orders of magnitude greater than that due to diffusion alone. This can be seen by comparing Eq. (5) with the simple diffusion cross-section (e.g. VINEYARD [6]). Using the low frequency expression for s (i.e.  $s = \alpha c_1^2 Q^2$ ) the two expressions are of the same form but the widths differ by the order of magnitude of the ratio of the kinematic viscosity to the diffusion constant. This ratio is between 10 and 100 for liquid metals in the range of a few hundred degrees above the melting point.

Near Q = 0 only the broader term can be observed and this was discussed in detail. At present the theoretical cross-sections are right only in a qualitative sense and more detailed calculations are required before a quantitative comparison is made. At the first peak of  $I_d^0$ , usually near  $Q = 2 \text{\AA}^{-1}$ , both terms should be important, and this would lead to a two component shape for the energy transfer distribution. A distribution of this type is suggested by the results of PALEVSKY [13] on liquid lead and tin and of COCKING and GUNER [3] on tin, taken at the principle peak in  $I_d^0$  for these liquids. In this case the broad component may spread into the low Q region and hence add a considerable background to the  $\tau = 0$  cross-section. An extension of the longitudinal mode calculated to  $\tau \neq 0$  is thus indicated, and may account for some of the discrepancy shown in Fig. 2.

The results given in this paper are a continuation of the attempt to relate features of the neutron scattering pattern to specific features of liquid models. The main contribution has been to show that there is a region of coherent scattering which should be sensitive to the model and to identify the most important properties which affect this region. Considerable further work on these lines, both experimental and theoretical, is required to establish the detailed properties which must be incorporated into a successful liquid model.

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#### DISCUSSION

P. SCHOFIELD: I would like to make a few comments regarding the coherent scattering of neutrons in liquids. There are, as I see it, two distinct problems to be considered: (a) the effect of interference on the "quasielastic" scattering (a question to be answered here is whether neutrons can detect the presence of clusters of atoms moving together - the "globules" of Egelstaff's theory\*); and (b) the inelastic scattering and the possibility of detecting local thermal excitations in the liquid corresponding to the correlated motions of sets of atoms. Let us consider (a) and (b) in turn.

(a) In considering this problem, it is best to work with the pair distribution function  $G_d(\underline{R}, t)$ . This can be written [VINEYARD, Phys. Rev. <u>110</u>, (1958) 999].

 $G_{d}(\underline{\mathbf{R}}, t) = \int g(\underline{\mathbf{R}}') H(\underline{\mathbf{R}}', \underline{\mathbf{R}}, t) d\underline{\mathbf{R}}'$ (1)

where  $g(\underline{R})$  is the static pair distribution function and  $H(\underline{R}^{\dagger}, \underline{R}, t)$  is the probability that, given an atom A at the origin at time zero, an atom B at  $\underline{R}^{\dagger}$  at time zero, moves to R in time t.

In the convolution approximation the motion of atom B is assumed to be independent of the presence of atom A, and  $H(\underline{R}^{1}, \underline{R}, t)$  is replaced by the self-correlation function  $G_{s}(R-R^{1}, t)$ . The most obvious defect of this ap-

<sup>\*</sup> EGELSTAFF, P.A., "Advances in Physics", 11 (1962) 203.

proximation is a geometrical one: if the distance of closest approach of two atoms is a, then if atom A has moved to  $\underline{R}^{"}$  in time t, atom B is excluded from a sphere of radius a around  $\underline{R}^{"}$  at this time.

It can be demonstrated fairly simply that the effect of modifying the convolution approximation to take account of this exclusion is to narrow  $S(Q, \omega)$  in energy at the peaks in the structure factor I(Q), and to broaden it in the valleys. This is in agreement with the data obtained by de GENNES from consideration of the energy moments of  $S(Q, \omega)$ ["Inelastic Scattering of Neutrons in Solids and Liquids", IAEA, Vienna (1961)239].

In order to see whether neutrons can detect clusters of atoms which move together, it is necessary to perform detailed calculations on this improvement of the approximation in which the minimum restriction is imposed upon the independence of the motion of atom B with a model in which, if atom A moves to  $\mathbb{R}^{\mu}$ , the probability of B being in the neighbourhood of  $\mathbb{R}^{\mu}$ is greatly enhanced.

(b) In his paper, Dr. Egelstaff proposes the use of the classical theory of damped waves in liquids, as given by Frenkel \* in the neutron scattering theory. Such an attempt was made by Butterworth and Marshall at the Stockholm conference, but this theory failed as it did not take account of diffusion. I should now like to show how the formalism can be cast in such a way that the Frenkel theory might be used.

We consider now the intermediate function  $I_d(\underline{Q}, t)$ . This can be written in the form

$$I_{d}(\underline{Q}, t) = \int g(\underline{R}) [\exp(i\underline{Q}, \underline{R})] \langle \exp(i\underline{Q} - \underline{u}(t)) \rangle_{\underline{R}} d\underline{R}$$
(2)

where  $\underline{u}(t)$  is the displacement of the atom originally at <u>R</u> and  $\langle . . \rangle_{\underline{R}}$  denotes a restricted thermal average - being the Boltzman weight average integrated over all momenta, and the positions of all but two of the atoms, the separation of these being equal to <u>R</u>. At t = 0,  $\underline{u}(t) = 0$ , while at long times the restricted average must fall off exponentially in time in the same way as I<sub>s</sub> (Q, t), i.e. at long times

$$\{I_{s}(\underline{Q},t)\}^{-1} \langle e^{i\underline{Q}\cdot u(t)} \rangle_{R} \to C(\underline{Q},\underline{R})$$
(3)

We may expect that  $C(\underline{Q}, \underline{R})$  tends to unity fairly rapidly as  $\underline{R}$  increases, and hope that it is not too different from unity for all  $\underline{R}$ . We can then make a 'quasi-phonon' expansion of  $I_d(\underline{Q}, t)$  by expanding the left-hand side of (3) in powers of  $\underline{Q}$ . Retaining the first two terms, we obtain

$$I_{d}(\underline{Q}, t) = I_{s}(\underline{Q}, t) \int g(\underline{R}) e^{i\underline{Q}\cdot\underline{R}} (1 + i\underline{Q}, \langle \underline{u}(t) \rangle_{R} d\underline{R}$$
(4)

(In the case of a solid, (4) contains the one-phonon peak correctly.) Note that the second term in the integral is of order  $Q^2$  since  $\int g(\underline{R}) \langle u(t) \rangle_R d\underline{R}$  vanishes.

In (4) we have an expression which should certainly be valid for small Q, in which we have introduced just one new function into the theory, namely

\* FRENKEL, J., "Kinetic Theory of Liquids", IV Oxford (1946).

 $\langle u(t) \rangle_{R}$ . As a function of time, this is the mean displacement of an atom, originally at R, given another atom at the origin at time zero.

It is tempting to identify  $\langle u(t) \rangle_R$  with the displacement of the Frenkel theory, but I cannot at present completely justify such a step.

P. EGELSTAFF: The analysis you propose seems to be consistent with mine and in particular it could be used to interpret the suggested "experimental dispersion law" for a liquid.

# FREQUENCY SPECTRUM OF LIQUIDS AND COLD NEUTRON SCATTERING\*

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#### Abstract — Résumé — Аннотация — Resumen

FREQUENCY SPECT RUM OF LIQUIDS AND COLD NEUTRON SCATTERING. An important question which arises in connection with slow neutron scattering by liquids is: does there exist a trequency spectrum for liquids analogous to that in solids? The answer to this question is given by showing that the width function  $\gamma(t)$  of the Gaussian space-time self-correlation function  $G_{s}(\mathbf{r},t)$  can be expressed, by using the frequency spectrum of the velocity auto-correlation function, in a form which is formally identical with that of a harmonic solid. Thus a knowledge of the frequency spectrum of the velocity auto-correlation function should enable one to calculate slow neutron scattering by liquids as has been emphasized by Egelstaff and co-workers.

Using a stochastic model of a liquid, the frequency spectrum  $f(\omega)$  of the velocity auto-correlation function is calculated for water at 300°K and for liquid lead at 620°K. In the case of water a maximum in  $f(\omega)$  corresponding to  $\hbar\omega$  75°K is predicted. For lead the maximum also occurs at nearly the same  $\omega$ -value. There also occurs a minimum in  $f(\omega)$  in both cases.

Larsson and Dahlborg have observed a maximum in  $f(\omega)$  at the above predicted  $\omega$ -value. A recent observation in liquid lead of Cotter et al. probably confirms our prediction too.

SPECT RE DE FRÉQUENCES DES LIQUIDES ET DIFFUSION DE NEUTRONS FROIDS. Dans le domaine de la diffusion des neutrons lents par des liquides une question importante se pose; existe-t-il un spectre de fréquences pour les liquides analogue au spectre pour les solides? On peut répondre à cette question en montrant que la fonction de largeur  $\gamma(t)$  de la fonction gaussienne spatio-temporelle d'auto-corrélation  $G_{s}(\underline{r},t)$  peut etre exprimée, en employant le spectre de fréquences de la fonction d'auto-corrélation des vitesses, sous une forme qui présente le même aspect formel que celle d'un solide harmonique. Par conséquent, la connaissance du spectre de fréquences de la fonction d'auto-corrélation des vitesses devrait permettre de calculer la diffusion des neutrons lents par les liquides comme l'ont souligné Egelstaff et ses collaborateurs.

Les auteurs calculent, à l'aide d'un modèle stochastique, le spectre des fréquences  $f(\omega)$  de la fonction d'auto-corrélation des vitesses dans l'eau à 300<sup>2</sup> K et dans le plomb liquide à 620<sup>6</sup> K. Dans le cas de l'eau ils prévoient un maximum de la fonction  $f(\omega)$  correspondant à  $\hbar \omega 75^{5}$  K. Dans le plomb, le maximum se manifeste à une valeur à peu près analogue. Il existe aussi un minimum de la fonction  $f(\omega)$  dans les deux cas.

Larsson et Dahlborg ont observé un maximum de la fonction  $f(\omega)$  à la valeur d' $\omega$  prévue ci-dessus. Des observations faites récemment dans du plomb liquide par Cotter <u>et al</u>. confirment vraisemblablement les prévisions des auteurs.

ЧАСТОТНЫЙ СПЕКТР ЖИДКОСТЕЙ И РАССЕЯНИЕ ХОЛОДНЫХ НЕЙТРОНОВ. В связи с изучением рассеяния медленных нейтронов жидкостями, возникает важный вопрос: существует ли частотный спектр для жидкостей, аналогичный спектру для твердых тел? Ответ на этот вопрос вытекает из того факта, что бушкция ширины  $\gamma(t)$  самокоррелиружщей функции пространство-время Гаусса G<sub>g</sub>(<u>r</u>,t) может быть выражена путем использования частотного спектра автокоррелиружщей функции скорости в форме, которая формально идентична форме гармонического твердого тела. Таким образом, знание частотного спектра автокорреляционной функции скорости должно позволить вычислить рассеяние медленных нейтронов жидкостями, как это отмечали Эгельштафф и другие.

С помощью стохастической модели жидкости, частотный спектр  $f(\omega)$  автокорредяционной функции скорости вычисляется для воды при 300°К и для жидкого свинца при 620°К. Для воды предвидится максимум f ( $\omega$ ), соответствующий fkm при 75°К. Для свинца максимум также имеет место почти при той же величине. В обоих случаях имеет также место минимум f( $\omega$ ).

<sup>\*</sup> Based on work performed under the auspices of the United States Atomic Energy Commission.

Ларссон и Дальборг наблюдали максимум f(ω) при вышеупомянутой предполагаемой величине ω. Последние наблюдения Коттра и др. при работе с жидким свинцом, видимо, также подтверждают наши предположения.

ESPECTRO DE FRECUENCIAS DE LOS LIQUIDOS Y DISPERSION DE NEUTRONES FRIOS. Una cuestión importante que se plantea respecto de la dispersión de neutrones lentos por los líquidos es la siguiente: (Existe un espectro de frecuencia de los líquidos análogo al de los sólidos? Para contestar a esta pregunta, basta demostrar que la función de amplitud y(t) de la función gaussiana de autocorrelación espacio-tiempo  $G_s(r, t)$  puede expresarse, utilizando el espectro de frecuencias de la función de autocorrelación de velocidad, en forma idéntica a la correspondiente a un sólido armónico. Es decir, si se conoce el espectro de frecuencias de la función de autocorrelación de velocidad, se debe poder calcular la dispersión de neutrones lentos por los líquidos, como han señalado Egelstaff y colaboradores.

Los autores calculan, utilizando un modelo estocástico de líquido, el espectro de frecuencia  $f(\omega)$  de la función de autocorrelación de velocidad, en el caso del agua a 300°K y del plomo líquido a 620 K. Predicen para la primera un máximo de  $f(\omega)$  correspondiente a  $\hbar \omega 75^{\circ}$ K. En el caso del plomo, el máximo se presenta también para el mismo valor de  $\omega$ , aproximadamente. Además, en ambos casos  $f(\omega)$  pasa por un mínimo.

Larsson y Dahlborg han observado un máximo de  $f(\omega)$  para el valor de  $\omega$  previsto por los autores. Al parecer una comprobación recientemente efectuada por Cotter y colaboradores en el caso del plomo líquido también confirma la previsión de los autores acerca de este metal.

#### 1. INTRODUCTION

The theory of slow neutron scattering by an interacting system in terms of the space-time correlation function has been given by VAN HOVE [1]. The scattering cross-section can be written in the following form

$$\frac{d^2\sigma}{d\Omega d\omega} = N \frac{k}{k_0} \left\{ a_{\rm coh}^2 S_{\rm coh} (\underline{\kappa}, \omega) + a_{\rm inc}^2 S_{\rm inc} (\underline{\kappa}, \omega) \right\}, \qquad (1)$$

where

$$S_{\rm coh}(\underline{\kappa},\omega) = \frac{1}{2\pi} \int e^{i(\underline{\kappa},\underline{1}-\omega t)} G(\underline{\mathbf{r}},t) \, d\underline{\mathbf{r}} dt, \qquad (2)$$

and

$$S_{inc}(\underline{\kappa},\omega) = \frac{1}{2\pi} \int e^{i(\underline{\kappa},\underline{r}-\omega t)} G_{s}(\underline{r},t) d\underline{r} dt.$$
(3)

 $a_{coh}$  and  $a_{inc}$  denote, respectively, the coherent and incoherent scattering lengths. N is the total number of atoms in the scattering system. hw and hk are, respectively, the energy and momentum transfers given by

$$\underline{\kappa} = \underline{\kappa}_0 - \underline{\kappa}, \tag{4}$$

and

$$\hbar\omega = \frac{\hbar^2}{2m} (k_0^2 - k^2),$$
 (5)

where  $\underline{k}_0$  and  $\underline{k}$  denote, respectively, the incident and final wave vectors of a neutron of mass 'm!

The introduction of the G functions by Van Hove was mainly due to the fact that they could be interpreted directly in terms of physical terms. In fact, such an interpretation has helped and guided many authors, during recent years, to propose dynamical models of the liquid state, which would explain the salient features of slow neutron scattering. For many purposes, as we shall see in the sequel, it is convenient to analyse the space transform of G(r, t), i.e.

$$\mathbf{F}(\underline{\kappa}, \mathbf{t}) = \int e^{\underline{i}\underline{\kappa}\cdot\underline{\mathbf{r}}} \mathbf{G}(\underline{\mathbf{r}}, \mathbf{t}) \, d\underline{\mathbf{r}}.$$
(6)

The scattering functions  $S_{coh}(\underline{\kappa},\omega)$  and  $S_{inc}(\underline{\kappa},\omega)$  are then simply the time transforms of  $F(\underline{\kappa}, t)$  and  $F_s(\underline{\kappa}, t)$ , respectively.

The F-functions are defined by

$$\mathbf{F}(\underline{\kappa}, \mathbf{t}) = \frac{1}{N} \sum_{ij} \langle \mathbf{e}^{-i\underline{\kappa}} \underline{R}_{j}(0) \rangle_{\mathbf{T}} \cdot \mathbf{e}^{i\underline{\kappa} \cdot \mathbf{R}} \underline{R}_{j}(\mathbf{t}) \rangle_{\mathbf{T}}$$
(7)

and

$$\mathbf{F}_{s}(\underline{\kappa}, \mathbf{t}) = \frac{1}{N} \sum_{\boldsymbol{\ell}} \langle \mathbf{e}^{-\mathbf{i}\underline{\kappa}.\underline{R}\boldsymbol{\ell}(0)}, \mathbf{e}^{\mathbf{i}\underline{\kappa}.\underline{R}\boldsymbol{\ell}(\mathbf{t})} \rangle_{\mathbf{T}}.$$
(8)

Here  $\underline{R}_{l}(t)$  is the position vector of the  $l^{th}$  atom in the Heisenberg representation  $\langle \ldots \rangle_{T}$  means that both quantum mechanical and statistical averages the should be taken. From the above definition, it follows that

$$\mathbf{F}(\kappa,-\mathbf{t}) = \mathbf{F}^{\mathbf{x}}(\kappa,\mathbf{t}), \qquad (9)$$

$$\mathbf{F}_{s}(\underline{\kappa},-t) = \mathbf{F}_{s}^{*}(\underline{\kappa},t). \tag{10}$$

For t = 0, we have from (7) and (8)

$$\mathbf{F}(\kappa, 0) = 1 + \int e^{\mathbf{i}\kappa \cdot \mathbf{r}} g(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \tag{11}$$

and

$$F_{s}(\kappa, 0) = 1,$$
 (12)

where g(r) is the instantaneous pair correlation function.

For  $t \to \infty$  both  $F(\underline{\kappa},t)$  and  $F_s(\underline{\kappa},t)$  tend to zero except in the case of a solid, in which case they tend to a finite limit. A consequence of this is that both  $S_{coh}(\underline{\kappa},\omega)$  and  $S_{inc}(\underline{\kappa},\omega)$  have a  $\delta(\omega)$  singularity. In a liquid where diffusion cannot be neglected we do not have any elastic scattering in the sense we have in a solid. What we do have is a pronounced peak with a finite width around the incident energy. The width of this so-called "quasi-elastic" peak depends sensitively on how these F-functions tend to zero for  $|t| \to \infty$ . On the other hand scattering corresponding to large energy transfers will mainly depend on the properties of these functions for small times.

#### 2. VELOCITY AUTO-CORRELATION FUNCTION

In what follows we shall be dealing with only the function  $F_s(\underline{\kappa}, t)$  corresponding to the self motion of an atom. It is convenient to express it in terms of a velocity-correlation function.  $F_s(\underline{\kappa}, t)$  can be written as [2];

$$F(\underline{\kappa},t) = e^{+i\kappa^2 \hbar t/2M} \exp\left[-\kappa^2 \gamma_1(t) + \kappa^4 \gamma_2(t) \dots \right], \qquad (13)$$

where

$$\gamma_{1}(t) = \int_{0}^{\infty} (t - t_{1}) \langle \mathbf{v}_{\kappa}(0) \mathbf{v}_{\kappa}(t_{1}) \rangle_{\mathbf{T}} dt_{1}, \qquad (14a)$$

and

$$\gamma_{2}(t) = \int_{0}^{t} dt_{1} \int_{0}^{t_{1}} dt_{2} \dots \int_{0}^{t_{3}} dt_{4} \langle v_{\kappa}(t_{4})v_{\kappa}(t_{3})v_{\kappa}(t_{2})v_{\kappa}(t_{1}) \rangle_{T} - \frac{1}{2} [\gamma_{1}(t)]^{2} \dots (14b)$$

<u>v</u> denotes the velocity of the atom and  $v_{\kappa}$  its component along the vector  $\kappa$ . In (13) terms of order  $\kappa^4$  and higher correspond to higher order velocity correlation functions as is evident from (14b). In the Gaussian approximation all these higher order terms are omitted.

An expansion of the type (13) would be useful if only the first few terms are important, in other words if the non-Gaussian correction is small. Now we know that in the case of a harmonic solid, and in the case of a particle

diffusing according to the Langevin equation all  $\gamma$  for n > 1 vanish. We also know that for both very small and very large times  $G_s(\mathbf{r}, \mathbf{t})$  for a liquid is a Gaussian function, and it is only in the intermediate time range that it is non-Gaussian. It was our conjecture [2] that on account of the random character of the motion of an atom in a liquid, all  $\gamma_n$  for n > 1 would be small and hence the Gaussian approximation should be good. This indeed is the case as has been demonstrated, within their experimental error, by the recent work of POPE et al. [3].

The  $\gamma$ -functions occuring in Eqs. (13), (14a) and (14b) have the following general properties; the details of their derivation are given in [2].

For  $t \rightarrow \infty$ 

$$\gamma_{\rm n}(t) \rightarrow D_{\rm n} t - C_{\rm n}, \tag{15}$$

where  $D_n$  and  $C_n$  are some constants. In particular

$$\mathbf{D_1} = -i\frac{\hbar}{2\mathbf{M}} + \int_0^\infty \langle \mathbf{v}_{\kappa}(0) \, \mathbf{v}_{\kappa}(t) \rangle \, \mathrm{d}t, \qquad (16)$$

and

$$C_{1} = -\int_{0}^{\infty} t \langle v_{\kappa}(0) v_{\kappa}(t) \rangle dt.$$
(17)

For  $t \to 0$ , we can expand  $\gamma_n(t)$  in a power series in 't' and it turns out that

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$$\gamma_{n}(t) \to t^{2n}.$$
 (18)

In the classical case, however,  $\gamma_2(t)$  starts as  $t^8$  and not as  $t^4$ , since in classical mechanics velocities have a Gaussian distribution and are uncorrelated with forces acting at the same time.

## 3. GAUSSIAN APPROXIMATION

In this approximation the scattering is completely determined by the function  $\gamma_1(t)$  given by (14a).  $\gamma_1(t)$  as it stands is a complex function. Since in the case of a liquid it is not possible to calculate  $F_g(\kappa, t)$  explicitly, recourse is taken to assuming a certain reasonable form of  $F_s(\kappa, t)$  to compute the scattering function  $S_{inc}(\kappa, \omega)$ . It is, however, not very convenient to deal with a complex  $F_g(\kappa, t)$ . If one assumes some real function for  $F_s(\kappa, t)$  then, as shown by SCHOFIELD [4] one violates the principle of detailed balance. The way out of this difficulty is to make use of the fluctuation-dissipation theorem, according to which the real and imaginary parts of  $F_g(\kappa, t)$  are related as follows [5]:

$$\int_{-\infty}^{+\infty} e^{-i\omega t} \operatorname{Im} F_{s}(\underline{\kappa}, t) dt = -i \tanh(\beta \omega) \int_{-\infty}^{+\infty} e^{-i\omega t} \operatorname{Re} F_{s}(\underline{\kappa}, t) dt$$
(19)

where

$$\beta = \frac{h}{k_B T}$$

Eq. (19) implies the following relation

Im 
$$F_s(\underline{\kappa}, t) = -\tan(\beta \frac{d}{dt}) \operatorname{Re} F_s(\underline{\kappa}, t)$$
 (20)

Let us now introduce a new function  $H_s(\kappa, t)$ , defined by

$$H_{s}(\kappa, t) = F_{s}(\kappa, t + i\beta).$$
(21)

Expanding  $F_s(\kappa, t+i\beta)$  in powers of  $\beta$  and making use of (20) we have

$$H_{s}(\underline{\kappa}, t) = \exp(i\beta \frac{d}{dt}) F_{s}(\underline{\kappa}, t) = \sec(\beta \frac{d}{dt}) \operatorname{Re} F_{s}(\underline{\kappa}, t).$$
(22)

 $H_s(\kappa,t)$  is thus real and an even function of 't'. The scattering function  $S_{inc}(\kappa,\omega)$  can now be written as

$$S_{inc}(\underline{\kappa}, \omega) = e^{\beta \omega}, \quad \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\beta \omega} H_s(\underline{\kappa}, t) dt, \quad (23)$$

where the integral is an even function of  $\omega$ . The exponential factor  $e^{\beta\omega}$  in (23) is essential to satisfy the condition of detailed balance.

From (21) and (14a) we have

$$H_{s}(\kappa, t) = \exp(-\kappa^{2} \rho(t)), \qquad (24)$$

where

$$\rho(t) = \gamma_1'(t + i\beta), \qquad (25a)$$

and

$$\gamma_{1}^{t}(t) = -\frac{ith}{2M} + 1/3 \int_{0}^{t} (t - t_{1}) \langle \underline{v}(0) . \underline{v}(t_{1}) \rangle_{T} dt_{1}.$$
(25b)

Now

$$\frac{\mathrm{d}^{2}\rho}{\mathrm{d}t^{2}} = \frac{\mathrm{d}^{2}}{\mathrm{d}t^{2}} \gamma_{1}^{!} (t+\mathrm{i}\beta) = 1/3 \langle \underline{\mathbf{v}}(0), \underline{\mathbf{v}}(t+\mathrm{i}\beta) \rangle_{\mathrm{T}}.$$
(26)

By making use of the fluctuation-dissipation theorem on the velocity correlation function above and performing the integration we have

$$\rho(\mathbf{t}) = \rho(\mathbf{0}) + 1/3 \int_{0}^{1} (\mathbf{t} - \mathbf{t}_{1}) \sec(\beta \frac{\mathrm{d}}{\mathrm{d}\mathbf{t}_{1}}) \operatorname{Re} \langle \underline{\mathbf{v}}(\mathbf{0}), \underline{\mathbf{v}}(\mathbf{t}_{1}) \rangle_{\mathrm{T}} \mathrm{d}\mathbf{t}_{1}. \qquad (27)$$

It was shown in [2] that to a high degree of accuracy  $\rho$  (0) is given by

$$\rho(0) = \frac{\hbar^2}{8 M k_B T}.$$
(28)

If we now retain only the first term in the expansion of the differential operator in (27), and further if we replace Re  $\langle v(0), v(t) \rangle_{\tau}$  by its classical analog  $\langle \underline{v}(0), \underline{v}(t) \rangle_{c_1}$ , we have

$$\rho(\mathbf{t}) = \frac{\hbar^2}{8 \mathbf{M} \mathbf{k}_{\mathbf{B}} \mathbf{T}} + 1/3 \int_0^1 (\mathbf{t} - \mathbf{t}_1) \langle \underline{\mathbf{v}}(\mathbf{0}) . \underline{\mathbf{v}}(\mathbf{t}_1) \rangle_{\mathbf{c}_1} d\mathbf{t}_1.$$
(29)

Eq. (29) should be a very good approximation for most liquids. The first term in (29) for slow neutron scattering is negligibly small and can be considered to represent a purely quantum mechanical correction [5] to  $\rho$  (t) at t = 0.

#### 4. SPECTRAL REPRESENTATION

From the foregoing it is thus clear that to calculate the scattering function  $S_{inc}(\underline{\kappa}, \omega)$  in the Gaussian approximation all that is necessary is the knowledge of the velocity auto-correlation function. It is very often useful and convenient to work in terms of the frequency distribution of this auto-correlation function.

Let us define two frequency spectra which are related to the real and imaginary parts of the velocity auto-correlation function in the following way

$$\operatorname{Im} \langle \underline{\mathbf{v}}(0), \underline{\mathbf{v}}(t) \rangle_{\mathbf{T}} = \frac{3\hbar}{2\mathbf{M}} \int_{0}^{\infty} \omega f(\omega) \sin(\omega t) d\omega$$
(30)

and

$$\operatorname{Re}\left\langle \underline{\mathbf{v}}(\mathbf{0}), \underline{\mathbf{v}}(\mathbf{t}) \right\rangle_{\mathrm{T}} = \frac{3\hbar}{2M\beta} \int_{0}^{\infty} g(\boldsymbol{\omega}) \cos(\boldsymbol{\omega} \mathbf{t}) \mathrm{d}\boldsymbol{\omega}. \tag{31}$$

Making use of the fluctuation-dissipation theorem Eq. (20), it follows from (30) and (31) that

$$g(\omega) = \beta \omega \coth(\beta \omega) f(\omega). \qquad (32)$$

On integrating both sides of Eq. (30) with respect to 't', 't' going from  $0 \text{ to} \infty$ , it is easy to show that

$$\int_{0}^{\infty} \mathbf{f}(\boldsymbol{\omega}) \mathrm{d}\boldsymbol{\omega} = 1. \tag{33}$$

The expression for  $\gamma_1^{i}(t)$ , on using (30) and (31) becomes

$$\gamma'_{1}(t) = \frac{\hbar}{2M} \int_{0}^{\infty} \frac{f(\omega)}{\omega} \left\{ \coth(\beta \omega) [1 - \cos \omega t] - i \sin \omega t \right\} d\omega.$$
(34)

If we compare the above expression with the corresponding expression for a harmonic solid it is seen that the two expressions are identical except that in each case the meaning of  $f(\omega)$  is different. In the case of a solid  $f(\omega)$  is the frequency distribution of the normal modes; whereas in the case of a liquid it is the frequency distribution of the velocity auto-correlation function. In a harmonic solid the two are identical. It must be emphasized that the particular form of  $\gamma_1$  (t) given by (34) is not a consequence of the harmonic nature of the motion but is a result of the fluctuation-dissipation theoreom.

The corresponding expression for  $\rho$  (t) is

$$\rho(t) = \frac{\hbar}{2M} \int_{0}^{\infty} f(\omega) \tanh\left(\frac{\beta\omega}{2}\right) d\omega + \frac{\hbar}{2M} \int_{0}^{\infty} \frac{f(\omega)}{\omega \sinh(\beta\omega)} [1 - \cos \omega t] d\omega.$$
(35)

The above form of  $\rho$  (t) (in their notation W(t)) has also been derived by EGELSTAFF and SCHOFIELD [16].

The inverse transforms using (30) and (31) are

$$\mathbf{f}(\boldsymbol{\omega}) = \frac{4\,\mathrm{M}}{3\,\pi\hbar} \cdot \frac{1}{\omega} \int_{0}^{\infty} \mathrm{Im} \langle \underline{\mathbf{v}}(0), \underline{\mathbf{v}}(t) \rangle_{\mathrm{T}} \sin \omega t \,\mathrm{dt}, \qquad (36a)$$

and

$$f(\omega) = \frac{4M}{3\pi\hbar} \frac{\tanh(\beta\omega)}{\omega} \int_{0}^{\infty} \operatorname{Re} \langle \underline{v}(0), \underline{v}(t) \rangle_{T} \cos \omega t \, dt, \qquad (36b)$$

where in (36b) use has been made of relation (32). Therefore

$$f(0) = \frac{2M}{3\pi k_{B}T} \int_{0}^{\infty} Re \langle \underline{v}(0) . \underline{v}(t) \rangle_{T} dt$$

 $\mathbf{or}$ 

$$f(0) = \frac{2 MD}{\pi k_B T},$$

(37)

since

$$D = 1/3 \int_{0}^{\infty} \operatorname{Re} \langle \underline{v}(0), \underline{v}(t) \rangle_{T} dt.$$

If we assume that  $\langle \underline{v}(0), \underline{v}(t) \rangle_T$  decreases rapidly enough for  $t \to \infty$ , then it follows from (36b) that  $f(\omega)$  can be expanded in powers of  $\omega^2$ .

$$\mathbf{f}(\boldsymbol{\omega}) = \frac{2\mathrm{MD}}{\pi \mathrm{k_B} \mathrm{T}} + \mathrm{C}_2 \,\boldsymbol{\omega}^2 + \mathrm{C}_4 \,\boldsymbol{\omega}^4 + \dots \qquad (38)$$

where

$$\mathbf{C}_{2n} = \frac{2\mathbf{M}}{3\pi\mathbf{k}_{\mathsf{B}}T} \frac{(-1)^{n}}{(2n)} \int_{0}^{\infty} \operatorname{Re} \left\langle \underline{\mathbf{v}}(\mathbf{0}), \underline{\mathbf{v}}(\mathbf{t}) \right\rangle_{T} t^{2n} \mathrm{d}t.$$
(39)

The function  $f(\omega)$  starts with a constant value f(0) given by (37) and goes as  $\omega^2$  for small  $\omega$ . The curvature at the origin is determined by the value  $C_2$ .  $f(\omega)$  is real and positive. Assuming that  $\langle \underline{v}(0), \underline{v}(t) \rangle_T$  has time derivatives which are continuous everywhere and tend to zero for  $t \to \pm \infty$ , it then follows from (36) that  $f(\omega)$  decreases more rapidly than any power of  $1/\omega$  for  $\omega \to \infty$ .

It would obviously be very desirable to know  $f(\omega)$  for a liquid from the experimentally determined scattering function  $S(\kappa, \omega)$ .

Now

$$S_{inc} (\kappa, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \cdot \exp\left\{-\kappa^2 \gamma_1'(t) + o(\kappa^4)\right\} dt.$$
(40)

Integrating the Root Mean Square of (40) twice and remembering that the integrand tends to sero for  $t \to \pm \infty$ , we have [6]

$$\mathbf{S}(\underline{\kappa},\omega) = \frac{1}{2\pi} \frac{\kappa^2}{\omega^2} \int_{-\infty}^{+\infty} \left\{ \dot{\gamma}_1'(\mathbf{t}) + \kappa^2 (\dot{\gamma}_1'(\mathbf{t}))^2 \right\} e^{-i\omega \mathbf{t} - \kappa^2 \gamma_1(\mathbf{t})} + o(\kappa^4).$$
(41)

In the limit of small momentum transfer (41) becomes

$$\omega^{2} S(\underline{\kappa}, \omega) / \kappa^{2} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \gamma_{1}^{*} (t) e^{-i\omega t} dt$$
$$= \frac{1}{2\pi} \frac{1}{3} \int_{-\infty}^{+\infty} \langle \underline{v}(0), \underline{v}(t) \rangle_{T} e^{-i\omega t} dt \quad (\text{from 14a})$$

$$= \hbar/4M \,\omega f(\omega) \left[1 + \coth \beta \omega\right], \qquad (42)$$

## using (36a) and (36b).

On comparing the above expression with that of EGELSTAFF and SCHOFIELD [6] one finds that our  $f(\omega)$  is identical with their  $\rho(\omega)$ . In a purely incoherent case  $f(\omega)$  can be obtained by extrapolation from measurements of  $S(\kappa, \omega)$  for small values of  $\kappa$ . Such a procedure has been adopted by Egelstaff and his co-workers.

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The actual form of  $f(\omega)$  depends on the nature of the motion in a scattering system. For example, if in a liquid we assume the motion of the atoms to be governed by the Langevin equation,  $f(\omega)$  has then a Lorentzian shape with a width  $k_BT/MD$ . In the case of a harmonic solid  $f(\omega) \sim \omega^2$  with a sharp cut off at  $\omega = \omega_D$ . If a liquid could be characterized for large values of  $\omega$  as a disordered solid and for small values of  $\omega$  as a system obeying Langevin's equation, we should expect  $f(\omega)$  for a liquid to be intermediate between these two extremes. That is to say  $f(\omega)$  would start at  $\omega = 0$  with a value f(0) and vary as  $\omega^2$  for small values of  $\omega$ . It might have a minimum for a certain value of  $\omega$  and would then increase reaching a certain maximum beyond which it would smoothly decrease and tend to zero.

In the case of a stochastic model [7] of a liquid given by the authors, the function  $f(\omega)$  has been computed for water at 300°K for values of the parameters occurring in the model which give the best fit with the scattering data of LARSSON and DAHLBORG [8]. We get a maximum in  $f(\omega)$  for an  $\omega$ -value corresponding to 75°K. Larsson and Dahlborg have attempted to extract an  $f(\omega)$  from their scattering data and they do find a maximum at the said value of  $\omega$ . We know from our computations that an incident spectrum corresponding to beryllium-filtered neutrons, as a result of integration over it, gives a broad maximum in the scattered spectrum in approximately the same  $\omega$ -region. Such a maximum does not occur with an incident monochromatic beam. And, hence, any agreement between our calculated  $f(\omega)$ and that of Larsson and Dahlborg could be fortuitous if the latter in their calculation did not take into consideration the shape of the incident spectrum.

It should be clearly understood that we have here been discussing a frequency spectrum which corresponds to the hindered translatory motions only of the water molecules. In reality the motion is much more complex involving hindered rotations and vibrations of the molecule, which would also show up as broad peaks in  $f(\omega)$ . It would be difficult in practice to separate unambiguously the  $f(\omega)$  for hindered translations from a complete  $f(\omega)$ .

In the case of liquid lead [7] the stochastic model gives a maximum in  $f(\omega)$  for  $\omega$  corresponding to 80°K. The parameters chosen in this case were those which gave the best fit with the experimental results of BROCKHOUSE and POPE [9] and of TURBERFIELD [10]. Recently COTTER et al. [11] have reported a peak at an energy gain of approximately 7.5 × 10<sup>-3</sup> eV in the scattered spectrum in liquid lead for beryllium filtered neutrons scattering at 90°.

As remarked ealier the integration over the incident spectrum can give rise to a broad maximum, thus making an interpretation of the maximum reported by Cotter et al. rather difficult.

## ACKNOWLEDGEMENTS

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#### DISCUSSION

B.N. BROCKHOUSE: I think the diagram you drew in your oral presentation is misleading for the case of jump-diffusion, representing non-Gaussian behaviour, since you are averaging over all the atoms in the liquid. In this case your diagram does not therefore cover all the physical facts.

K.S. SINGWI: When I drew the curve flat I didn't mean that it is really flat; but the change that has occurred in the mean square displacement in this short time is very small compared with the chango that has really occurred. So in any case it is not going to make any difference to the scattering except that it will give you comparatively larger broadening in one case than in the other. I don't know how the Gaussian and the non-Gaussian question came in, but you can have an entirely Gaussian plot of  $\rho(t)$ . Actually I worked solely in the Gaussian approximation and  $\rho(t)$  in our paper is based purely on the Gaussian approximation. Now another thing, with Dr. Brockhouse's conception of simple diffusion, in the case where C is positive instead of negative he will have to make the Fourier transformation and then he will get a very funny sort of  $S(Q, \omega)$ , in the shape of a fairly broad quasi-elastic line.

P. SCHOFIELD: The <u>intercept</u> C given by Dr. Singwi does not determine the variation of the width of the quasi-elastic peak with  $Q^2$ . The determining feature here is how  $\rho(t)$  approaches its asymptotic linear behaviour. However, in the theory of Rahman, Singwi and Sjölander, this is related to C. In fact, one can show that

$$C \sim \int_{0}^{\infty} t < v(0) \cdot v(t) > dt \sim \int_{0}^{\infty} \frac{1}{\omega} \frac{\partial f(\omega)}{\partial \omega} d\omega$$

i.e. it covers the whole range of  $\omega$ , and hence is related to the overall intensity of the peak. The half-width on the other hand is determined by the very-low-frequency part of  $f(\omega)$ .

K.S. SINGWI: I agree with you. In fact it is possible to show that the main contribution to C comes from small values of  $\omega$  and that  $\Delta \times a$ , where  $\Delta$  is the width of  $f(\omega)$  for small  $\omega$  and a is the curvature of  $f(\omega)$  for  $\omega = 0$ .

A. SJÖLANDER: There are two basic considerations I would like to stress. The first is whether  $G_s$  (<u>r</u>, t) is very near to a Gaussian function or not. If it is Gaussian, this will probably have an important effect as to the type of stochastic motions we have in the liquid. I don't think enough experimental evidence is available as yet to determine this. The second question concerns the frequency function introduced by Egelstaff, which

showed a diffusive as well as a vibrating part. If a deep dip occurs in between, this should indicate that two types of motion are going on simultaneously without essentially interfering dynamically. I doubt whether it is settled that such a deep dip really exists.

K.S. SINGWI: The expansion in  $K^2$ , discussed in my paper, is of practical utility provided terms containing  $K^4$  and higher powers of  $K^2$  are small. I understand from the recent experimental work of Brockhouse and Pope that the  $K^4$  term is only a few per cent and hence the non-Gaussian correction is small. As regards your second question I have the feeling that the two types of motion are not quite independent and this would lead to the filling-up of the valley in  $f(\omega)$ .

B.N. BROCKHOUSE: Yes, the non-Gaussian component should not be more than 10%.

P. SCHOFIELD: And is this also on a time scale that is long compared with the case of platinum?

B.N. BROCKHOUSE: Well, I don't think it is relevant as far as the upper limit is concerned because the jump diffusion only has to occur to a very small amount to contribute. The frequency need only be very small and so the amount of the other component that grows in can be very small and it is very difficult to see it.

# STUDIES OF LIQUID SODIUM BY INELASTIC SCATTERING OF SLOW NEUTRONS

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#### Abstract — Résumé — Аннотация — Resumen

ST UDIES OF LIQUID SODIUM BY INELASTIC SCATTERING OF SLOW NEUTRONS: The scattering 4.1Å neutrons by liquid sodium at 108°C, 153°C and 198°C has been compared with scattering from solid sodium (80°C) at six scatter angles between 20° and 90°. Sodium provides a simple monatomic liquid with coherent and incoherent scattering cross-section 1.55 and 1.85 b respectively. Due to the range of momentum transfers covered it is possible to distinguish and discuss coherent and incoherent effects separately. Three interesting features of the scattered spectra are evident:

(a) The near elastic scattering is largely incoherent and in the liquid state show broadening by diffusive motion less than that expected from a simple (Fick's Law) model. Comparison with estimates from alternative interpretations by Egelstaff and Schofield and by Rahman, Singwi and Sjölander are presented.

(b) The wide spreading sprectrum for solid and liquid are similar.

(c) At high scatter angles coherent effects appear near the elastic peak and a direct test of Vineyard's "convolution" approximation is made.

ÉTUDE DU SODIUM LIQUIDE PAR LA DIFFUSION INÉLASTIQUE DE NEUTRONS LENTS. L'auteur a comparé la diffusion de neutrons de 4,1Å de longueur d'onde par du sodium liquide aux températures de 108, 153 et 198°C, à la diffusion dans du sodium solide (80°C) pour six angles de diffusion compris entre 20 et 90°. Le sodium fournit un liquide monoatomique simple ayant des sections efficaces de diffusion cohérente et incohérente de 1,55 et de 1,85 b respectivement. Etant donné la gamme d'impulsions considérée, il est possible de distinguer les effets cohérents et incohérents et de les examiner séparément. Les spectres de diffusion présentent trois caractéristiques intéressantes;

a) La diffusion quasi-élastique est dans une large mesure incohéreme et accuse, à l'état liquide, moins d'élargissement dû au mouvement de diffusion qu'un modèle simple ne le laissait prévoir (loi de Fick). L'auteur compare ses observations aux estimations découlant d'autres interprétations données par Egelstaff et Schofield et par Rahman, Singwi et Sjölander.

b) Le spectre de dispersion large est semblable pour l'état solide et l'état liquide.

c) Pour les angles de diffusion ouverts il apparaît des effets de cohérence au voisinage des pics élastiques; l'auteur essaie de vérifier directement l'approximation de "convolution" de Vineyard.

ИССЛЕДОВАНИЕ ЖИДКОГО НАТРИЯ МЕТОДОМ НЕУПРУТОГО РАССЕЯНИЯ МЕДЛЕННЫХ НЕЙТРОНОВ. Рассеяние нейтронов с длиной волны, равной 4,1 Å в жидком натрии при температурах 108, 153 и 198°С было сравнено с рассеянием в твердом натрии (при 80°С) для нести углов рассеяния, летацих между 20 и 90°. Натрий дает простур моноатомнур жидкость с когерентным и некогерентным поперечными сечениями рассеяния соответственно 1,55 и 1,85 барнов. Благодаря рассмотренному диапазону переноса моментов представляется возможным опознать и обсудить раздельно когерентные и некогерентные воздействия. Выявляются три интересные особенности спектров рассеяния:

а) Почти упругое рассеяние является в значительной мере некогерентным и в жидком состоянии обнаруживает благодаря диффундирующему движению меньшее расширение, чем этого можно было бы ожидать для простой модели (закон Фикка). Дается сравнение результатов в свете предполо-

жений, сделанных Энгельстаффом и Шофильдом, а также Рахманом, Сингви и Сьеландером.

- б) Широко распространенные спекторы для твердого и жидкого состояния аналогичны.
- в) При более значительных углах расседния когерентные воздействия наблодаются вблизи упругого пика; произведена непосредственная проверка приближения по методу Вайнярда.

ESTUDIO DEL SODIO LÍQUIDO POR DISPERSIÓN INELÁSTICA DE NEUTRONES LENTOS. El autor compara la dispersión de neutrones de 4,1Å por sodio líquido a 108°C, 153°C y 198°C, con la dispersión por sodio sólido (a 80°C) en seis ángulos comprendidos entre 20 y 90°. El sodio constituye un líquido monoatómico simple cuyas secciones eficaces de dispersión coherente e incoherente se elevan a 1,55 y 1,85 b, respectivamente. Debido a la gama de transferencias de cantidad de movimiento observada, es posible distinguir los efectos coherentes e incoherentes y estudiarlos separadamente. Cabe señalar tres particularidades interesantes de los espectros de dispersión:

1. La dispersión cuasi elástica es en gran parte incoherente y en el estado líquido presenta un ensanchamiento por movimiento de difusión menor que el que cabe esperar de un modelo sencillo (Ley de Fick). El autor hace una comparación con los cálculos realizados basándose en otras interpretaciones de Egelstaff y Schofield y de Rahman, Singwi y Sjölander.

2. Los espectros, considerablemente ensanchados, son análogos para el estado sólido y para el estado líquido.

3. Para ángulos de dispersión grandes, se observan efectos coherentes en las proximidades del pico elástico; el autor efectúa una comprobación directa del método de aproximación de Vineyard por "circonvolución".

#### INTRODUCTION

The ideal liquid for studying the diffusive motion of atoms by slow neutron scattering would have incoherent scattering properties and the scattering atoms would be in a simple (chemically-unbound)state. Such a liquid is not readily available; liquid vanadium would fulfil these conditions but is a very troublesome subject for experiment. Liquid sodium has therefore been chosen for experiment as a monatomic liquid with a high ratio of incoherent to coherent cross-sections (1.85 and 1.55 b respectively). Further, neutron absorption is low ( $\sigma_a = 0.5$  b at 2200 m/s) and the macroscopic diffusion coefficient and the static structure factor from X-ray measurements are known.

A principle object of the present work was the study of the near elastic peak to provide data on diffusive motion in the liquid state. The liquid has therefore been studied at three temperatures 108°C, 153°C and 198°C where the values of the diffusion coefficient are 4.4, 6.3,  $8.3 \times 10^{-5}$  cm<sup>2</sup>/s [1] respectively.

The use of slow neutrons (wavelengths  $4.0\text{\AA}$  and  $4.5\text{\AA}$ ) enables the region of small momentum transfer to be studied and in this region the coherent effects can be, to some extent, separated from the near elastic peak. However, in order to gain more detailed information on the coherent effects in the liquid state, similar comparative measurements were made on the solid and liquid states of a metal with predominantly coherent scattering. Tin was chosen for this purpose and the results on it are reported in the following paper by COCKING ("Comparative studies of slow neutron scattering by solid and liquid tin<sup>1</sup>). Data over the wider scattered energy spectrum has been obtained and a comparison of this spectrum for the solid and liquid will be made.

At the highest scatter angles used in this work the near elastic peak is markedly affected by coherent scattering effects and here a test of VINEYARD convolution approximation [2] has been made.

#### EXPERIMENTAL METHOD

The sodium sample (99.99% pure) was contained in a 0.010-in wall stainless steel cylinder 1.5-in diam.by 3-in long in an atmosphere of helium. For safety this cylinder was in turn sealed in a helium filled cylinder also with 0.010 in stainless steel walls. Small heaters mounted at the ends maintained the sample at the required temperature within 1°C. Measurements were made with the sample at roomtemperature and at 80°, 108°, 153°C, using 4.0Å incident neutrons and 198°C using 4.5Å incident neutrons. The measurements at 80° and 108° were made to examine the solid and liquid states within a small temperature difference from the melting point, 97.5°C.

This sample was supported in an evacuated enclosure in the neutron beam so that the beam crossed parallel to a diameter of the cylinder. An identical empty container maintained at the sample temperature was used to measure the scattering from the container. The sample absorbed  $\sim 6\%$ of the incident neutrons and scattered  $\sim 10\%$  as solid and  $\sim 16\%$  as liquid.

The incident neutron selector and time-of-flight apparatus used is described in the paper by HARRIS <u>et al</u>. ("A cold neutron monochromator and scattering apparatus"). The velocity spectrum of the neutrons scattered by the specimen as solid and liquid were measured at scatter angles of 20°,  $30^{\circ}$ ,  $45^{\circ}$ ,  $60^{\circ}$ ,  $75^{\circ}$  and  $90^{\circ}$ .

Unfortunately the liquid hydrogen loop which gives a large increase in slow neutron flux was not operating at the time of this work so that the statistical accuracy of these measurements (shown by the scatterer of the points in Fig. 1) is not high. For the same reason measurements at a longer wavelength than 4.5Å were not practicable.

#### RESULTS

In Fig. 1 the scattered spectra from the solid  $(80^{\circ}C)$  and the liquid  $(108^{\circ}C)$  are shown plotted as corrected counts per time channel versus time-of-flight. The ordinates ("corrected counts") are the experimental counts per time channel after correction for counter background and scatter by the container; small factors to correct for the different efficiencies of the six detector arrays are included and the calculated efficiency variation with energy of the detectors has been allowed for. Finally the incident beam monitor reading is used to give the results for solid and liquid normalized to the same number of incident neutrons.

Similar results taken at 155°C and 198°C are not shown in full here. They are used in detail in analysis of the diffusion broadening of the near elastic peaks, and at larger energy transfers they confirm conclusions drawn from the data of Fig. 1.

Several effects are apparent in Fig. 1, viz:

- (a) The similarity of the broad energy spectrum for solid and liquid at energy transfers greater than about 4 meV;
- (b) The broadening of the near elastic scattering for the liquid over the elastic peaks in the solid;
- (c) As the two highest scatter angles used, the shape and intensity of the near elastic peaks in the liquid are markedly affected by coherent effects. These three effects are discussed separately.

#### BROAD ENERGY SPECTRUM FOR THE SOLID

First we discuss the coherent effects expected in the inelastic spectrum for the solid. As shown (from EGELSTAFF'S [3] theory) in the following





Detected counts per time channel corrected for instrumental effects (see text) versus time-of-flight. Results for solid and liquid sodium normalized for equal numbers of incident neutrons. Vertical lines give the results of calculations of spectra using a frequency distribution of BHATIA [5]. Vertical arrows marked Q + q and Q - q are explained in the text.

paper by COCKING the coherent scattering appears for the polycrystalline solid with a rather sharp step at an energy transfer given by  $Q + q = 2\pi\tau$ (hQ is the momentum transferred to the neutron, 'q' is the wave number of the phonon excited and  $\tau = 1/d$  where 'd' is the crystal plane spacing). 'q' can be calculated using the approximation  $q = c\omega$  where 'c' is the velocity of sound in the solid and  $\hbar\omega$  is the energy transfer to the neutron. The coherent scattering extends from  $Q + q = 2\pi\tau$  and the intensity which is maximum at the position  $Q + q = 2\pi\tau$  falls with decreasing scatter angle. The region  $Q + q = 2\pi\tau$  to  $Q - q = 2\pi\tau$  is marked for the three higher angles in Fig.1, for the plane in sodium having the highest spacing [the (011) plane].

In comparison with the distinct steps observed for tin (see following paper by COCKING) the steps in sodium are expected to be small since the coherent cross-section is relatively small and for tin two planes with almost coincident spacings contribute to the cross-section.

If Fig. 1 the highest angle detector ( $\theta = 90^{\circ}$ ) shows a rise in cross-section in the region expected and for  $\theta = 75^{\circ}$  a small edge at the position where  $Q + q = 2\pi\tau$ . In other detectors no coherent effect can be distinguished.

Other planes in sodium can be shown to contribute to the scattering less than the plane discussed.

The incoherent part of the inelastic spectrum can be calculated using the method of EGELSTAFF and SCHOFIELD [4] if a frequency distribution of vibrational modes is known. The vertical lines on Fig. 1 give the results of such a calculation where the frequency distribution calculated by BHATIA [5] for sodium has been used. The normalization to the experimental results has a possible error of  $\pm$  40%. The points on the calculated spectra are within  $\pm$  15% of the experimental values except in the region near energy transfers of 2 meV where the calculated spectra are 50% too high.Better agreement is obtained using a frequency distribution calculated by JOSHI [12] but calculations using this data are not yet complete.

#### BROAD ENERGY SPECTRUM FOR THE LIQUID

As already discussed, coherent effects are small compared with the incoherent scattering. Thus for the present, we disregard small differences between the interference effects in the solid and liquid for energy transfers greater than  $\sim 4$  meV. The marked similarity of the spectra from the solid and liquid then suggests that similar motions of the atoms in the two phases exists in this energy region. This idea is consistent with the small change in specific heat on melting. Further the small change in density on melting ( $\sim 2\%$ ) suggests that the interatomic forces are not markedly different in the two phases.

The results on tin suggest that while the high energy part of the scattered spectra arising from coherent scattering are similar for solid and liquid, the liquid actually gives increased scattering in the low energy region. This conclusion is confirmed in the results of Fig. 1 where the liquid shows slightly higher total counts.

#### ELASTIC SCATTERING FROM THE SOLID

Coherent elastic scattering by the sodium sample falls outside the angular range of the present detectors. The elastic peaks for the solid therefore arise from incoherent elastic scattering and small contributions from the inelastic spectrum. The inelastic spectrum is calculated using the Bhatia frequency distribution and is subtracted from the experimental results. (This contribution is marked in Fig. 1).

The remaining elastic peaks fall in amplitude as the scatter angle increases, by the Debye-Waller factor. The observed peak heights are consistent (within 4%) with the Debye-Waller factor calculated from the Bhatia spectrum. The shape of the elastic peaks is taken as a measure of the resolution of the apparatus.

#### QUASI-ELASTIC SCATTERING FROM THE LIQUID

Several theoretical models [4, 6, 7] have been suggested for calculation of the broadening of the near elastic peak due to diffusive motion of the atoms in a liquid. These calculations are first made ignoring the interference effects which arise with coherent scatterers. VINEYARD [2] has suggested an approximation in which the interference term is expressed as a product of the cross-section calculated assuming incoherent scattering and the static structure factor.

In Fig. 2 the static structure factor for liquid sodium at 110°C is shown. This curve has been derived from recent X-ray scattering measurements by ORTON and WILLIAMS [8] who give results covering the whole temperature range of the present work. The values of momentum transfer for elastic scattering at the six scatter angles used are also marked on Fig. 2. It



Fig.2

Static structure factor calculated from X-ray scattering measurements [8].

is clear that while marked coherent elastic scattering is expected for the two higher angle detectors as observed, the lower angle detectors will have small coherent elastic contributions in comparison with the incoherent elastic scattering. The analysis of the four lower angle detectors is considered first. The broadening of the near elastic peaks has been predicted by the two theoretical models and has been calculated for the present experimental conditions and folded with the experimental resolution function. These calculations have been compared with the observed results.

Calculations using the broadening predicted by Fick's Law for diffusive motion[2] gave a greater broadening than those observed. This is in agreement with the results of measurements reported on other liquids [9, 10]. Calculations have therefore been made using the theory of EGELSTAFF and SCHOFIELD [4]. In the expression given by these authors a parameter 'c' is introduced, in addition to the diffusion coefficient. A full discussion of the interpretation of the parameter c is given in these authors' paper, and by EGELSTAFF [11]. A single value at each temperature for the parameter 'c' has here been chosen which gives the best fit to the experimental data at all scatter angles. Results taken with the sample at 155°C are compared with the predictions using c =  $1.3 \times 10^{-12}$  s in Fig. 3. Similar comparisons are made for the other sample temperatures, the agreement between calculated and observed data being comparable to that shown in Fig. 3. (Note: the high intensity on the energy loss side for  $\theta = 45^{\circ}$  is found at the two higher temperatures used and is unexplained.)



Fig.3

Experimental data on quasi-elastic peaks (points) compared with calculations using theory of EGELSTAFF and SCHOFFELD [4] (full lines).

The choice of the correct 'base' level for the 'quasi-elastic' peak is always a difficulty in interpreting measurements such as these. Since the 'bound' contributions from the incoherent scattering and the coherent scattering (see the results on tin) both give a small and continuous spectrum across the elastic region, the base levels (shown in Fig. 3) have been chosen in the wings of the quasi-elastic peak. This particular choice gives the greatest uncertainty in making a comparison between theory and experiment.

The values of the parameter 'c' which gives the best fit to the experimental data at the three temperatures are given in Table I. (The present values are lower than the values derived by EGELSTAFF [11] from preliminary data by the present author. The trend of increasing values of 'c' with increasing temperature is the same for both data.)

Also tabulated are the values of the parameter corresponding to the parameter c for the models of 'free diffusion' and for 'jump diffusion' as calculated by Egelstaff. The trend with increasing temperature is more reliable for the calculated values than their absolute values. It is clear that the experimental values for 'c' tend to increase with increasing temperature favouring the idea of the dominance of 'free diffusion' in liquid sodium at these temperatures.

In Figs 4(a) to (d) results are shown for four detectors at the higher scatter angles with the peak calculated for incoherent scattering, using the parameters which gave the best fits for the lower angle peaks (dashed line).



Fig.4

Experimental data on quasi-elastic peaks (points) compared with calculations using theory of EGALSTAFF and SCHOFIELD [4] (broken lines) and including interference effects using "convolution approximation" [2] (full lines).

The incoherent scoherent scattering (full lines) is calculated using Vineyard's approximation. The incoherent scattering used is that shown (full lines), the static structure factor is taken from the X-ray data [8]. The arrows give

(,							
Temperature	'c'(exptl data)	au (jump diffusion)	'c'(free diffusion)				
108°C	1.0 ± 0.4	3, 6	1. 9				
153°C	1.3 ± 0.4	2, 9	2, 5				
198°C	1.6 ± 0.5	2.2	3. 1				

# TABLE I CALCULATED AND EXPERIMENTAL PARAMETERS (in units of 10<sup>-12</sup> s)

the position of the main peak in the static structure factor, here referred to as  $[1+\gamma(Q)]_{max}$ , where the major coherent effects are expected in the convolution approximation. The agreement with the experimental data is within the expected uncertainty in 4(b) and 4(d) where  $[1+\gamma(Q)]_{max}$  falls within 1 meV of the elastic position. The agreement becomes less satisfactory when  $[1+\gamma(Q)]_{max}$  occurs at higher energy transfer.

#### CÓNCLUSIONS

Spectra of neutrons scattered by the solid and liquid states of sodium have been compared. In the spectra at energy transfers greater than~4 meV, incoherent scattering dominates. For the solid, this region of the spectrum may be calculated within the present experimental error using the frequency distribution given by BHATIA [5]. The corresponding spectrum for the liquid is similar to that for the solid suggesting that the frequency distribution of motions of the atoms in the two phases are similar for times less than ~1.5  $\times$  10<sup>-13</sup> s.

Due to the range of momentum transfer used, coherent effects are unimportant for near elastic scattering at the lower scatter angles. Here the experimental quasi-elastic peaks have been compared with predictions of the theory of Egelstaff and Schofield and values for the parameter 'c', the interaction time, at three temperatures have been derived. The trend of 'c' increasing with increasing temperature suggests the dominance of 'free diffusion' in the liquid.

At the highest scatter angles, where coherent effects appear in the quasi-elastic scattering, a test of Vineyard convolution approximation is made. It is shown that the approximation gives agreement with the observed data when the coherent effects appear at small energy transfers.

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# COMPARATIVE STUDIES OF SLOW NEUTRON SCATTERING BY SOLID AND LIQUID TIN

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#### Abstract — Résumé — Аннотация — Resumen

COMPARATIVE STUDIES OF SLOW NEUTRON SCATTERING BY SOLID AND LIQUID TIN. The scattering of 4.0Å and 6.2Å neutrons by tin as solid (210°C) and liquid (240 C) has been measured. The scattered spectra at six scatter angles between  $20^{\circ}$  and  $90^{\circ}$  was analysed by time-of-flight methods.

At the longer wavelength the low intensity elastic scattered peaks are used to derive the incoherent crosssection for tin  $(0.04 \pm 0.01 b)$ .

Sharp steps in scattered spectra for the solid can be identified and similar but broadened steps for the liquid are seen. Using a theory due to Egelstaff, the steps for the solid can be interpreted as the excitation of particular phonons. The single phonon theory for the solid is modified to attempt to account for the different behaviour of the liquid. The appreciable scattering observed in the liquid at low energy transfers is not explained in this way.

ET UDE COMPARÉE DE LA DIFFUSION DE NEUTRONS LENTS PAR DE L'ÉTAIN SOLIDE ET DE L'ÉTAIN LIQUIDE. Les auteurs ont mesuré la diffusion de neutrons de 4,0Å et de 6,2Å de longeur de'onde dans de l'étain à l'état solide (210°C) et de l'étain à l'état liquide (240°C). Ils ont analysé par des méthodes du temps de vol les spectres de diffusion pour six angles de diffusion compris entre 20° et 90°.

Pour la plus grande longueur d'onde, ils ont utilizé les pics de diffusion élastique à faible intensité pour déterminer la section efficace incohérente dans l'étain  $(0,04\pm0,01b)$ .

On peut observer des paliers étroits dans les spectres de diffusion pour l'état solide et des paliers analogues mais plus larges pour l'état liquide. D'après une théorie établie par Egelstaff, on peut interpréter les paliers pour l'état solide comme étant dus à l'excitation de phonons particuliers. La théorie du phonon simple pour l'état solide a été modifiée pour essayer d'expliquer le comportement différent de l'état liquide. La diffusion appréciable observée dans l'état liquide pour de faibles transferts d'énergie ne s'explique pas pour autant.

СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ РАССЕЯНИЯ МЕДЛЕННЫХ НЕЙТРОНОВ ТВЕРДЫМ И ЖИДКИМ ОЛОВОМ. Было измерено рассеяние нейтронов с длиной волны, соответствующей 4,0 и 6,2 Å, оловом в твердом (210°С) и жидком (240°С) состояниях. Были проанализированы по методу времени пролета спектры рассеяния при шести углах рассеяния между 20 и 90°.

При более значительных длинах волн пики упругого рассеяния низкой интенсивности были использованы для того, чтобы вывести некогерентное поперечное сечение для одова (0,04 ± 0,01 баря).

Опознаваемы резкие когерентные пики для твердого состояния, аналогичные, но расширенные пики, видны для жидкого состояния. На основании теории Эгельстаффа эти пики для твердого состояния могут быть охарактеризованы как возбуждение особых фононов. Изменяется единая теория фононов для твердого состояния с целью дать объяснение различным поведениям жидкости. Этим путем не объясняется заметное рассеяние, наблюдаемое в жидком состояния при переносах малых энергий.

ESTUDIO COMPARATIVO DE LA DISPERSIÓN DE NEUTRONES LENTOS POR ESTAÑO SÓLIDO Y LÍQUIDO. Los autores han medido la dispersión de neutrones de 4,0Å y 6,2Å por estaño sólido (210°C) y líquido (240°C). Han analizado, por el método del tiempo de vuelo. los espectros de dispersión en seis ángulos distintos, comprendidos entre 20° y 90°.

En el caso de la longitud de onda más elevada, utilizan los picos de dispersión elástica de baja intensidad para deducir la sección eficaz incoherente del estaño  $(0,04 \pm 0,01 b)$ .

<sup>\*</sup> Attached from Turkish Atomic Energy.

En el estano sólido es posible identificar saltos acusados, en tanto que en el estaño líquido se observan saltos análogos, pero de base más ancha. Aplicando una teoría debida a Egelstaff, es posible atribuir lossaltos correspondientes al estaño sólido a la excitación de determinados fonones. Para poder aclarar el comportamiento diferente del estaño líquido, los autores modifican la teoría del fonón único correspondiente al sólido. Sin embargo, queda sin explicar la considerable dispersión observada en el estaño líquido en el caso de transferencias de baja energía.

#### 1. INTRODUCTION

Several studies of liquids using the technique of slow neutron scattering have been reported, for example on water, lead and tin. Hydrogenous liquids have the advantage in interpretation that the scattering is largely incoherent but have the complication of the effect of chemical binding of the hydrogen in comparatively complex molecules. Metals, while providing in some cases a simple monatomic liquid, have usually a large coherent component in the scattering.

In this paper and in the previous paper by HARRIS ("Studies of liquid sodium by inelastic scattering of slow neutrons") the liquid states of tin and sodium have been studied using the scattering of cold neutrons ( $\geq 4$ Å wavelength) and have been compared with the results from the solid metals.

The first measurements were made on sodium for which the coherent and incoherent scattering cross-sections are 1.55 b and 1.85 b respectively. In interpreting the results with sodium it became clear that further understanding of the effect of the coherent scattering was needed. Similar studies on a liquid having predominantly coherent scattering were therefore undertaken, and for experimental convenience tin was chosen. One result of this work was a measurement of the incoherent cross-section of tin (viz. 0.04  $\pm$  0.01 b) so that the coherent cross-section comprises > 99% of the total cross-section (4.6 b).

At the long neutron wavelengths used, it will be shown that coherent elastic scattering is not possible at the angles of scatter used and because the incoherent cross-section is small for tin, elastic scattering is virtually absent.

The differential cross-section and average energy transfer for the scattering by metals has been compared, by EGELSTAFF [2, 5], with calculations based on simple models. Our more detailed measurements will be compared to the same models, and the liquid model will be shown to be inadequate at low energy transfers.

#### EXPERIMENTAL METHOD

The tin specimen was contained in a 0.010-in wall stainless steel cylinder of 1.5-in diam. by 3-in long. Small heaters mounted at the ends maintained the sample at 210°C or 240°C for the solid and liquid state studies respectively (tin melting point 232°C). This sample was supported in an evacuated enclosure in the neutron beam so that the beam crossed parallel to a diameter of the cylinder. An identical empty container, maintained at the sample temperature, was used to measure the background scattering.

The incident neutron selector and time-of-flight apparatus used is described in the paper by HARRIS et al. ("A cold neutron monochromator and scattering apparatus"). The velocity spectrum of both 4.0Å and 6.2Å neutrons scattered by the specimen as solid and liquid were measured at scatter angles of 20°, 30°, 45°, 60°, 75° and 90°.

The transmission of the sample was measured roughly at both wavelengths. At 4.0Å incident neutron wavelength the sample absorbs 14% of the incident neutrons and scatters 16% at 210°C (solid) changing sharply on melting to 32% at 240°C. With 6.2Å incident neutrons (greater than twice the largest plane spacing for solid tin) the change of transmission on melting is smaller - the sample absorbed 22% of the beam and scattered 10% as solid (210°C) and 13% as liquid (240°C).

## RESULTS

The results of these measurements are shown in Figs. 1 and 2. The ordinate ("corrected counts") are the experimental counts per time channel after correction for counter background and scatter by the container; small factors to correct for the different efficiencies of the six detector arrays are included and the calculated efficiency variation with energy of the detectors has been removed. Finally the incident beam monitor reading is used to give the results for solid and liquid normalized to the same number of incident neutrons.

In Fig.3 the static structure factor for liquid tin derived from recent X-ray measurements [1] is shown together with the diffraction lines for solid white tin (body-centred tetragonal structure). It is seen that for elastic scattering the values of momentum transfer lie below the region of the main peak in the structure factor. For this reason little elastic scattering is expected to be observed in either solid or liquid cases. From a comparison of the small elastic scattered intensity for the solid with that from a thin vanadium sample the incoherent cross-section 0.04  $\pm$  0.01 b for the tin was derived, taking the incoherent cross-section for vanadium to be 5.1 b. The discussion which follows will relate principally to the results taken with 6.2Å neutrons, because they are simpler to interpret and there may be appreciable multiple coherent scattering present in the results with the 4.0Å neutrons.

The scattering from the solid in all detectors extends to energy transfer of 25 meV corresponding to a temperature of 290°K (the Debye temperature for white tin is 190°K). At lower energy transfers the scattered spectra for the solid are marked by a sharp fall, the scattering being nearly zero below this "cut-off". The sharp "cut-offs" are explained in the next section; below the "cut-off", destructive interference makes coherent scattering negligible.

The spectra for the liquid show a broadly similar shape and spread to the solid but the sharp "cut-offs" are now broadened. An interesting and surprising result is the appreciable scattering at small energy transfers down to almost zero energy transfer. Since on melting the special order of the solid is destroyed, one is tempted to suggest that in the liquid the destructive interference is no longer complete and as a result incoherent scattering is seen. However, the appearance of incoherent scattering in the liquid should lead to a strong elastic peak and no increase in the elastic scattering is seen on melting.


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Incident neutrons - 2.1 meV, 6.25Å, 1584 µs/m.

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Static structure factor for liquid tin at 245°C.

In the following section a simplified calculation of the cross-section is presented. The cross-section is expressed as a product of two terms. The first term is the cross-section calculated from the "incoherent approximation" while the second term gives a structure factor for the coherent scattering. Presentation of the results as the structure factor allows the data on the solid to be understood and emphasises the marked difference in the results on the liquid.

## THE ONE-PHONON CROSS-SECTION FOR A POLYCRYSTAL

A simple theoretical treatment for inelastic scattering of slow neutrons by polycrystals was given in an early paper by EGELSTAFF [2]. Starting from the expression by WEINSTOCK [3] [Eqs (35) and (36)] for the coherent differential cross-section of a microcrystal for single phonon absorption, he performs an average over all orientations of Q and q with respect to  $2\pi\tau$ (definitions below). The resulting expression for the cross-section of the polycrystalline solid is

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E}, = \frac{\mathrm{\sigma}\mathrm{coh}}{4\pi}. \ \mathrm{I} \ \mathrm{Z} \tag{1}$$

where

$$I = (B/4M\pi^{2})(k'/k)e^{-2W}[(Q^{2}xq^{2})/\omega(1-x)](dq/d\omega)$$
(2)

and

$$Z = \sum_{\sigma} (\pi F_{\tau} / 2B\tau 2q)$$

B is the volume per nucleus in the crystal; M is the mass of the scattering nucleus; k' and k are the scattered and incident neutron wave numbers; hw and hq are the energy and momentum of the phonon;

 $x = \exp \{\hbar \omega / K_B T\};$ 

 $\mathbf{Q} = \mathbf{k'} - \mathbf{k};$ 

 $\overline{\tau}$  is the reciprocal lattice vector of a given plane;

 $\mathbf{F}_{\mathbf{r}}$  is the structure factor for the plane including the multiplicity. Equation (2) may be written as

I =  $(1/2m) (k'/k) e^{-2w} (Q^2/\omega) [x/(1-x)] \rho(\omega)$ 

where  $\rho(\omega)$  is the frequency distribution of normal modes. It may be shown [2] that  $(\sigma_{coh}/4\pi)I$  is the cross-section in the "incoherent approximation". Z may then be seen as a structure factor for coherent scattering from the polycrystal. When the summation is made over several planes the form factor approaches the value unity as expected.

It is therefore convenient in presenting our results to isolate the structure factor by dividing the observed cross-section by the cross-section calculated using the incoherent approximation. For the frequency distribution  $\rho(\omega)$  we have used the Debye approximation  $\rho(\omega) = 3\omega^2/\omega_D$  where  $\omega_D$  is the frequency corresponding to the Debye temperature. This approximation should be satisfactory for the low energy part of the spectrum, discussed later.

## DISCUSSION OF THE POLYCRYSTALLINE STRUCTURE FACTOR (Z)

The permissible range of Q for energy gain from a phonon is illustrated in Fig.4. The vectors Q, q and  $2\pi\tau$  must form a triangle to satisfy the con-



Fig.4

Construction to illustrate condition for single phonon coherent scattering.

dition  $\underline{Q} + \underline{q} = \underline{2\pi\tau}$ . It is clear therefore that the permissible range of Q is given by

$$\mathbf{Q} - \mathbf{q} < 2\pi\tau < \mathbf{Q} + \mathbf{q}$$

Using a fixed incident energy, each scattered energy gives for each scatter angle definite values for vector  $\underline{Q}$  and for  $\omega$  and therefore from the dispersion relation  $\omega = \omega(q)$  a single value for q for each branch of the dispersion relation. Thus at scattered energies below a certain value given by  $Q + q = 2\pi\tau$  coherent single phonon inelastic scattering is not possible. In addition the scattering falls again to zero at the upper limit  $Q-q = 2\pi\tau$ . This upper limit is usually beyond the limit of the spectra observed here, that is, beyond the upper limit of the frequency distribution,  $\rho(\omega)$ . A step in the structure factor occurs for each value of  $\tau$ . For tin the planes are sufficiently separated so that in the 6.2Å results only the two planes at  $2\pi\tau = 2.13$  and  $2.22\text{\AA}^{-1}$  need be considered



Fig.5

Polycrystalline structure factor for 90° scatter angle (incident energy - 2.1 meV).

In Fig. 5(a) the polycrystalline structure factor is shown for the first plane in solid tin  $(2\pi\tau = 2.13\text{\AA}^{-1})$  for scattering through 90° for 6.2Å incident neutrons. Only one of the two closely spaced planes in tin is shown for clarity of presentation.

In calculating q the assumption  $\omega = cq$  has been made, where c is the velocity of sound (c = 2470 m/s [4] has been used for both longitudinal and transverse modes.) The components due to longitudinal and transverse phonons (taken parallel and perpendicular to <u>q</u>, respectively) is also shown. It is clear that under these conditions the sharp rise in the cross-section at

 $Q + q = 2\pi\tau$  corresponds to longitudinal phonons. In Figs. 1 and 2 the position of the sharp rise predicted at  $Q + q = 2\pi\tau$  is marked with arrows for the first two planes of tin; the position of the fall at  $Q - q = 2\pi\tau$  is also marked where relevant.

The experimental shape for the polycrystalline structure factor is shown in Fig. 5(b). The agreement with the calculations of Fig. 5(a) is qualitatively correct but in unsatisfactory quantitatively.

In practice the longitudinal and transverse components should be calculated separately.

The contributions from longitudinal modes may be calculated by including in Eq.(1) the factor  $\cos^2 \theta_L$  where  $\theta$  is the angle between Q and q, i.e.

$$\cos \theta_{\rm L} = [(2\pi\tau)^2 - Q^2 - q_{\rm L}^2]/2Qq_{\rm L}$$

The contribution from transverse modes is obtained similarly using the factor  $(1 - \cos^2 \theta_T)$  where

$$\cos \theta_{T} = [(2\pi\tau)^{2} - Q^{2} - q_{T}]/2Qq_{T}$$

 $\boldsymbol{q}_L$  and  $\boldsymbol{q}_T$  are obtained using  $\boldsymbol{\omega}=\boldsymbol{c}_L \; \boldsymbol{q}_L$  or  $\boldsymbol{\omega}=\boldsymbol{c}_T \; \boldsymbol{q}_T$ . Calculations based on these results are given in Fig. 5(c) where the transverse sound velocity is less than the longitudinal velocity. A factor of 0.7 between the two has been used, which is the calculated ratio for the bulk solid. The effect of the lower transverse velocity is to increase and displace the transverse component to yield a sharply peaked curve similar to that found in the experimental results.

The difficulty of assigning the absolute scale for the experimental results (possible error of  $\pm$  45%), the uncertainty in the correct sound velocity to use and the assumptions made in deriving the theoretical expression make an exact comparison of experiment and calculation meaningless. However, the general features of the present results of the scattering by the polycrystal may be understood in terms of the usual formulations of neutron scattering by solids. We now test the possibility of modifying this theory to account for the results for the liquid.

#### STRUCTURE FACTOR FOR THE LIQUID

We follow the approach of EGELSTAFF'S "pseudo-phonon" model [5] in which the idea of "phonons" in the liquid is retained. The static structure factor of Fig.3 is then taken to be a continuous distribution of the value of  $2\pi\tau$ .

The polycrystalline structure factor  $\Sigma(\pi F_{\tau}/2B\tau Q_{g})$  then becomes

$$(1/2Qq) \int 2\pi\tau [d + \gamma (2\pi\tau)] d(2\pi\tau)$$

where  $[1 + \gamma(2\pi\tau)]$  is the static structure factor of Fig. 3. The limits of integration are taken as Q + q and Q - q where q is given by  $\omega$  = cq.

At large values of Q and  $\omega$  the structure factor approaches the value unity as required in the incoherent approximation. In the limit as  $\omega \rightarrow 0$ , i.e.

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near elastic scattering the liquid structure factor reduces to the static structure factor  $[1 + \gamma(Q)]$ . However, the near elastic scattering is dominated by the effect of diffusive motion which cannot be treated by the single "phonon" approximation which we are using here. The present discussion is therefore restricted to the results at energy transfers greater than 1 meV.

So far only the known spacial distribution of atomic positions in the liquid has been used, but in addition there will be further broadening of the liquid structure factor by the diffusive motion of the atoms. We take the broadening in energy to be given roughly by the half-width of the Lorentzian function given by Fick's Law, viz.  $2hDQ^2[5]$  (where D is the diffusion coefficient). Over the range of Q of interest here, i.e. at energy transfers below the sharp drops in the scattered intensity, the broadening in energy due to diffusive motion is of the order 0.2 meV. Thus the calculated structure factor is very little changed by including the effects of diffusive motion.



Fig.6

Comparison of calculated structure factor and experimental results at two angles.

The calculated structure factors including this estimated diffusive broadening are shown for two scatter angles in Fig. 6. The smearing of the sharp "cut-off" of the solid is apparent. Also in Fig. 6 are the liquid structure factors derived from the experimental results. These are derived, as explained above, by dividing the observed cross-section by that predicted by the incoherent approximation using a frequency distribution  $\rho(\omega) \sim \omega^2$  as for the solid in the region where the present "phonon" calculation can be considered to have some meaning (taken as  $\hbar \omega > 1 \text{ meV}$ ) The experimental results show a marked increase in the structure factor at low energy transfers, this increase becoming continuously more pronounced as the scatter angle decreases. Clearly the calculations given are quite inadequate to explain the present experimental results.

Further discussion is reserved until more analysis of the results is completed.

## BRIEF DESCRIPTION OF RESULTS WITH 4.0Å NEUTRONS

The experimental results taken with 4Å neutrons show broadly a similar behaviour to the results already described. The cut-off for the polycrystalline scattering (calculated positions marked with arrows in Fig. 1) appears in the expected position at scatter angles less than 75°. The scattering appearing below the cut-offs is probably due to multi-phonon scattering. The agreement with the present simple theory for the high peak at  $\theta = 75^{\circ}$  is not satisfactory. At  $\theta = 90^{\circ}$  the two lower spaced planes appear as Bragg scattering, the inelastic peak at this angle being associated with the third plane in solid tin.

In the liquid, for which the structure factor does not fall to zero at low energy transfers, appreciable inelastic scattering is again seen.

At  $\theta = 90^{\circ}$  the momentum transfer for elastic scattering is equal to the value for the first peak of the structure factor of Fig.3 and the strong elastic peak is seen in the experimental results.

#### CONCLUSIONS

Experimental data on the scattering of cold neutrons by solid and liquid tin are compared to approximate calculation for single phonon coherent scattering by a polycrystal and its extension to liquids. The cross-section is represented as a coherent structure factor times the cross-section derived using the incoherent approximation. The structure factor gives a step in the cross-section corresponding to the appearance of the different planes in the crystal, analogous to the steps seen in the total cross-section arising from the appearance of Bragg scattering from the crystal planes. Steps corresponding to the planes in tin are demonstrated in the present experiment. The calculated structure factor gives an acceptable description of the experimental results for the polycrystalline solid. More detailed interpretation would be possible with results on a solid having a simple Bravais lattice for which dispersion relations were available, aluminium being a possible material.

The experimental results on the liquid are similar to those obtained with solid tin at high energy transfer, but show much more scattering at low energy transfers. This result cannot be explained using the calculated structure factor for a "pseudo-phonon" model together with the assumption of a Debye frequency distribution of modes in the liquid. This conclusion is similar to that of the early work of EGELSTAFF [5] who compared differential cross-sections and average energy transfers with the predictions of these models.

#### S.J. COCKING and Z. GUNER

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## DISCUSSION

### (On the two foregoing papers)

B. N. BROCKHOUSE: It should be pointed out that Vineyard's convolution approximation contravenes the second moment theorem very badly, especially in the region of small or medium momentum transfer. The second moment theorem is so soundly based theoretically that it is almost inconceivable that it should be wrong, and in any case it was experimentally verified several years ago.\*

P. EGELSTAFF: The results on sodium and tin which Mr. Cocking has just used to test the Vineyard approximation may also be used to test the de Gennes narrowing effect. This effect is based on the moment theorems and essentially arises from the fact that the  $t^2$  term is absent from the time expansion of the interference function. In order to see the  $t^2$  term one has to work in the multiphonon region, and hence de Gennes<sup>1</sup> narrowing would not be observed in the one-phonon region. The fact that a strong effect is observed only a few millivolts from the zero energy transfer position shows that the narrowing is much stronger than predicted by de Gennes.

K. S. SINGWI: It is true that the convolution approximation violates the condition that Dr. Brockhouse has mentioned, but in all fairness to Vineyard, I must say that it is never meant to be applied in the entire region. It is true only in the region of small Q, and in that region I have a feeling it should not be really much at fault.

P. SCHOFIELD: I might point out that, apart from violating the moment theorem, the convolution approximation also fails at long times. In fact one can show that it can only be true if  $I_s$  (Q, t) falls off exponentially with time at all times.

S. COCKING: May I add a more elementary point here. Sodium is a favourable case for testing the convolution approximation since the ionic radius is small compared with the lattice spacing.

B. N. BROCKHOUSE: With regard to what was said by Dr. Singwi, I must say that in my view it is in the region of small Q that the convolution approximation fails especially badly.

<sup>\*</sup> BROCKHOUSE and POPE, Phys. Rev. Lett. 3 (1962) 259.

## SCATTERING OF NEUTRONS BY LIQUID BROMINE\*

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#### Abstract — Résumé — Аннотация — Resumen

SCATTERING OF NEUTRONS BY LIQUID BROMINE. Neutrons of 0.037 eV and 0.0088 eV were scattered from a thin sample of liquid bromine at room temperature, and the energy distributions of the scattered neutrons measured at angles from 10° to 160° by the time-of-flight method. The angular distribution contirms the results of a previous study by Caglioti.

Spectra were expressed in the form of the "scattering law"  $S(\alpha, \beta)$  of Egelstaff and analysed to derive the generalized frequency distribution  $p(\beta)$  of atomic motions in the liquid. The function  $p(\beta)$  has a broad smooth peak centred at  $\beta \approx 0.3$ , and shows no evidence for discrete levels in the measured range  $0 < \beta < 0.8$ ; the general shape of the curve supports the "quasi-crystalline" picture of the liquid. Difficulty in the absolute normalization of  $p(\beta)$  is discussed.

DIFFUSION DES NEUTRONS PAR LE BROME LIQUIDE. Des neutrons de 0,037 eV et 0,0088 eV ont été diffusés par un échantillon mince de brome liquide à la température ambiante; on a mesu-é, par la méthode du temps de vol, les distributions d'énergies des neutrons diffusés, pour des angles compris entre 10° et 160°. La distribution angulaire confirme les résultats d'une étude antérieure faite par Caglioti.

Les spectres ont été exprimés d'après la «loi de dispersion»  $S(\alpha, \beta)$  d'Egelstaff et analysés pour déterminer la distribution généralisée des fréquences  $p(\beta)$  des mouvements atomiques dans le liquide. La fonction  $p(\beta)$  comporte un pic large et à faible pente dont le centre est à  $\beta \approx 0,3$  et ne présente aucune indication de niveaux discrets dans la gamme mesurée  $0 < \beta < 0,8$ ; la forme générale de la courbe confirme l'image «quasi cristalline» du liquide. Les auteurs examinent les difficultés qui s'opposent à la normalisation absolue de  $p(\beta)$ .

РАССЕЛНИЕ НЕЙТРОНОВ ЖИДКИМ БРОМОМ. Нейтроны с энергией 0,037 и 0,0088 эв рассеивались тонким образцом жидкого брома при комнатной температуре, измерялось распределение энергий рассеянных нейтронов при углах от 10 до 160° методом времени пролета. Угловое распределение подтверждает результаты предыдущих исследований Каглиотти.

Спектры были выражены в форме "закона рассеяния" S ( $\alpha$ , $\beta$ ) Эгельстаффа и анализировались для выведения обобщенного распределения частот р ( $\beta$ ) движений атомов в жидкости. Функция р ( $\beta$ ) имеет широкий гладкий пик, соответственно значению  $\beta \approx 0,3$  и не показывает никаких данных для дискретных уровней в измеренном диапазоне 0 <  $\beta$  < 0,8; общая конфигурация петли подтверждает "квазикристаллическую" картину жидкости. Рассматривается проблема абсолютной нормализации р ( $\beta$ ).

DISPERSIÓN DE NFUTRONES POR BROMO LÍQUIDO. Los autores han estudiado la dispersión de neutrones de 0,037 eV y 0,0088 eV en una muestra de bromo líquido de espesor reducido, a temperatura ambiente. La distribución energética de los neutrones dispersos fue medida para ángulos comprendidos entre 10° y 160°, mediante el método del tiempo de vuelo. La distribución angular confirma los resultados obtenidos en un estudio anterior por Caglioti.

Los espectros fueron expresados en la forma correspondiente a la "ley de dispersión"  $S(\alpha,\beta)$  de Egelstaff y analizados para derivar la distribución generalizada de frecuencias  $p(\beta)$  de los movimientos atómicos en el líquido. La función  $p(\beta)$  tiene un pico poco pronunciado, cuyo máximo corresponde a  $\beta \approx 0.3$  y no parece presentar saltos en el intervalo  $0 < \beta < 0.8$  medido; la forma general de la curva confirma la descripción del líquido como "cuasi-cristalino". Los autores examinan las dificultades que presenta la normalización absoluta de la función  $p(\beta)$ .

<sup>\*</sup> Joint project between AECL Chalk River and AERE, Harwell.

<sup>\*\*</sup> Natural Research Council of Canada Post-Doctoral Fellow.

<sup>\*\*\*</sup> On attachment from AERE, Harwell.

## 1. INTRODUCTION

Studies by neutron scattering of molecular motions in liquids have been confined mainly to monatomic liquids, such as molten metals [1] and lique-fied inert gases [2,3]. Investigation of polyatomic liquids has concentrated largely on light and heavy water, in which the hydrogen atoms do most of the scattering.

A point of considerable interest in the case of diatomic molecules is the extent to which vibrations and rotations in the gas phase can still occur in the liquid. Energy levels for these processes may be difficult to observe even if they are present, as they may be greatly broadened by thermal motions of the molecules; De GENNES [4] has given some guidance on neutron energies to be used in such a search. There is also much interest in the details of diffusive motion, e.g. whether this occurs continuously or in a series of jumps, and whether the diffusing units are single molecules or large rotating groups as suggested by EGELSTAFF [5]. A further property to be investigated is the relationship between the solid and liquid phases of a substance, and the charges which occur on melting.

One previous study of neutron scattering by liquid bromine was made by CAGLIOTI et al.[6], using a crystal spectrometer. From the angular distribution of coherently scattered neutrons they computed by a Fourier transformation the molecular density distribution function  $\rho$  (r). The major peak in this quantity showed clearly the presence of the second atom in each molecule, and gave an interatomic distance in good agreement with other measurements in the solid and gaseous states. It was shown that the main features of the parent solid were preserved during the melting process. As no analysis of the distribution of inelastically scattered neutrons was made, it was not possible to study molecular motions in detail, though it was shown from the available free volume that the molecules could not be freely rotating.

The aim of the present experiment was to search for rotational and vibrational levels in liquid bromine and to study the diffusion process. Such results could then be compared with those from studies of water and monatomic liquids.

#### 2. THEORETICAL TREATMENT

The theoretical developments of EGELSTAFF and SCHOFIELD [7] will be briefly described here, with the application to the present work.

The experimental data, when correctly normalized, give the double differential scattering cross-section as a function of scattering angle and the energy  $\epsilon = E' - E$  which is transferred in the collision. This is related to the "scattering law"  $S(\alpha, \beta)$  for the material by:

$$S(\alpha, \beta) = \frac{d^2\sigma}{d\Omega d\epsilon} \left[ e^{\beta/2} \left( \frac{k}{k'} \right) \right] \frac{4\pi}{\sigma_b} k_B T.$$
(1)

The dimensionless quantities  $\alpha$  and  $\beta$  are related respectively to the momentum change hQ and the energy change h $\omega$  by

## SCATTERING OF NEUTRONS BY LIQUID BROMINE

$$\alpha = \frac{\hbar^2 Q^2}{2Mk_B T}$$
 and  $\beta = \frac{\hbar \omega}{k_B T}$ ,

where M is the mass of the scattering atom and  $\sigma_b$  its bound scattering crosssection, k and k' are the initial and final wave numbers of the neutron,  $k_B$ is Boltzmann's constant and T the absolute temperature. Expression of the data in the form of S ( $\alpha$ ,  $\beta$ ) has the advantages of reducing the number of explicit variables from three to two and including implicitly the condition of the thermal equilibrium of the scatterer. Further analysis is conveniently performed in terms of S( $\alpha$ ,  $\beta$ ).

Although the space-time correlations of the atoms are related to the scattering law by a Fourier transformation [8], it is preferable to obtain them by other means, as the range of  $\alpha$  and  $\beta$  which can be covered experimentally is too small to make direct transformation an accurate method. Egelstaff shows that a useful alternative procedure is to obtain the quantity  $[S(\alpha, \beta)/\alpha]_0 = \lim_{\alpha \to 0} [S(\alpha, \beta)/\alpha]$  for all available  $\beta$ . In practice this is done by plotting log  $[S(\alpha, \beta)/\alpha]$  against  $\alpha$  at constant  $\beta$  and extrapolating the linear portion of the plot to  $\alpha = 0$ . This method separates the "self" and "interference" terms of  $S(\alpha, \beta) [9]$ ; interference effects, which are important only for distances of the order of one atomic spacing, cause the curves to rise rapidly as  $\alpha$  tends to zero but are not significant in the linear region.

The quantity  $p(\beta) = \beta^2 [S_S(\alpha, \beta)/\alpha]_0$ , where  $S_S$  is the "self" portion of  $S(\alpha, \beta)$ , is related by Fourier transformation to the velocity autocorrelation function of the molecules;  $p(\beta)$  has been called the "generalized frequency distribution" of the molecular motions and shows characteristic variations with  $\beta$  for different states of matter. For a liquid it shows the general nature of the motions, in particular whether rotational or vibrational levels are present. Information on diffusion can be derived from the behaviour of  $p(\beta)$  as  $\beta \rightarrow 0$ , but it is difficult to make accurate measurements in this region.

#### 3. EXPERIMENTAL METHOD

The experimental apparatus has been described in detail [10], and only a brief outline will be given here. A system of four phased rotors produces bursts of monoenergetic neutrons, collimated to a beam size of 1 1/2-in wide by 1-in high. Twenty scintillation detectors are placed around the target at angles from 10° to 159°, with a flight path of 1.30 m. Pulses from each detector are time-sorted into 270 channels of width  $6\mu$  s and recorded on magnetic tape, which is scanned after a 24-h run. Pulses from three fission chambers in the line of the beam are also time-sorted, for calculation of beam intensity, velocity of the incident neutrons and transmission of the sample.

Fig. 1 shows the bromine sample holder. The liquid was contained within a teflon ring of internal diameter  $2 \ 1/2$  in and thickness 0.2 in, with a small filling hole sealed by a teflon screw. Teflon film 0.002-in thick,backed for further strength by 0.005-in vanadium foil, made up each of the two faces. This containing assembly was clamped between aluminium rings. The sample and an empty duplicate were automatically interchanged every 15 min, to allow accurate subtraction of background.





Bromine scattering specimen. The specimen is in the form of a thin circular disk, oriented at  $45^{\circ}$  to the neutron beam. Flight path to the detectors is 1.30 m.

The incident neutron energies were 0.037 eV and 0.0088 eV ( $\lambda = 1.49$  and 3.06Å), with about 200 h of running time at each energy. Transmission of the bromine layer was 86% at 0.037 eV and 74% at 0.0088 eV. At the higher energy, the standard deviation in neutron arrival times at the sample was 3.5  $\mu$ s, and their incident energies was 0.6%.

An absolute cross-section scale was established by comparing the known scattering cross-section  $\sigma_b$  with the total number of scattered neutrons; to obtain this quantity the net count in each detector was multiplied by  $\sin \theta$  and plotted against  $\theta$ , and the smoothed curve integrated numerically over all angles. The absolute detector efficiencies had been previously determined by measuring the almost completely incoherent scattering from vanadium.

## 4. RESULTS

Typical spectra obtained with 0.037 eV neutrons are shown in Fig. 2. Backgrounds were very significant, with the ratio (net count/background)



The net scattered intensity and the background are shown, for detectors at 82° and 142° to the beam. Incident neutron energy was 0.037 eV.

equal to 0.93 at 142° and 1.03 at 85°. Owing to the poor statistics and the good energy resolution in the incident pulse, resolution corrections were not applied to these spectra.

Such data were converted to the form of  $S(\alpha, \beta)$  and analysed to derive the frequency distribution function  $p(\beta)$ , in the manner described in Section 2. Plots were prepared of  $S(\alpha, \beta)$  versus  $\alpha$  at constant  $\beta$ , i.e. for each time channel or averaged group of three time channels. Some typical examples are shown in Fig. 3. Points for which  $\alpha$  was less than 0.02 were ignored in the straight-line extrapolations, because a measured angular distribution (to be discussed below) showed that such points would contain significant coherent contributions. In fitting the straight lines, the slopes of the lines were constrained to vary smoothly with  $\beta$ .



Scattering law for bromine at 20°C. Plots of  $(S/\alpha)$  versus  $\alpha$  are shown for some representative values of  $\beta$ . The intercept of each fitted straight line is the quantity  $[S/\alpha]_{\alpha}$  for the given  $\beta$ .

The final results were the averages from two series of measurements at 0.037 eV, each lasting about 100 h; data taken at 0.0088 eV could not be used in this way as  $\alpha$  was always less than 0.02. Data with  $\beta$  +ve and -ve were treated separately and the resulting extrapolations compared later as a check on consistency of the results. Corresponding extrapolations were always consistent within estimated errors and no distinction was made between them in producing the final smoothed curve of  $[S(\alpha, \beta)/\alpha]_0$  versus  $\beta$ . From this smoothed curve was formed the function  $p(\beta) = \beta^2 [S(\alpha, \beta)/\alpha]_0$ ; it is shown in Fig. 4, with estimated uncertainties which are believed to be rather conservative.

Angular distributions of the total number of scattered neutrons were obtained by summing the counts in each detector. The resulting distribution from 0.088 eV neutrons is shown in Fig. 5, where the abscissa is the value of  $\alpha$  for elastic scattering at the given angle. For comparison is shown the curve of Caglioti et al. measured with neutrons of 0.15 and 0.091 eV. As the agreement is quite good, the present results confirm their picture of the structure of this liquid.



Fig.4

Frequency distribution for liquid bromine. This curve of  $p(\beta)$  was prepared from a smoothed plot of  $[S/\alpha]_0$  versus  $\beta$ . Estimated uncertainties in the curve are shown.

#### 5. DISCUSSION

Egelstaff shows from the moment theorems of PLACZEK [11] that

$$\int_{0}^{\infty} 2\beta \sinh (\beta/2) [S_{S}(\alpha,\beta)/\alpha]_{0} d\beta = 1 ,$$

where  $S_S(\alpha, \beta)$  is the "self" term only, i.e. interference terms have been excluded. The area enclosed by the function  $p(\beta)$  should therefore be less than unity, but that contained by the present curve, integrated to  $\beta = 0.9$ only, is 2.1. A similar tendency towards over-estimation of  $p(\beta)$  has arisen in studies of  $D_2O[12]$  and  $UO_2[13]$ . Three possible explanations for such a discrepancy are the following:

(1) The abolute cross-section scale in the experiment is too high by a factor of 2 or more;



Angular distribution. The full curve is the angular distribution of the total scattered intensity for incident neutrons of 0.0088 eV, with the results of Caglioti shown for comparison. The two curves have been arbitrarily normalized.

- (2) The procedure for extrapolation of  $S(\alpha, \beta)/\alpha$  curves has not completely removed coherent contributions;
- (3) Multiphonon effects at high energy transfer are keeping  $p(\beta)$  high at high  $\beta$ .

The absolute cross-section scale is based on the published scattering cross-sections for bromine and for vanadium (used to calibrate the detectors), and seems unlikely that this scale could be incorrect by more than 40%. Further experimental and theoretical work is needed to check the other two possibilities. Small errors in  $[S(\alpha, \beta)/\alpha]_0$  at large  $\beta$  would cause significant errors in  $p(\beta)$ , owing to the large scaling factor  $\beta^2$ .

Results so far have shown no evidence of discrete levels in the liquid. Although this may be due to inadequate statistical accuracy, it seems clear that there are no dominant levels in the range of energy transfer covered. Rotational levels of the bromine molecule are probably too closely spaced to be resolvable. The vibrational level in the free bromine molecule occurs at 0.04 eV [14], corresponding to  $\beta$  = 1.6 at room temperature. To extend the presently explored range of  $\beta$ , measurement is needed at higher neutron energies.

The general shape of  $p(\beta)$  is similar to that found previously for  $H_2O$  [15] and  $D_2O$  [12], and is nearer to that expected for a solid than for a purely diffusing system.. It therefore supports the "quasi-crystalline" model of a liquid.

Further work on bromine will include measurements at higher values of energy transfer, in a search for discrete vibrational levels. The problem of the incorrect area under  $p(\beta)$  will be studied more closely.

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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.

## NEUTRON SPECTROMETRY WORK AT THE CNEN

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#### Abstract — Résumé — Аннотация — Resumen

NEUTRON SPECTROMETRY WORK AT THE CNEN. In this communication the main features of the triple axis spectrometer recently installed at the Ispra-1 reactor are presented. Preliminary results in the quasi elastic angular distribution of 1.4 Å neutrons scattered in liquid bromine are shown and briefly discussed.

LA SPECTROMÉT RE NEUTRONIQUE AU CNEN. Dans ce mémoire, l'auteur décrit les principales caractéristiques du spectromètre triaxial installé récemment au réacteur Ispra-1. Il donne et examine brièvement les résultats préliminaires des expériences sur la distribution angulaire quasi élastique de neutrons de 1,4 Å diffusés dans du brome liquide.

РАБОТЫ ПО НЕЙТРОННОЙ СПЕКТРОМЕТРИИ В НКЯЗ. В этом сообщении приводятся основные характеристики трехосного спектрометра, установленного недавно на реакторе "Испра-1". Показываются и кратко обсуждаются предварительные результаты по квазиупругому угловому распределению 1,4 Å нейтронов, рассеянных в жидком броме.

TRABAJOS DE ESPECTROMETRÍA NEUTRÓNICA REALIZADOS EN EL CNEN. La memoria describe las principales características del espectrómetro triaxial recientemente instalado en el reactor Ispra-1. Asimismo, expone brevemente los resultados iniciales de las determinaciones de distribución angular de neutrones de 1,4 Å dispersados en forma cuasi elástica por bromo líquido.

A conventional triple axis spectrometer has been very recently put into operation at the 5 MW CP-5 type reactor of the Ispra Centre.

The spectrometer, shown in Fig. 1, allows automatic measurements of neutron scattering in solids and liquids at fixed values of the momentum (or of the energy) transfer, through programmed increments of the scattering angle  $\phi$ , the analysing angle  $2\vartheta_A$  and the orientation angle  $\Psi$  of the (crystal) sample. Furthermore the spectrometer may be easily converted into a nominal double axis unit and into an instrument suitable for the beryllium filtered detector technique.

In the design of such a spectrometer particular care was taken in order to keep the ratio background signal as low as possible. To this end, we found it convenient to provide a bulky shielding 60-cm diam. all around the counter, and to adjust the counter efficiency to the wavelength so as to make it as directional as possible.

Preliminary results on phonon peaks by a brass crystal, showed a background level of approximately 2 counts/min when a counter 15-cm long, 5-cm diam., filled with enriched  $BF_3$  at a pressure of 70 cm Hg was utilized; a background level as low as 0.4 counts/min was reached with a counter of the same characteristics, but filled with natural  $BF_3$ , during some mea-



Fig.1

The triple axis spectrometer in operation at the Ispra-1 reactor.

surements on the molecular modes of liquid bromine performed with the inverse beryllium filter technique \*.

A preliminary analysis was undertaken on the quasi-elastic scattering in liquid bromine at room temperature with the following purposes:

- (a) To study the reliability of the information on the radial distribution function of a diatomic liquid obtained utilizing the static approximation through the usual Fourier inversion of a conventional neutron diffraction pattern;
- (b) To devise a dynamical model of the liquid based on known values of macroscopic parameters, useful for an understanding of the behaviour of the liquid during a time controlled by the energy resolution of the experimental set-up.

An angular distribution of the intensity diffracted by a cylindrical sample 2-cm diam. was obtained by pivoting the analysing spectrometer set at the

<sup>\*</sup> The measurements quoted above will be reported elsewhere at their completion; they were performed with J. J. Antal and M. Antonini.

wavelength of 1.4 Å associated with the neutrons impinging on the liquid sample. The energy resolution (full width at half maximum)of the monochromating and analysing spectrometers were set at  $\Delta E_{\widetilde{M}}$  1.4 10<sup>-3</sup> eV and  $\Delta E_A \simeq 2.3 \, 10^{-3}$  eV respectively [1]. Therefore the quasi-elastic angular distribution is physically connected with a sort of time average [2] of the VAN HOVE's [3] correlation function G (<u>r</u>, t) over a period  $\Delta t$  of the order of 1.3  $\times 10^{-12}$ s.

The quasi-elastic angular distribution obtained for liquid bromine is shown in Fig.2. At present the pattern reaches a maximum value of the wave-vector transfer  $Q = 5.85A^{1}$ .



Angular distribution of 1.4A neutrons quasi-elastically scattered from liquid bromine at room temperature. The bars represent the experimental data, corrected for the contribution of the quartz container. The dashed horizontal line is the estimated level of multiple and incoherent scattering. The full line, labelled  $u^2=0.6_5$  Å<sup>2</sup>, is the fit obtained through the model discussed in the text. The lines labelled 0.06 Å<sup>2</sup> and 0.07 Å<sup>2</sup> show how sensitive if the fit to the choice of the mean square value  $6u^2$  of the nuclear displacement associated with the solid-like part of the self correlation function. The fit and the experimental data have been arbitrarily normalized at the (triangular) point corresponding to  $Q = 5 Å^{-1}$ .

A comparison of the present, limited amount of data with the corresponding conventional distribution [5] confirms that, even for a heavy liquid element, the neutron scattering process is mainly inelastic, with the exception, perhaps, of events associated with wave-vector transfers underlying the first diffraction peak [6]. Therefore it appears that since the scattering angle is not uniquely related with the wave vector transfer when dealing with monochromatic neutron radiation [4, 7], an experiment should be performed measuring the integrated intensity associated with all of the possible energy transfers at any fixed value of the momentum transfer. Measurements of this sort could help to clearly establish some limits on the reliability of the static approximation when used in conjunction with the determination of the radial distribution function of a liquid.

An attempt to fit the experimental data of Fig. 2 has been done utilizing VINEYARD's convolution approximation.c.f.Eq.(14) of [4] together with

a model of the liquid which, in its simplicity, is perhaps appropriate to the nature of the information obtainable by this kind of technique. The Fourier transform of the self-correlation function in liquid bromine is assumed to be made up of two contributions, gas-like plus solid-like, weighted (in analogy with the vacancy theory of liquids [8]) on the basis of the knowledge of the molar volumes of solid bromine at its melting temperature and liquid bromine at room temperature. In the gas-like term (wt. 23%), the effective mass of a bromine, atom is assumed to be 6/5 times the nuclear mass [9]. The solid-like Gaussian self correlation function (wt. 77%) is tentatively assumed to have a width  $2\mu$  independent of time, whose value is left free in order to optimize the fit. The interference effects due to instantaneous space correlations among nuclei within the liquid are supposed to be conveniently expressed by the conventional neutron diffraction pattern [5]. In comparing the experimental points (Fig. 2) with the average of Vineyard's expression over the energy resolution function of our spectrometer, no attempt was made to put the intensity data in an absolute scale.

There are reasons to think that the relatively small discrepancies between the experimental data and the fit could be partly attributed (a) to the use of the static approximation we implicitly made when specifying the interference effects and (b) to the assumption of a <u>time-independent</u> mean square nuclear displacement  $6\mu^2$  associated with the solid-like contribution.

It appears from Fig.2 that the quality of the fit depends sensitively on the amount of local relaxation one attributes to the structure of the liquid through the value of  $\mu^2$ . In the present case the latter should be about  $0.06_5 \text{ A}^2$  in order to produce a reasonable fit. This amount is much larger than the one computed on the basis of a Debye model of the system, and could be partly explained by hindered rotations.

As we mentioned above, experiments are now under way at Ispra to explore other regions of the  $(Q, \omega)$  space, so as to reach eventually a more detailed picture of the molecular motions possibly present within this liquid.

## ACKNOWLEDGEMENTS

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For Discussion see p. 271.

# DYNAMICS OF LIQUID HYDROGEN BY NEUTRON SCATTERING\*

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#### Abstract — Résumé — Аннотация — Resumen

DYNAMICS OF LIQUID HYDROGEN BY NEUTRON SCATTERING. The total scattering cross-section of liquid para-hydrogen for neutrons below about 0.014 eV is found to conform approximately to the Schwinger-Teller theory for para-hydrogen gas, indicating very weak intermolecular forces. A minimum of about 3 b per hydrogen atom is reached at about 0.014 eV as a result of coherence of scattering from oppositely oriented atoms in the molecule. A sharp rise with increasing neutron energy above this threshold corresponds to inelastic collisions in which the neutron spin is reversed and the molecule is thus converted from para - to ortho-hydrogen, absorbing the energy difference between the J=0 and J=1 ground rotational levels of the para and ortho states. Preliminary measurements of the neutron energy loss in both energy regions confirm these interpretations and are being continued for more detailed investigation of liquid dynamics.

ETUDE DE LA DYNAMIQUE DE L'HYDROGÈNE LIQUIDE PAR LA DIFFUSION NEUT RONIQUE. La section efficace totale de diffusion des neutrons dans du para-hydrogène liquide pour une énergie inférieure à 0,014 eV concorde approximativement avec les résultats donnés par la théorie de Schwinger-Teller pour le para-hydrogène gazeux, ce qui montre que les forces intermoléculaires en présence sont très faibles. Cette section efficace atteint un minimum d'environ 3 b par atome d'hydrogène à 0,014 eV environ, par suite de la diffusion cohérente sur des atomes ayant des orientations opposées dans la molécule. L'augmentation brusque qui se produit au-dessus de ce seuil correspond à des collisions inélastiques dans lesquelles le spin est inversé; la molécule d'hydrogène est ainsi transformée de la forme para à la forme ontho, absorbant la différence d'énergie entre les niveaux fondamentaux de rotation J=0 et J=1 des états ortho et para. Des mesures préliminaires de la perte d'énergie neutronique dans les deux domaines d'énergie confirment ces interprétations; les expériences se pousuivent en vue d'une étude plus détaillée de la dynamique de l'hydrogène liquide.

ДИНАМИКА ЖИДКОГО ВОДОРОДА ПРИ РАССЕЯНИИ НЕЙТРОНОВ. Найдено, что поперечное сечение рассеяния нейтронов с энергией ниже 0,014 электронвольт жидким параводородом соответствует приблизительно теории Швингер-Теллера для параводородного газа, при этом виявлены очень слабие междумолекулярные силы. Приблизительно при 0,014 эв достигнут минимум примерно в 3 барка на атом водорода в результате когерентности рассеяния от противоположно ориентированных атомов в данной молекуле. Крутой скачок с увеличением энергии нейтровов над этим порогом соответствует неупругим столкновениям, в которых нейтронный спин делается обратным и молекула таким образом превращается из параводорода в ортоводород, поглощая разницу энергии между J = 0 и J = 1 основных вращательных уровнений пара- и орто-состояний. Предварительные измерения потери энергии нейтронами в обоих энергических районах подтвеорили эту интерпретацию. Опыты продолжаются.

ESTUDIO DE LA DINÁMICA DEL HIDRÓGENO LÍQUIDO POR DISPERSIÓN NEUTRÓNICA. Los autores comprueban que la sección eficaz total de dispersión del para-hidrógeno líquido correspondiente a neutrones de energía inferior a 0,014 eV se ajusta aproximadamente a la teoría de Schwinger-Teller relativa al parahidrógeno gaseoso, lo que indica la intervención de fuerzas intermoleculares muy débiles. A unos 0,014 eV se alcanza un mínimo del orden de 3 b por átomo de hidrógeno, resultante de la dispersión coherente por áto-

<sup>\*</sup> Work performed at General Dynamics/General Atomic.

mos orientados en direcciones opuestas en la molécula. Al aumentar la energía neutrónica por encima de ese valor umbral se observa un incremento brusco que corresponde a los choques inelásticos en que el espín neutrónico es invertido, con lo que la molécula de para-hidrógeno se convierte en molécula de orto-hidrógeno, absórbiendo la diferencia de energía existente entre los niveles rotatorios fundamentales J=0 y J=1 de los estados para y orto. Las mediciones iniciales de la pérdida de energía neutrónica en ambas regiones energéticas confirman estas interpretaciones, Dichas mediciones continúan efectuándose con miras a investigar con más detalle la dinámica de los líquidos.

## I. INTRODUCTION

Liquid hydrogen has several special features of structure and dynamics which distinguish its neutron scattering properties from those of other liquids, and also of other hydrogenous materials. In general these result from its being a molecular liquid, characterized by strong binding between the two atoms of the molecule but by relatively weak inter-molecular forces, so that its behaviour is similar to the gaseous form.

In all other hydrogenous solids and liquids, the nuclear spins may be considered completely randomly-oriented. The large difference in the singlet and triplet scattering amplitudes,  $a_s = -23.67 \times 10^{-13}$ , and  $a_t = 5.40 \times 10^{-13}$  cm, respectively, therefore leads to a large incoherent and small coherent cross-section. Since liquid hydrogen exists in the two forms of ortho (parallel nuclear spins) and para (anti-parallel nuclear spins) coherent scattering is much more important. In para-hydrogen, destructive interference of the scattered waves leads to a low total cross-section.

The effect of weak intermolecular binding is that the individual molecule is relatively free in both translational and rotational motion. Evidence from specific heat measurements indicates that the molecule rotates rather freely in liquid and even in solid state. The quantum mechanically-allowable rotation states are given by the equation

$$E = (h^2 / ma^2) J(J + 1) = 0.015(J/2)(J + 1)$$
(1)

where even J values correspond to the para state and odd to the ortho state, as given in Table I. In addition, there is to be expected a continuum of transitional energy levels, corresponding to the motion of the molecule within the shallow potential well determined by the surrounding molecules. Levels corresponding to relative vibrations of the two atoms in a molecule of course occur at energies substantially above the rotational energy levels.

1		E
Para	Ortho	eV
0		<b>.</b> 0
	1	0.015
2		0.045
	3	0.090
4		0.150

TABL	ΞI
111000	

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These general aspects of the dynamics of liquid hydrogen have been investigated experimentally by the scattering of low energy neutrons from an electron linear accelerator. The present paper discusses the general features of neutron scattering in liquid  $H_2$  as compared to  $H_2$  gas, and particularly the conclusions which may be derived from the simple measurement of total scattering cross-section. The accompanying paper reports further and more detailed information from inelastic scattering measurements.

## II. NEUTRON SCATTERING FROM GASEOUS HYDROGEN

There was a special and fundamental interest in the study of neutron scattering from molecular hydrogen very early in the history of neutron physics to determine the spin dependence of n-p interactions. For scattering of thermal neutrons - energy in the range 0.025 eV - from H<sub>2</sub> molecules, reference to Table I shows that four different elastic or inelastic scattering interactions are energetically possible:

- $0 \rightarrow 0$  para-para (elastic);
- $0 \rightarrow 1$  para ortho (inelastic);
- $1 \rightarrow 1$  ortho-ortho (elastic);
- $1 \rightarrow 0$  ortho para (inelastic).

On the basis of an assumed spin dependence of the n-p interaction SCHWINGER and TELLER [2] derived the theoretical relation of total cross-section to neutron energy for each of these four cases, as shown in Fig. 1. Two of these cases, para - para and ortho - ortho, correspond to simple elastic scattering in which no rotational energy level is concerned. The two inelastic cases,





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para - ortho and ortho - para, combine two effects. The neutron is scattered with reversed spin orientation, having exchanged with one of the hydrogen atoms, but with negligible energy associated with the spin reversal. At the same time, however, the molecule must gain or lose an amount of energy equal to the difference between the J = 0 and J = 1 ground rotational states of the para and ortho orientation. The cross-section for scattering from parahydrogen therefore has a threshold at the energy necessary for excitation of the first rotational level. Above the threshold the cross-section rises rapidly with increasing probability of inelastic scattering; below, the cross-section is much lower than the 20 b free H value, as a result of destructive coherence between the scattered amplitude from the oppositely-oriented hydrogens.

The curves, as shown in Fig. 1 are of course only qualitatively correct, as they were based on values of the scattering amplitudes only inaccurately known at the time, but were sufficient to demonstrate the spin dependence of n-p scattering. More careful measurements of the molecular cross-sections were later made by SUTTON, LONG <u>et al.</u> [3] for the purpose of more precise determination of the individual scattering amplitudes. These measurements were carried out intentionally at energies low enough [4] to avoid inelastic scattering by excitation of rotational levels, and on H<sub>2</sub> gas to avoid possible effects of inter-molecular binding. No measurements have been previously made, however, on liquid hydrogen, or on gaseous parahydrogen in a higher range of incident neutron energy.

Referring again to Fig. 1, it is seen that the effects of inter-molecular binding on translational motions may be investigated by neutron scattering in the low energy region, where no rotational excitation occurs; the degree of hindrance of rotational motion should be revealed particularly by the sharpness of the threshold, as well as by the form of the cross-section curve with increasing energies.

A liquid nitrogen temperature paraffin moderator was used to increase flux of the low energy neutrons, and liquid hydrogen as a cold moderator was briefly investigated [4].

## III. TOTAL CROSS-SECTION MEASUREMENTS

The general experimental method has been described elsewhere and is here only briefly outlined. Neutron pulses of about  $5 \times 10^{10}$  neutrons were produced in a Pb target by bombardment with an 80 mA beam of 24-28 meV electrons from the linear accelerator, and were moderated in a small block of liquid nitrogen temperature polyethylene. Time-of-flight over a 3 meter path from source to BF<sub>3</sub> detectors was recorded on a 256 channel recorder, with 16, 32 or 64µs channels. For energy calibration, primarily a more precise determination of the average emission time of the neutron pulse from the cold moderator, the positions of the 0.005, 0.010, 0.015, and 0.020 eV Bragg diffraction cut-offs in iron were determined by transmission of the beam through a polycrystalline sample.

The liquid hydrogen samples were in flat aluminium containers of several thicknesses ranging from 8 to 40 mm, placed inside a previously described [5] vacuum cryostat with multiple aluminium and stainless steel walls, and so arranged that samples of different hydrogen thickness and dummy containers of the same aluminium wall thickness could be interchanged by rotation of the cryostat. Two types of samples were studied, the 75% - 25% ortho-para mixture which characterizes room temperature hydrogen and which persists, in approximately this ratio, for a reasonable time after liquefaction, and the approximately 99. 75% para-hydrogen mixture, which is the equilibrium distribution to which the liquid reverts with a halflife period of several hours, in the absence of catalysts. In all cases measurements were made on the liquid at its boiling point of approximately 20. 4°K for normal atmospheric pressure. To obtain these two distributions, therefore, the samples were liquified either immediately before measurement or a period of several days before.

Figure 2 shows the total transmission cross-section versus energy for these two mixtures, which are indicated as ortho-para and as para, respectively. The insert on that figure shows data determined with higher instrumental resolution over the restricted energy range 0.010 to 0.020 eV in order to



- (a) Theoretical elastic (0 → 0) and inelastic (0 → 0) scattering cross-sections of para-hydrogen molecules calculated in 1937 by SCHWINGER and TELLER [2]. Doppler broadening is neglected.
- (b) Theoretical elastic (1 → 1) and inelastic (1 → 0) scattering cross-sections of ortho-hydrogen molecules calculated by Schwinger and Teller.

investigate the sharpness of the threshold for inelastic scattering. For comparative purposes Fig. 1 includes two lines, labelled para-H<sub>2</sub> gas and ortho-H<sub>2</sub> gas, and representing the results of SUTTON, LONG <u>et al.</u> [3]. The solid portions of these lines are curves of the Schwinger-Teller form best fitted to their experimental data, over the energy range of their measurements, and the dotted portions are extrapolations to higher and lower energies, still following the Schwinger-Teller form. It should be noted that these curves apply to the hypothetical, but experimentally unobtainable, pure para and ortho gases, whereas our data apply to the mixtures as described above, and in the ortho-para case to a somewhat indeterminate mixture ratio, since reversion to the para state was taking place slowly during the several hours of the experiment. These differences are not significant, however, to the qualitative conclusions derived.

#### IV. DISCUSSION OF RESULTS

A general comparison of the experimental data of Fig. 2 with the theoretical curves of Fig. 1 indicates that the neutron scattering properties of  $H_2$  liquid approximately follow those predicted for  $H_2$  gas by the Schwinger-Teller theory.

For incident neutron energies too low to excite the first rotational level, scattering by the para-hydrogen molecule is an elastic process for which the total cross-section is

$$\sigma_0 = k_0 (3a_1 + a_0)^2$$

where  $k_{0,0}$  is an energy dependent factor as derived by Schwinger and Teller. and at are the singlet and triplet scattering amplitudes, and the combination  $3a_1 + a_0$  is proportional to the coherent scattering amplitude. Using the more recent value 3,  $74 \times 10^{-13}$  for the coherent scattering amplitude [6], the curve shown in Fig. 2 would be lower by about 10%. If the molecule were completely bound, this total cross-section should be increased by the reduced mass factor  $(3/2)^2$ . The fact that experimental data for the liquid agree rather closely with the values for para-hydrogen gas may be taken as an indication that translational recoil motion of the para molecule is practically unaffected by binding forces. Effects in ortho-hydrogen for low incident neutron energy are similar but somewhat more difficult to interpret. for several reasons. The total cross-section is the sum of an elastic scattering term  $\sigma_{1,1}$  and an inelastic term  $\sigma_{1,0}$ , the latter representing orthopara conversion, with neutron energy gain, which is possible at all incident energies. The measured values also represent an average of ortho and para molecules in a ratio of approximately 75% - 25% but not accurately known.

At higher energies, in the range 0.010 to 0.020 eV there is a sharp rise in the liquid para-hydrogen cross-section, evidently corresponding to an additional term  $\sigma_{0, 1}$  for inelastic scattering by para-ortho conversion. The theoretical form of the  $\sigma_{0, 1}$  term for H<sub>2</sub> gas is shown in Fig.1. Although the energy required to raise the molecule to the ortho ground state is 0.015 eV, the threshold neutron energy is (3/2).015 = 0.023 eV, since conservation of momentum for collision of the mass 1 neutron and mass 2 molecule requires that at threshold 1/3 of the energy remains in translational motion of the neutron and recoil molecule. Differences between the experimental data and the theoretical curve are to be expected both in sharpness and in position of the threshold.

Even in the case of the gas, the curve in Fig. 1 is derived on the assumption of a stationary molecule and takes no account of Doppler broadening. Since at the boiling temperature of 20. 4°K, kt = 0.0017 eV, the shape of the minimum should be significantly modified by Doppler effect. For liquid, inter-molecular binding forces are expected to introduce further broadening, increasing according to the extent of hindrance of rotation of the molecule. The measurements shown in Fig. 2 were not at very high resolution, and no attempt has been made to correct for Doppler broadening; however, preliminary higher resolution measurements in the region of the threshold, shown in the insert at the top of Fig. 2, show a sharpness which qualitatively indicates free rotation.

The position of the cross-section minimum for liquid para-hydrogen is definitely below the 0.023 eV value expected for a free gas, and more nearly at 0.015 eV. This would indicate that the molecule is bound in the sense that, for an inelastic neutron collision, its centre of mass is fixed with respect to the surrounding molecules, allowing the neutron momentum to be transferred to the entire system and the neutrons' total kinetic energy to go into raising the molecule from the J = 0 para to the J = 1 ortho state. This conclusion seems somewhat in conflict with the free molecule behaviour at lower neutron energies and indicates the need for more carefully quantitative measurements near the cross-section minimum.

The sharp minimum of the neutron scattering cross-section of liquid para-hydrogen is similar in shape to the minimum in the cross-section of metallic hydrides. There is, in fact a strong analogy between these cases. In the case of zirconium hydride, it was shown [7,8] that, since the individual hydrogen atoms are isolated from each other, being isotropically bound at the centre of a tetrahedron of zirconium atoms, they act as independent oscillators with discrete energy levels at multiples of 0.13 eV. The hydrogen atoms bound in a metallic hydride were thus shown to act as an Einstein crystal and to behave very closely in accordance with the Fermi[9] bound harmonic oscillator theory. The present experiments show that, since the individual hydrogen molecules are nearly isolated from each other, being weakly bound to the surrounding liquid; they act as independent rotators, with the discrete energy level 0.015 eV. The hydrogen molecules bound in the liquid are thus shown to behave very nearly in accord with the Schwinger-Teller theory for a free molecular gas.

## V. LIQUID HYDROGEN MODERATORS AND FILTERS

Liquid hydrogen is an almost uniquely useful moderator to serve as a source of cold neutrons. The present results verify several significant points concerning its moderating properties. From 0.015 eV up through the thermal energy range, it is seen that liquid para-hydrogen has a high cross-section for inelastic scattering by which the neutron loses a relatively large amount, 0.015 eV, of its energy. More important for the low temperature moderating properties, even below the 0.015 eV threshold, there is an effective means of neutron energy loss, since the molecules behave approximately as a free gas of mass 2 scatterers. More precisely, there is a continuum of very low energy states of tranlational motion, so that a mechanism exists for the neutron to reach thermal equilibrium with the moderator. This is in contrast to other hydrogenous moderators, all of which are solids at  $20^{\circ}$ K and therefore lack low energy states for energy exchange with neutrons.

It should also be noted that liquid hydrogen has some uniquely useful properties as a filter for slow neutrons. The cross-section minimum of liquid para-hydrogen is in the vicinity of 0.015 eV and is lower by a factor of 8 to 10 than the cross-section above 0.060 eV. While beryllium filters

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can be used to transmit neutrons in the energy range 0 to 0.005 eV, a liquid para-hydrogen filter extends this range three-fold to 0 to 0.015 eV. It has already been possible to work in this range with single crystal filters such as lead and quartz, but with the considerable disadvantage that the filter transmission is not a smooth function of energy but depends in a complicated way on the energy and the orientation of filter crystals. The liquid hydrogen cross-section is, of course, a smooth function of energy and independent of direction. Although there are some disadvantages in the requirement of a double-walled storage cryostat and some safety precautions, these may in many cases be warranted by the favourable filter characteristics. A still higher energy "cut-off" of the filter could be attained by using gaseous parahydrogen, for which the inelastic threshold is at 0.023 eV. In this case, a rather large volume of filter would need to be maintained at low temperature, to retain the para-state.

### VI. CONCLUSIONS

From the observed total neutron scattering cross-section of liquid para and ortho-hydrogen, it may be concluded that:

- (1) The cross-section of liquid para-hydrogen agrees generally with the Schwinger-Teller theory for gaseous para-hydrogen, indicating weak intermolecular binding in the liquid, in particular.
- (2) Agreement with the gaseous values in the region, 0 to 0.015 eV, of coherent elastic scattering indicates freedom of translational recoil motions.
- (3) A sharp rise in cross-section at about 0.015 eV corresponds to inelastic scattering by para to ortho conversion, accompanied by neutron spin reversal, and indicates freedom of rotation of molecules.
- (4) Both para- and ortho-hydrogen should act as effective neutron moderators even at neutron energies too low for excitation of rotational levels, since neutron energy can be absorbed by nearly free recoil of molecules.

### VII. FURTHER MEASUREMENTS

Although the total cross-section measurements give a good qualitative picture of the liquid dynamics, two types of more difficult measurements are clearly of value. Measurements with polarized neutrons, to observe the spin reversal of scattered neutrons, would more clearly verify the interpretations and distinguish between elastic and inelastic scatterings. but would be difficult for intensity reasons. A more quantitative picture of the spectrum of vibrational energies of molecules in the liquid, and of the degree of hindrance of rotations, can be obtained from the differential scattering crosssection as a function of angle and energy. Measurements of this type are described in an accompanying paper.

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#### DISCUSSION

## (On paper by G. Caglioti and P. Ascarelli)

B. N. BROCKHOUSE: I would just like to comment that I don't think you are actually using the Vineyard convolution approximation - what you're using is certainly not forbidden by the moment theorem because you are applying it to the quasi-elastic part of the scattering only. The Vineyard approximation applies to the whole scattering pattern and this is forbidden by the moment theorem. I think recent experimental data suggests that the approximation you are using is not too good, but it is not absolutely forbidden.

K.S. SINGWI: I do not understand your comment. When the question of Vineyard convolution approximation came up I said that for small Q, small energy transfer, and when the time is large and the distance is large, the approximation should give good results. It seems you do not agree? Or do you?

B. N. BROCKHOUSE: It <u>is</u> a question of energy transfer and not momentum transfer.

K.S. SINGWI: It is both. If Q is small, R is large. It means that when the atoms are far apart then the self part is quite good. That is what I meant.

A. SJOLANDER: In your experiment, Dr. Caglioti, you average over a fairly long time, so one might expect simple diffusion theory to give reasonable agreement. Have you tried this most simple model and, if so, have you found bad agreement?

G. CAGLIOTI: This attempt to fit the experimental results should be regarded as preliminary. Since the agreement of our simple model with the present amount of data may be regarded as satisfactory, we have not yet tried any other models, but it is possible that we will have to have recourse to other models when more experimental data is suitable.

# NEUTRON INTERACTIONS IN LIQUID PARA- AND ORTHO-HYDROGEN\*

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## Abstract — Résumé — Аннотация — Resumen

NEUTRON INTERACTIONS IN LIQUID PARA- AND ORTHO-HYDROGEN. An experimental method is described which utilizes a simple Fermi-type chopper and conventional time-of-flight techniques in conjunction with an electron linear-accelerator pulsed neutron source to study inelastic scattering of thermal neutrons from liquid para- and ortho-para-hydrogen. The overall general agreement between theory and experiment supports the concept that the molecules in liquid hydrogen behave nearly as they would in a "perfect" gas. For liquid ortho-para-hydrogen, however, the extra broadening of the energy distribution of scattered neutrons suggests that some effects of the liquid state may be present. Similar observations on para-hydrogen indicate that, in this liquid as well, the motion of the molecules is affected by weak intermolecular forces.

INTERACTIONS NEUTRONIQUES DANS L'ORTHO-HYDROGÈNE ET LE PARA-HYDROGÈNE LIQUIDES. Les auteurs décrivent la méthode expérimentale, fondée sur l'emploi d'un sélecteur simple de Fermi et de techniques classiques de temps de vol, qu'ils ont employée pour étudier, au moyen d'une source de neutrons pulsés produits par un accélérateur linéaire d'électrons, la diffusion inélastique des neutrons thermiques dans du parahydrogène et de l'hydrogène ordinaire liquides. La concordance générale entre les résultats théoriques et expérimentaux confirme l'hypothèse selon laquelle les molécules dans l'hydrogène liquide se comportent à peu près comme dans un gaz «parfait». Toutefois, pour l'hydrogène ordinaire liquide, le plus grand élargissement de la distribution d'énergies des neutrons diffusés donne à penser qu'il pourrait se produire certains effets de l'état liquide. Des observations semblables sur le para-hydrogène indiquent que, dans ce liquide également, le mouvement des molécules est influencé par des forces intermoléculaires faibles.

НЕЙТРОННЫЕ ВЗАИМОДЕЙСТЕИЯ В ЖИДКОМ ПАРА- И ОРТОВОДОРОДЕ. Описывается экспериментальный метод, при котором используется простой прерыватель типа Ферми и обичные методи времени продета в связи с использованием злектронного динейного ускорителя в качестве пульсирундего источника нейтронов для изучения неупругого рассеяния тепловых нейтронов жидким пара- и ортопараводородом. Хорошее соответствие теории и эксперимента подтверждает концепций о том, что молекули в жидком водороде ведут себя почти так же, как если би они были "идеальным" газом. Для жидкого ортопараводорода знергетический спектр рассеянных нейтронов увеличивается, как полагается, в результате некоторого влияния жидкого состояния вещества. Подобные же наблюдения за параводородом указывают, что в этой жидкости движение молекул также находится под влиянием слабых межнолекулярных сил.

INTERACCIONES NEUTRÓNICAS EN PARA-HIDRÓGENO Y ORTO-HIDRÓGENO LÍQUIDOS. Los autores describen un método experimental en el que se utiliza un selector sencillo tipo Fermi y el procedimiento clásico del tiempo de vuelo, junto con un acelerador lineal de electrones como fuente pulsada de neutrones, para estudiar la dispersión inelástica de neutrones térmicos por para-hidrógeno y orto-para-hidrógeno líquidos. La concordancia general entre los resultados obtenidos experimentalmente y los valores teóricos confirma la hipótesis de que las moléculas se comportan en el hidrógeno líquido casi como si se tratara de un "gas perfecto". Sin embargo, en el caso del orto-para-hidrógeno líquido, el considerable ensanchamiento de la distribución energética de los neutrones dispersos sugiere la intervención de algunos de los efectos correspondientes al estado líquido. Observaciones análogas en el caso del para-hidrógeno indican que, también en este líquido, el movimiento de las moléculas se ve afectado por fuerzas intermoleculares débiles.

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#### INTRODUCTION

The techniques of neutron inelastic scattering have been applied to the study of liquid para-hydrogen and liquid ortho-para-hydrogen. This preliminary report covers the early phases of this research. An important goal is to investigate the respect in which the behaviour of liquid para and liquid ortho-para-hydrogen differs from a perfect gas. In order to do this, certain aspects of the scattering system have been examined theoretically to select proper experimental conditions.

### THEORY

The scattering of low energy neutrons from liquid hydrogen has been investigated theoretically by G. SARMA [1]. His treatment utilizes the formalism of VAN HOVE [2] to describe, in Born approximation, the scattering by a system of particles subject to the assumptions that (a), the Hamiltonian is independent of the spins and (b), there are no correlations between the position and orientation of a particular molecule nor between the orientations of different molecules. Moreover, the hydrogen molecule is approximated by a simple rigid rotator and thus possesses the rotational states

$$\mathbf{E}_{\rm L} = (\hbar^2 / \mathrm{ma}^2) \mathbf{J} (\mathbf{J} + 1) = 0.015 (\mathbf{J}/2) (\mathbf{J} + 1) \mathbf{eV}$$
(1)

where m is the proton mass and a = 0.75 Å, the distance between the two protons in the hydrogen molecule. Consideration of the vibrational modes is neglected since the incident neutron energies in the range of interest are much smaller than the minimum energy necessary to excite the lowest of these modes.

Under the above assumptions, the differential cross-sections for "coherent" and "incoherent" scattering may be written respectively as the fourdimensional Fourier transforms of the "distinct" and "self" parts of the Van Hove pair distribution function  $G(\underline{r}, t)$ . The differential "coherent" crosssection, which accounts for that part of the coherent scattering arising from different molecules, is negligibly small, so that the "incoherent" crosssection alone defines the scattering. Direct comparison between theory and experiment depends on the form of  $G_S(\underline{r}, t)$ . As a first approximation, Sarma considers the case where intermolecular forces may be neglected and takes for  $G_S(\underline{r}, t)$  the auto-correlation function of a perfect gas. With this model the differential "incoherent" cross-section takes the form:

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}E} = \left(4 \frac{\mathrm{m}}{\pi \mathrm{k}_{\mathrm{B}} \mathrm{T}}\right)^{1/2} \frac{\mathrm{k}}{\hbar \mathrm{k}_0} \frac{\mathrm{f}_{\mathrm{I} \to \mathrm{I}'}}{\mathrm{K}} \exp\left\{-\mathrm{m} \frac{\left[\hbar\omega - (\mathrm{E}_{\mathrm{I}'} - \mathrm{E}_{\mathrm{I}}) - \frac{\hbar^2 \mathrm{K}^2}{4\mathrm{m}}\right]^2}{\mathrm{k}_{\mathrm{B}} \mathrm{Th}^2 \mathrm{K}^2}\right\}$$
(2)

In this expression  $\underline{K} = \underline{k} - \underline{k}_0$ , where  $\underline{k}_0$  and  $\underline{k}$  are the neutron wave vectors before and after scattering. The term  $f_{J_{\rightarrow}J_1}$ , is a function of Ka/2 (and therefore of angle) and its value depends strongly on the initial and final states of the hydrogen molecule; i.e. upon the transition considered.

In the para and ortho-modifications of liquid hydrogen, all of the molecules are assumed to be in their lowest states (J = 0 and J = 1, respectively). Thus, for incident neutron energies less than 0.1 eV, the following are the only values of  $f_{I \rightarrow I}$  that need be considered:

$$f_{0 \to 0} = 4p_0 A_{coh}^2 B_0^2$$

$$f_{0 \to 1} = 12p_0 A_{incoh}^2 B_1^2$$

$$f_{1 \to 1} = 4p_1 (A_{coh}^2 + 2/3A_{incoh}^2)(B_0^2 + 2B_2^2)$$
(3)
$$f_{1 \to 0} = (4/3)p_1 A_{incoh}^2 B_1^2$$

$$f_{1 \to 2} = (4/3)p_1 A_{incoh}^2 (2B_1^2 + 3B_3^2)$$

Here  $p_I$  is the statistical weight of the molecules in the state J and the B's are spherical Bessel functions of the argument (Ka/2). These values of f can differ by several orders of magnitude because of the difference in the values  $A_{coh}^2 = 3.57 \times 10^{-2}$  b and  $A_{incoh}^2 = 1.59$  b.

The numerator of the exponent in Eq.(2) expresses the conservation of energy in terms of the energy transfer  $\hbar \omega = (E_{J'} - E_J)$  and the momentum transfer  $\hbar K$ . Expressing these in terms of energy, i.e.:

$$\hbar \omega - (\mathbf{E}_{J'} - \mathbf{E}_{J}) = \mathbf{E}_{0} - \mathbf{E} - (\mathbf{E}_{J'} - \mathbf{E}_{J})$$

$$\hbar^{2} \mathbf{K}^{2} = 2\mathbf{m}(\mathbf{E} + \mathbf{E}_{0} - 2\sqrt{\mathbf{E}\mathbf{E}_{0}}\cos\varphi)$$
(4)

where  $E_0$  and E are the initial and final energies of the neutron and  $\phi$  is the angle of scattering, Eq.(2) can be rewritten:

$$\frac{d^{2}\sigma}{d\Omega dE} = \frac{4(2\pi k_{B}T)^{-1/2}(E/E_{0})^{1/2}(f_{J\rightarrow J})}{[E + E_{0} - 2\sqrt{EE_{0}}\cos\varphi]}\exp - \frac{9[\frac{1}{3}(E_{0} - 2\Delta E_{J}) + 2\sqrt{EE_{0}}\cos\varphi] - E]^{2}}{8k_{B}T(E + E_{0} - 2\sqrt{EE_{0}}\cos\varphi) - E]^{2}}$$
(5)

Thus,  $\frac{d^2\sigma}{d\Omega dE}$  takes on its maximum value when

 $E = 1/3(E_0 - 2\Delta E_{J'J} + 2\sqrt{EE_0}\cos\varphi)$ (6)

is in agreement with what one would expect from simple classical considerations. The exponential term in Eq. (5) describes an intrinsic broadening associated with each of the scattering components and, as a consequence of the initial assumptions, this broadening is due entirely to the thermal motions of the hydrogen molecules.

Inasmuch as our initial measurements have been obtained with  $\varphi = 90 \deg$ , further consideration will be limited to this special case. Eq.(5) then reduces to

$$\frac{d^{2}\sigma}{d\Omega dE}\Big|_{\varphi = \pi/2} = 4(2\pi k_{B}T)^{-1/2} \left(\frac{E}{E_{0}}\right)^{1/2} \frac{f_{I \to I'}}{(E + E_{0})^{1/2}} \exp -\frac{9[\frac{1}{3}(E_{0} - 2\Delta E_{I'}J) - E]^{2}}{8k_{B}T(E + E_{0})}$$
(7)
If the average energy after scattering,

$$E = (E_0 - 2\Delta E_{1'1})/3$$

is assigned to all values of E, except in the numerator of the exponent, the exponential in Eq. (7) is a simple Gaussian with its full-width at half-maximum given by

δξ = 
$$(4/3)(2k_BT\ln 2)^{1/2}$$
 (E + E<sub>0</sub>)<sup>1/2</sup> (8)

To the same degree of approximation and letting  $\epsilon = 1/3(E_0 - 2\Delta E_{J'J}) - E$ , we can integrate (7) obtaining

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\Big|_{\varphi=\pi/2} = \frac{8}{3} \left( \frac{\mathrm{E}_{0} - 2\Delta\mathrm{E}_{\mathrm{I}'\mathrm{I}}}{3\mathrm{E}_{0}} \right)^{1/2} \mathrm{f}_{\mathrm{I}\to\mathrm{J}'}\left( \frac{\mathrm{K}_{a}}{2} \right) \tag{9}$$

where the argument Ka/2 has the value  $0.3(E_0 - \Delta E_{J'J}/2)^{1/2}$  when the energies are expressed in units of milli-electron volts (meV):

The broadening  $\delta \xi$  depends both on the incident neutron energy and on the transition considered. This dependence is shown in Fig. 1 where the



Fig.1

Theoretical broadening of the distribution in energy of neutrons scattered by liquid hydrogen.

energy broadening for 90 deg scattering is plotted as a function of  $E_0$  for the various scattering components. It is seen that in all cases the broadening is quite large for all but the lowest energies. The dotted portions of the two lower curves represent the energy ranges where the incident neutron energy is insufficient to excite these transitions.

In applying Eq. (9) to the case of para-hydrogen, it is necessary to consider only the two scattering components associated with the transitions

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 $0 \rightarrow 0$  ("elastic") and  $0 \rightarrow 1$ . By substituting the appropriate values of  $f_{J \rightarrow J'}$  from Eq.(3) with  $p_0 = 1$  into Eq.(9), the magnitudes of the partial cross-sections at  $\varphi = 90$  deg for these scattering components are easily calculated. The results are shown in Fig.2 as a function of the incident neutron energy. The "elastic" component is proportional to  $A^2_{coh}$  and is so small that ten times its value has been plotted. It is of interest to note that both cross-sections vanish for particular values of  $E_0$ .





Theoretical differential cross-sections for scattering at 90° from para-hydrogen.



Fig.3

Theoretical differential cross-sections for scattering at 90° from ortho-para-hydrogen.

Fig. 3 shows a similar plot of the differential cross-sections evaluated at  $\varphi = 90$  deg for the various components scattered from ortho-para-hydrogen. In this case all of the transitions listed in Eq.(3) are possible and the curves shown were calculated assuming a 2:1 ortho-to-para mixtures (i.e.p = 0.67 and  $p_0 = 0.33$ ). Although this relative concentration has not been measured for the present experiment, this assignment is reasonable for the present experimental conditions.

It should be noted that the approximations made in the derivation of Eqs.(8) and (9) are not generally valid. When  $E \rightarrow 0$  or when its value is small and comparable with the expected broadening, the representation of a scattered component as a simple Gaussian is not sufficiently accurate. In such cases an exact evaluation of Eq.(7) has been made in comparing theory with the experimental results. An example of such an analysis is shown in Fig.4 where the scattering components,  $(0 \rightarrow 1)$ ,  $(1 \rightarrow 0)$ ,  $(1 \rightarrow 2)$ , and  $(0 \rightarrow 0, 1 \rightarrow 1)$ , are exhibited for 0.065 eV neutrons incident on ortho-para-hydrogen.



Fig.4

Four components of the scattering from ortho-hydrogen at 90° for neutrons with  $E_n = 65 \text{ meV}$ .

#### EXPERIMENT

The experimental method employed is closely related to the conventional double chopper, the essential difference being the substitution of an electron linear accelerator pulsed neutron source for the first chopping element. A schematic drawing of the experimental arrangement is shown in Fig. 5. Five  $\mu$ s bursts of high energy neutrons are produced when electrons from the accelerator strike an electron-neutron converter. A fraction of these are moderated and directed toward the chopper located 2.8 m from the moderator. The neutrons transmitted by the chopper strike the sample and those scattered at 90 deg are detected by a BF<sub>3</sub> counter bank 1.6 m from the sample. The time distribution of the scattered neutrons is recorded by a 256-channel analyser operated with 16  $\mu$ s channel widths.

The repetition rate of the accelerator and the rotational speed of the chopper are operated at the same frequency and the energy of the neutrons incident on the sample is determined by the phase of the accelerator pulse with respect to the instant that the chopper is open. This phase can be continuously varied electronically by changing the delay of the chopper control pulse which triggers the accelerator. In practice, the useful range of energies



Fig.5

Experimental arrangement for neutron inelastic scattering measurements using an electron linear accelerator.

is limited by the available intensity and the chopper transmission function but extends from  $\sim 0.0005$  eV to  $\sim 0.25$  eV.

For the present measurements, the apparatus outlined above has been used to select those incident energies which eliminate one or more of the scattering components. In order to facilitate the discussion these energies are summarized in Table I. In the case of para-hydrogen the scattering is effectively due to a single component for the incident energies chosen. For  $E_0 < 0.030 \text{ eV}$ , the neutron energy is insufficient to excite the first rotational level while above this threshold the  $(0 \rightarrow 1)$  is predominant due to the very small cross-section of the "elastic"  $(0 \rightarrow 0)$  scattering. The situation with ortho-para-hydrogen is more complicated since at least one inelastic component is present in addition to the "elastic"  $(0 \rightarrow 0, 1 \rightarrow 1)$  scattering.

#### TABLE I

SELECTED OPTIMUM INCIDENT ENERGIES,  $E_0$ , TO REDUCE CERTAIN CONTRIBUTIONS TO THE SCATTERING AT 90 DEG. FROM VARIOUS ROTATIONAL LEVELS IN LIQUID HYDROGEN

Scatterer	~ E <sub>0</sub> (eV)	Contributions
р-Н	< 0. 030	0 →0
	~ 0.065	0→1
	<b>~</b> 0. 170	0 →0
о-р-Н	< 0. 030	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 0$
	0.030 > 0.060	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 0, 0 \rightarrow 1$
	~ 0. 170	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 2$

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The instrumental resolution was measured over the range of incident energies employed by measuring the elastic scattering from a thin sheet of vanadium.  $\Delta T$  is the width at half maximum for the observed scattered distribution and T is the flight time for the flight path from the scatter to the detector. The values found for  $\Delta T/T$  vary between 0.05 and 0.10 depending upon the exact experimental conditions; i.e. chopper speed, beam divergence, and moderator used as the neutron source. Although the resolution is inadequate for many applications, it is satisfactory in the case of liquid hydrogen due to the large intrinsic thermal broadening associated with the various scattering components. Finally, the calibration of the energy scale was determined by measuring the different flight times for elastic scattering from vanadium over different known flight paths with other experimental conditions held constant.

Fig.6 shows the measured distribution of initially mono-energetic 0.065 eV neutrons scattered at 90 deg from a sample of liquid para-hydrogen



Experimental data for 0.065 eV neutrons scattered by a 1 mm layer of para-hydrogen. Theoretical predictions based on a perfect gas model are also shown.

having a nominal thickness of 1 mm. Here, as in all subsequent measurements, the data have been corrected for the background measured with cadmium interposed between the moderator neutron source and the chopper. This method of measuring background was adopted because it includes the moderation of the general "fast" neutron background by the sample. It does not, however, account for the elastic scattering from the container which appears as the relatively sharp peak centered at  $E_0$  in the data. The dashed curve represents the predicted theoretical scattering corrected for instrument resolution and plotted with an arbitrary normalization. Though the experimental and theoretical curves agree in position, the observed broadening, 0.020 eV, is approximately 20% greater than the predicted value of 0.017 eV.

Similar representations of the scattering from ortho-para-hydrogen are shown in Figs. 7 and 8 where the incident neutron energies were 0.065 eV and



Fig.7





Experimental data for 0.04 eV neutrons scattered by a thin layer of ortho-para-hydrogen. Theoretical predictions based on a perfect gas model are also shown.

0.040 eV respectively. Comparable measurements have also been made utilizing higher incident neutron energies and in all cases the observed broadening is greater than predicted on the basis of a perfect gas model. Although the

theoretical curves were plotted in Figs.6, 7 and 8 with arbitrary normalization, it may be useful for future reference to compare for two cases the relative theoretical and experimental values. For  $E_0 = 0.065$  eV and for the peak of the scattered neutron distributions

$$\left(\frac{d\sigma}{d\Omega dE}\right)_{p-H} \left/ \left(\frac{d\sigma}{d\Omega dE}\right)_{o-p-H} \right| = 1.93 \text{ and } \sim 3.7$$

respectively for the theoretical and experimental curves.

1

Since the sample thicknesses were chosen to have a neutron transmission greater than or equal to 0.85, the effects of multiple scattering are believed to be small in most of the cases examined. This assumption has been reinforced by measuring the distribution of neutrons scattered from a sample of para-hydrogen having half the thickness used in obtaining the data in Fig.6. The observed widths agree within the experimental error. On the basis of these considerations, the observed additional broadening of the distributions appears to be a feature of the liquid state of hydrogen.

## DISCUSSION

The overall agreement between theory and experiment supports the generally accepted concept that the molecules in liquid hydrogen behave very nearly as they do in a "perfect" gas. The absence of appreciable binding forces is evident from the agreement between the observed and calculated energies of the various scattering components. Such would not be the case if even moderate binding forces were operative, since then the effective mass of the recoiling molecule would be increased with a substantial reduction in the energy of the recoiling molecule. The position of the scattering distribution peaks is thus relatively sensitive to the recoil mass. Moreover, any tendency of liquid hydrogen to exhibit solid state characteristics would be reflected in a reduction of the width of the scattered distribution.

The present data, though not sufficiently accurate to permit final conclusions, indicate that the scattering components are broader than one would expect from the "perfect" gas model. One interpretation of this additional broadening is that the effective translational energy of a hydrogen molecule in the liquid state is larger due to molecular interactions. Theoretical conclusions of PAULING [3] and measurements of Raman spectra [4] support the supposition that the molecules in liquid hydrogen rotate freely. However, the motion of the hydrogen molecules may involve at least two different aspects of the liquid. On the one hand, if there are general nearest-neighbour collisions between molecules, additional broadening of all scattering components should be observed. On the other hand, if the main effect of the liquid state is to reduce the lifetime of the excited states thus introducing a further lack of sharpness in the excited levels, then the (0 - 0) scattering distribution in para-hydrogen should not be additionally broadened but all other neutron interactions involving excited states should exhibit extra broadening. Nuclear magnetic resonance measurements [5] of the dependence of the nuclear relaxation time on different concentrations of ortho-hydrogen have shown

that an interaction exists between ortho and para-hydrogen molecules. In view of this interaction, the final state of the neutron scattering event which consists of a single ortho-molecule surrounded by para-molecules is not well defined and may be an explanation for the extra broadening observed in the present experiment on para-hydrogen. The broadening of the distribution from ortho-para-hydrogen (Fig. 7) appears to be greater than that from para-hydrogen (Fig. 6). Nuclear magnetic resonance measurements have provided clear evidence that the ortho-ortho quadrupole interaction is very strong and much stronger than the ortho-para interaction. This strong orthoortho interaction could be the mechanism by which neighbouring molecules interact and hence give an extra broadening to the distribution in energy of neutrons scattered by ortho-hydrogen. A future experiment on the "elastic" scattering (0  $\rightarrow$  0) of neutrons in para-hydrogen with E<sub>0</sub> < 0.030 eV should provide considerable clarification of these effects and may give evidence of an interaction of para-molecules with other para-molecules, an interaction which cannot be studied directly by the techniques of nuclear magnetic resonance. The experiment has not been performed as yet with the present experimental arrangement due to the very small cross-section of the  $(0 \rightarrow 0)$ scattering in para-hydrogen.

The positional discrepancy between experiment and theory shown in Fig.8 has not been confirmed by repeating the measurements. A crude estimate of multiple scattering indicates only a small effective displacement of the peak to be expected for this scattering (with perhaps the main effect being an enhanced low energy tail). A definitive check on this will be made by observing the scattering from a thinner scattering layer. Assuming the validity of the discrepancy, an explanation is that the liquid state of hydrogen alters the relative cross-sections for excitation and de-excitation. If this explanation is correct, the data of Fig.8 indicate that the (0  $\rightarrow$ 1) transition is enhanced and/or the (1  $\rightarrow$  0) transition is suppressed in liquid ortho-parahydrogen. The relative cross-sections for scattering by para-hydrogen and ortho-para-hydrogen, noted in the previous section for E<sub>0</sub> = 0.065 eV, offer additional evidence that the liquid state affects the magnitude of the partial cross-sections.

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  - Both of these include extensive additional references to pertinent literature.

## DISCUSSION

D.G. HURST: I might mention that calculations of the complete type shown on the screen during Mr. Whittemore's oral presentation were done by us a great many years ago in connection with measurements in heavy hydrogen. At that time this Gaussian approximation looked very attractive since calculations had to be done by hand, but it never quite gave the accuracy required. I am wondering whether you have any figures for the error introduced by this approximation.

W.L. WHITTEMORE: I don't have them at my fingertips, but I have some calculations with me. Perhaps we could show you in some detail that the Gaussian approximation is reasonably good, but when dealing very closely with the excitation of the various levels, one has to be just a little bit careful. In the case of hydrogen, however, since the molecule is very light and thermal effects are very great, you smear over any sharp excitation levels, in the same way that in the paper that Dr. McReynolds presented, although there is a sharp onset in the total cross-section, it is still smeared out, mainly owing to the thermal effects. I suppose one has the same kind of phenomenon here.

**D.T. GOLDMAN:** Is there any evidence on how well Sarma's theory agrees with experiment in the case of gaseous hydrogen?

W.L. WHITTEMORE: Not as yet. I would very much like to make such a comparison, but we have used liquid measurements only.

P. EGELSTAFF: There may be a simple explanation of the fact that the observed width in liquid hydrogen is greater than that given by Sarma's model. Since the observations indicate that your experimental conditions are such that the liquid looks like a gas, the width may be calculated from the moment theorems; and these give the width as  $2 \overline{k}(\overline{k})$  is the average kinetic energy in the system). This is always greater for a liquid than a gas owing to zero point motion.

W.L. WHITTEMORE: We haven't yet put this to the test, but will do so in due course when the statistics of the data are improved.

K.S. SINGWI: I was just going to say what Dr. Egelstaff has said. I would also like to know what is the difference in the position of the maximum as computed theoretically and as you have seen.

W.L. WHITTEMORE: I am afraid that's not a meaningful experimental question at the present time. I would say that the patterns overlap within the statistics at the present time. They agree, but within statistics which are rather poor.

## SLOW NEUTRON SCATTERING BY BENZENE

## V.C. BOFFI AND V.G. MOLINARI COMITATO NAZIONALE PER L'ENERGIA NUCLEARE, ROME, ITALY AND

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#### Abstract — Résumé — Аннотация — Resumen

SLOW NEUTRON SCATTERING BY BENZENE. We have calculated the scattering of slow neutrons by the benzene molecule. The calculations are carried out within the framework of the time dependent formalism of Zemach and Glauber. Detailed account is taken of the effects of the molecular vibrations on the neutron scattering. Among the results explicitly calculated are the slow neutron total scattering cross-section as a function of energy and the energy angular distribution of singly scattered sections.

DIFFUSION DES NEUTRONS LENTS PAR LE BENZENE. Les auteurs ont calcule la diffusion des neutrons lents par les molécules de benzène. Ils l'ont fait en se fondant sur le formalisme dépendant du temps, mis au point par Zemach et Glauber. Ils ont tenu soigneusement compte des effets des vibrations moléculaires sur la diffusion neutronique. Parmi les résultats calculés de façon explicite, il faut citer la section efficace totale de diffusion des neutrons lents en fonction de l'énergie ainsi que la distribution angulaire.

РАССЕЯНИЕ МЕДЛЕННЫХ НЕЙТРОНОВ БЕНЗОЛОМ. Авторы определили рассеяние медленных нейтронов молекулой бензола. Расчеты произведены в рамках зависящего от времени формального механизма по Земаху и Глауберу. Подробно учитывается воздействие молекулярных вибраций на рассеяние нейтронов. Определены общие поперечные сечения рассеяния медленных нейтронов в зависимости от энергии и угловое распределение энергии по отдельно выбранным сечениям.

DISPERSIÓN DE NEUTRONES LENTOS POR EL BENCENO. Los autores han calculado la dispersión de neutrones lentos por la molécula de benceno. Los cálculos se han efectuado con arregio a las fórmulas de dependencia del tiempo de Zemach y Glauber. Se han tenido debidamente en cuenta los efectos ejercidos por las vibraciones moleculares sobre la dispersión neutrónica. Entre los resultados explícitamente calculados, figuran la sección eficaz total de dispersión de neutrones lentos en función de la energía y la distribución energética angular de las secciones dispersadas aisladamente.

#### INTRODUCTION

Inelastic neutron scattering data and the corresponding Scattering Law,  $S(\alpha, \beta)$ , are now becoming available for many moderators at several temperatures.

The difficulty connected with the Scattering Law is related to the circumstance that it is not possible to cover the entire range of the  $\alpha$  and  $\beta$ space at the present stage of development of the experimental techniques. From the point of view of reactor calculations, it would be desirable to obtain Scattering Laws at large values of  $\alpha$  and  $\beta$ . In this respect, analytical and semi-analytical expressions for the Scattering Laws could be very useful for interpolating the experimental data and for extrapolating them to larger values of  $\alpha$  and  $\beta$ . In this paper we present a theoretical calculation of the scattering of slow neutrons by benzene. We expect that an understanding of neutron scattering by benzene would provide a reasonable basis for a quantitative understanding of scattering by polyphenyls.

In Section I we give a summary of the results obtained in a previous paper [1] in which the time-dependent formalism of ZEMACH and GLAUBER [2] is used to study the effects of the molecular vibrations on the neutron scattering by benzene.

In Section II curves representing the total neutron scattering cross-sections as a function of energy and at different temperatures are shown. The effects of the translations and rotations are included in an approximate manner.

In Section III the Scattering Law in benzene is discussed in the polyatomic gas approximation. The relative curves are shown and compared with experimental results of BRUGGER [3] for some polyphenyls.

## I. SCATTERING OF NEUTRONS BY PROTON BOUND IN BENZENE

For a molecule consisting of  $n_H$  hydrogen atoms, the general expression for the cross-section per hydrogen atom for transfer to final momentum <u>K</u> of a neutron with initial momentum <u>K</u><sub>0</sub> is given, in the notations of ZEMACH and GLAUBER [2] (h = Planck's constant = 1) and upon the assumption that the scattering is completely incoherent, by

$$\frac{\mathrm{d}}{\mathrm{d}\underline{K}} \sigma(\underline{K} \to \underline{K}_0) = \frac{\sigma_b}{8\pi^2 K_0 n_H} \int_{-\infty}^{\infty} \mathrm{dt} \, \mathrm{e}^{\mathrm{i}\epsilon t} \sum_{k=1}^{n_H} \chi_k(\underline{k}, t), \qquad (1)$$

where  $\sigma_b$  is the bound atom n-p cross-section,  $\epsilon = (K^2 - K_0^2)/2$  represents the energy transfer and  $\kappa = \underline{K} - \underline{K}_0$  the momentum transfer.

The function  $\chi_k(\underline{\kappa}, t)$ , which contains the dependence of the scattering on the dynamics of the atoms in the molecule, is given by

$$\chi_{k}(\underline{\kappa}, t) = \langle e^{i\underline{\kappa}\underline{t}_{k}(t)} e^{-i\underline{\kappa}\underline{t}_{k}(0)} \rangle_{T}$$
(2)

where  $\underline{r}_{k}(t)$ , the time-dependent position operator of the kth nucleus in the incleude at the time t, satisfies the Heisenberg equation of motion

$$i \frac{d}{dt} \underline{r}_{k}(t) = \underline{r}_{k}(t)H - H\underline{r}_{k}(t), \qquad (3)$$

in which H is the molecular Hamiltonian. The symbol  $\langle \dots \rangle_T$  means that an average is to be taken over the equilibrium distribution of initial states of the molecule and over molecular orientation.

From Eq. (2) the relevance of the molecular dynamics for the neutron scattering becomes clear. The precise calculation of the momentum transfer cross-section requires a detailed knowledge of the molecular dynamics. In general, it is at best extremely difficult to describe the motion of a hydrogen atom moving in the actual force field of all its neighbours. If we

ignore interactions between molecules, between vibration and rotation, and use the harmonic approximation for internal molecular vibrations, the dynamical problem is well defined and can be solved in principle. Nevertheless, the calculation of the neutron scattering is still a very complex problem. Its complexity lies in the dependence of the scattering on the timedependent nuclear displacements rather than on the dependence of the displacements on time. However, the large mass and moments of inertia of the benzene molecule allow us to make an approximation which considerably simplifies the problem of calculating  $d\sigma/dK$ . As pointed out in our previous paper [1], this approximation consists in neglecting the contributions to  $r_k(t)$  from translations and rotations during the time of interaction between the neutron and the molecule. This is equivalent to neglecting the contribution to the inelastic scattering which results from excitation of translational and rotational degress of freedom by the neutron. We shall show later how to account in an approximate manner for the contribution of rotations and translations. These contributions become important for small energy and momentum transfers.

At this stage, the problem we must consider is that of the harmonic vibrations of hydrogen bound in benzene and their interaction with slow neutrons. We consider a molecule composed of N atoms, and denote by  $u_k(t)$  the displacement of the kth atom from its equilibrium position at time t. Following ZEMACH and GLAUBER [2], for small vibrations we separate the displacements into normal modes and introduce the corresponding expression into Eq. (2). The thermal average indicated in Eq. (2) can be carried out by using a well-known theorem due to BLOCH [4].

$$\chi_{k}(\underline{\kappa},t) = \langle \exp \left\{ \frac{\kappa^{2}}{2M_{k}} \stackrel{e}{=} \frac{\kappa}{\kappa} \cdot \left[ \Gamma_{kk}(t) - \Gamma_{kk}(0) \right] \cdot \stackrel{e}{=} \frac{\kappa}{\kappa} \right\} \rangle_{\Omega}, \quad (4)$$

where  $M_k$  is the mass of the kth atom,  $\underline{e}_{\underline{\kappa}} = \underline{\kappa}/\kappa$  and the symbol  $\langle \dots \rangle_{\Omega}$ means that an average over molecular orientation is to be performed. The tensors  $\Gamma_{kk}(t)$  are related to the normal modes of vibration by

$$\underline{\underline{\mathbf{e}}}_{\underline{\kappa}} \cdot \Gamma_{\mathbf{k}\mathbf{k}}(\mathbf{t}) \cdot \underline{\underline{\mathbf{e}}}_{\underline{\kappa}} = \sum_{\mathbf{j=1}}^{3\mathbf{N}-6} g_{\mathbf{j}}(\mathbf{t}) \left|\underline{\underline{\mathbf{e}}}_{\underline{\kappa}} \underline{\underline{\mathbf{C}}}_{\mathbf{j}}^{(\mathbf{k})}\right|^{2} , \qquad (5)$$

where

$$g_{j}(t) = \frac{(\overline{n}_{j} + 1) e^{i\omega_{j}t} + \overline{n}_{j} e^{-i\omega_{j}t}}{\omega_{j}}$$
(6)

and  $(K_{B} = Boltzmann's constant = 1)$ 

$$\overline{n}_{i} = (e^{\omega_{j}/T} - 1)^{-1}$$
(7)

is the background of thermally-excited oscillators of frequency  $\omega_j$ . In Eqs. (5), (6) and (7)  $\omega_j$  and  $\underline{C}_j^{(k)}$  are the frequency and the amplitude vectors, respectively, of the kth particle in the jth normal mode of vibration.

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Now the problem is to bring Eq. (4) into a form which will allow us to evaluate the Fourier transform appearing in Eq. (1). We first consider the average over molecular orientations indicated in Eq. (4). The approximation which we make consists in setting

$$\chi_{k}(\underline{\kappa}, t) = \exp\left\langle \frac{\kappa^{2}}{2M_{k}} \frac{e}{\underline{\kappa}} \left[ \Gamma_{kk}(t) - \Gamma_{kk}(0) \right] \frac{e}{\underline{\kappa}} \right\rangle_{\Omega}.$$
(8)

This amounts to averaging the molecular motion over molecular orientation before computing the cross-section instead of averaging the cross-section after having computed it for a particular orientation. Using Eq. (5) and doing the average required for use in Eq. (8) gives the result

$$\langle \underline{\mathbf{e}}_{\underline{\kappa}} \Gamma_{\mathbf{kk}}(t) \underline{\mathbf{e}}_{\underline{\kappa}} \rangle_{\Omega} = \frac{1}{3} \sum_{j=1}^{3N-6} g_j(t) \left( C_j^{(k)} \right)^2$$
 (9)

At this point the approximation, Eq. (8), is not necessary but since it will be made in the final analysis, nothing essential is lost in making this approximation now.

By introducing the notations

$$\rho_{k}(\omega) = \frac{1}{3} \sum_{j=1}^{3N-6} \delta(\omega - \omega_{j}) \left(C_{j}^{(k)}\right)^{2}, \qquad (10)$$

Eq.(9) becomes

$$\langle \underline{\mathbf{e}}_{\underline{\kappa}} \Gamma_{\mathbf{k}\mathbf{k}}(\mathbf{t}) \underline{\mathbf{e}}_{\underline{\kappa}} \rangle_{\Omega} = \int_{0}^{\infty} g(\omega, \mathbf{t}) \rho_{\mathbf{k}}(\omega) d\omega$$
 (11)

By putting Eq. (11) into Eq. (9), we obtain

$$\chi_{k}(\underline{\kappa}, t) = \exp \left\{ \frac{\kappa^{2}}{2M_{k}} \int_{0}^{\infty} \rho_{k}(\omega) \left[ g(\omega, t) - g(\omega, 0) \right] d\omega \right\}^{-}.$$
 (12)

Finally, for the case where  $\mathbf{M}_k$  is independent of k, we make the approximation that

$$\chi(\underline{\kappa}, t) = \frac{1}{n_{\rm H}} \sum_{k=1}^{n_{\rm H}} \chi_k(\underline{\kappa}, t)$$
(13)

with  $X(\kappa, t)$  obtained from Eq. (12) by replacing  $\rho_k(\omega)$  by

$$\rho(\omega) = \frac{1}{n_{\rm H}} \sum_{k=1}^{n_{\rm H}} \rho_k(\omega) . \qquad (14)$$

Now the equation for the scattering of neutrons by benzene is formally equivalent to the equation for the incoherent scattering of neutrons by atoms bound in an isotropic cubic crystal having one atom per unit cell. The advartage of having Eq. (5) cast into the form of Eq. (11) is that in this case there exist extensively developed methods [5, 6, 7] for carrying out the Fourier transform indicated in Eq. (1). It remains only to determine the values of the frequencies  $\omega_j$  and amplitudes  $\underline{C}_j^{(k)}$  in order to evaluate the scattering cross-section. This has been done in our previous paper [1]. For the details of these calculations, the reader should refer to the mentioned reference. There numerical calculations of the benzene kernel were carried out using IBM-7090 code SUMMIT [8].

# II. TOTAL SCATTERING CROSS-SECTION PER HYDROGEN ATOM BOUND IN BENZENE

The scattering kernel is integrated numerically to yield the total scattering cross-section per hydrogen atom bound in benzene. The total scattering cross-section per hydrogen atom bound in benzene at 300°K is plotted in Fig. 1 in two cases:





Total scattering cross-section a 300°K per hydrogen atom bound in benzene versus energy.

(a) The effects of translations and rotations are neglected;

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(b) These effects are taken into account as free translations and rotations, the latter being treated in the short collision time approximation.

The effective mass,  $M^*$ , associated with the translations is determined by [1]

$$M^{*} = \frac{1}{1 - \frac{1}{n_{H}} \sum_{j=1}^{3N-6} \frac{n_{H}}{k=1}} = 15.04.$$
(15)

which gives  $M^* = 15.04$  neutron masses. The mass  $M^*$  associated with the rotations and translations differs from the effective mass introduced by KRIEGER and NELKIN [9], which turns out to be 21.3 neutron masses. The behaviour exhibited in Fig. 1 is what one expects on the basis of qualitative physical considerations.

In Fig. 2 the total scattering cross-section per hydrogen atom bound in benzene is compared with the preliminary experimental values obtained by



Fig.2

Total cross-section at 300°K per hydrogen atom bound in benzene.

PAULI and ANTONINI [10]. The temperature is again 300°K. The agreement between theory and experiment is generally quite good. The low value for the calculated cross-section at 0.003 eV is attributed to errors in the computation procedure. Further investigation of the long wave length cross-section is being carried out. In this connection we remark that at sufficiently low energies the measured cross-section should be proportional to the wave length  $\lambda$ . Because of the large mass of benzene, however, one must go to energies much smaller than 0.001 eV before one reaches the region where the  $\lambda$  law is valid. The same statement applies to other heavy molecules.

In Fig. 3 the total scattering cross-sections per hydrogen atom bound in benzene at three different temperatures ( $300^{\circ}$ K,  $600^{\circ}$ K and  $900^{\circ}$ K) are plotted. The influence of the Doppler effect is evident at low energies. Here, however, we do not know of any experimental results with which to compare.



Total scattering cross-section per hydrogen atom bound in benzene at different temperatures.

## III. SCATTERING LAW PER HYDROGEN ATOM BOUND IN BENZENE

We now turn our attention to a more detailed study of the Scattering Law for hydrogen atoms bound in benzene. The differential energy transfer cross-section, Eq. (1), can be written as

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d} \mathrm{E} \mathrm{d} \Omega} = \frac{K}{K_0} \frac{\sigma_b}{4\pi} \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d} t \, \mathrm{e}^{\mathrm{i} \epsilon t} \, \chi(\underline{\kappa}, t) \, . \tag{16}$$

It is a function of  $E_0$ , E,  $\theta$ , T, which are, respectively, the incident neutron energy, the final neutron energy, the scattering angle in the laboratory system and the temperature of the scatterer (measured in units of energy). The dependence on T and on the physical state of the scatterer is contained in  $\chi(\underline{\kappa}, t)$ . By applying the condition of the detailed balance and introducing the new dimensionless variables [11, 12],

$$\boldsymbol{\alpha} = \frac{(K^2 + K_0^2 - 2\sqrt{KK_0} \cos \theta)}{2MT} = \frac{\kappa^2}{2MT}$$

$$\boldsymbol{\beta} = \frac{\mathbf{E} - \mathbf{E}_0}{T} = \frac{\boldsymbol{\epsilon}}{T} , \qquad (17)$$

where M is the mass of the atom in units of neutron mass, one gets from Eq. (16)

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d} \mathrm{E} \mathrm{d} \Omega} = \frac{\mathrm{K}}{\mathrm{K}_0} \,\mathrm{e}^{-\beta/2} \,\frac{\sigma_\mathrm{b}}{4\pi\mathrm{T}} \,\mathrm{S}(\alpha,\beta) \,, \tag{18}$$

where the dimensionless quantity  $S(\alpha, \beta)$  is the Scattering Law.

Let us now construct the expression of  $S(\alpha, \beta)$  on the basis of the theoretical model for the scattering by benzene described in Section I. For this purpose we start by approximating  $\chi(\underline{\kappa}, t)$ , defined by Eq. (13), as a product of two terms, i.e. as

$$\chi(\underline{\kappa}, t) = \chi_{R,T} (\underline{\kappa}, t) \chi_{V}(\underline{\kappa}, t)$$
(19)

where  $\chi_{R,T}$  ( $\underline{\kappa}$ , t) and  $\chi_V(\underline{\kappa}$ , t) are associated, respectively, with the rotations and translations and with the vibrations. Now we may approximate the factor  $\chi_{R,T}$  ( $\underline{\kappa}$ , t) by means of the short collision time approximation, at the same time making the "phonon" expansion of the factor  $\chi_V(\underline{\kappa}, t)$ . Under these assumptions, we obtain

$$\chi_{R,T}(\underline{\kappa},t) = \exp\left[\frac{\kappa^2}{2M^*}(it - Tt^2)\right];$$

$$\chi_{V}(\underline{\kappa},t) = \exp\left\{\frac{\kappa^2}{2}[\gamma(t) - \gamma(0)]\right\},$$
(20)

where  $M^*$ , the mass associated with the rotations and translations, was evaluated in a first approximation in Section II, and

$$\gamma(t) = \overline{\langle \underline{e}_{\underline{\kappa}} \Gamma_{kk}(t) \underline{e}_{\underline{\kappa}} \rangle}$$
$$= \frac{1}{3} \sum_{j=1}^{3N-6} g_{j}(t) \frac{1}{n_{H}} \sum_{\Sigma}^{n_{H}} \left( C_{j}^{(k)} \right)^{2}$$
$$= \frac{1}{3} \sum_{j=1}^{3N-6} A_{j}g_{j}(t)$$
(21)

with  $g_i(t)$  given by Eq. (6).

The "phonon" expansion for the function  $\chi_{V}(\underline{\kappa},t)$  consists simply in setting

$$\chi_{V}(\underline{\kappa}, t) \simeq \exp\left[-\frac{\kappa^{2}}{2}\gamma(0)\right] \left[1+\frac{\kappa^{2}}{2}\gamma(t)+\ldots\right]$$
 (22)

Introducing the first of Eqs. (20) and Eq. (22) (in which only the first two terms of the "phonon" expansion are indicated) into Eq. (16), making use

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of Eqs. (17) with M = 1 and separating the result of the integration as in Eq. (18), we obtain for the function  $S(\alpha, \beta)$  the expression

$$S(\alpha,\beta) = \sqrt{\frac{M^*}{4\pi\alpha}} \exp\left[-\frac{M^*}{4\alpha} \left(\frac{\alpha^2}{M^{*2}} + \beta^2\right)\right] \exp\left[-\gamma(0)T\alpha\right]$$

$$\left[1 + \frac{2T\alpha}{3} \sum_{j=1}^{3N-6} \frac{A_j}{\omega_j} \frac{e^{-\frac{1}{2}\frac{\omega_j}{T}} \left[\frac{M^*}{2\alpha} \left(\frac{\omega_j}{T}\right) - 1\right]}{e^{\frac{\omega_j/T}{T}} - 1} \cosh\left(M^*\frac{\beta}{\alpha} \frac{\omega_j}{2T}\right) + \dots, \right\} (23)$$

which can be written in a more compact form as

$$S(\alpha,\beta) = S_{C}(\alpha,\beta) e^{-\gamma(0)T\alpha} [1 + C(\alpha,\beta)].$$
 (24)

 $S_{G}(\alpha, \beta)$  is the Scattering Law for an ideal monoatomic gas having mass M\*. The factor exp  $[-\gamma(0)T\alpha]$  is the Debye-Waller factor associated with the vibrations. One had at 300°K [1]

$$\gamma(0) = \frac{1}{3} \sum_{j=1}^{3N-6} \frac{A_j}{\omega_j} \frac{e^{\omega_j/T} + 1}{e^{\omega_j/T} - 1} = 20.19.$$
 (25)

 $C(\alpha, \beta)$  depends on both the vibrations and the mass M\* associated with the rotations and translations. In Eq. (23) we explicitly exhibit only the terms representing zero and one-quantum transitions. In the actual computations, however, all transitions which contribute significantly to  $S(\alpha, \beta)$  are taken into account.

In Fig. 4 we compare the theoretical results for a benzene gas with the room temperature data taken by BRUGGER [3] for solid Santowax-R. For comparison, we also give  $S(\alpha, \beta)$  for a monoatomic hydrogen gas.

#### DISCUSSION

For all values of  $\beta$  which we have considered, the theoretical  $S(\alpha, \beta)$  curves for free benzene molecules agree reasonably well for  $\alpha \geq 2$  with Brugger's room temperature data on Santowax-R. The disagreement that persists for  $\alpha \leq 2$  is to be expected. For such low values of  $\alpha$ , the Scattering Law is much more sensitive to the differences in the solid Santowax-R and the gaseous benzene that we have considered.

It would be interesting to compare the model considered in this paper with the liquid Santowax-R data that exists at temperatures above room temperature, and with liquid benzene Scattering Law data which does not yet exist in any great quantity. Such comparisons are currently being undertaken.

We conclude by remarking that the theory just presented appears to be sufficiently realistic and accurate to account for the thermalization of neutrons in organic-moderated reactors. This is expected to be the case since.



Fig.4

Scattering Law at 300°K for benzene.

the neutron spectrum in a reactor is not very sensitive to the behaviour of  $S(\alpha, \beta)$  in the region of  $\alpha (\alpha \leq 2)$  where our theory has difficulty. This expectation is borne out by the accuracy with which we can calculate such integral properties as the total cross-section. A more realistic treatment, including liquid and solid state effects, is required to understand the measured  $S(\alpha, \beta)$  curves at low values of  $\alpha$ .

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# ИССЛЕДОВАНИЕ НЕУПРУГОГО РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ НА НЕКОТОРЫХ ВОДОРОДОСОДЕРЖАЩИХ ВЕЩЕСТВАХ

## М.Г. ЗЕМЛЯНОВ и Н.А.ЧЕРНОПЛЕКОВ ОРДЕНА ЛЕНИНА ИНСТИТУТ АТОМНОЙ ЭНЕРГИИ ИМ. И.В. КУРЧАТОВА АКАДЕМИИ НАУК СССР, МОСКВА СССР

#### Abstract — Résumé — Аннотация — Resumen

A STUDY OF COLD NEUTRON INELASTIC SCATTERING ON CERTAIN HYDROGENOUS SUBSTANCES. Working with a beryllium filter for separating the spectral line of cold neutrons, and using the time-of-flight method, the authors studied the spectrum of inelastically-scattered cold neutrons in benzene, diphenyl and in irradiated and non-irradiated polyethylene.

The results obtained are compared with the results of optical measurements.

ÉTUDE DE LA DIFFUSION INÉLASTIQUE DES NEUTRONS FROIDS DANS CERTAINES SUBSTANCES CON-TENANT DE L'HYDROGÈNE. Les auteurs ont étudié, par la méthode de la mesure du temps de vol, le spectre de diffusion inélastique des neutrons froids dans le benzol, le diphényle et le polyéthylène irradié et non irradié, en utilisant un filtre de béryllium pour mieux faire apparaître la bande spectrale de ces neutrons.

Ils comparent les données obtenues aux résultats des mesures optiques.

ИССЛЕДОВАНИЕ НЕУПРУГОГО РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ НА НЕКОТОРЫХ ВОДОРОДОСОДЕРЖАЩИХ ВЕЩЕСТВАХ. При помощи бериллиевого фильтра для выделения спектральной линии холодных нейтронов и метода времени пролета быд исследован спектр неупруго рассеянных холодных нейтронов на бензоле, аифениле, облученном и необлученном полиэтилене.

Полученные данные сравниваются с результатами оптических измерений.

ESTUDIO DE LA DISPERSIÓN INELÁSTICA DE NEUTRONES FRÍOS EN ALGUNAS SUSTANCIAS HIDRO-GENADAS. Los autores utilizaron un filtro de berilio que permite poner de relieve la raya espectral correşpondiente a los neutrones fríos, para estudiar por el método del tiempo de vuelo el espectro de los neutrones lentos dispersos inelásticamente en el benceno, el difenilo y el polietileno irradiado y sin irradiar.

Comparan los datos obtenidos con los resultados de las mediciones ópticas.

#### 1. ВВЕДЕНИЕ

Исследование неупругого рассеяния холодных нейтронов на водородосодержащих веществах - бензоле, дифениле и полиэтилене представляет двоякий интерес. С одной стороны, полифенилы и полиэтилен приобретают все возрастающее значение как материалы замедлителей в реакторостроении, и решение задачи термализации нейтронов в указанных веществах требует прямого исследования процессов неупругого взаимодействия. С другой стороны, изучение неупругого рассеяния холодных нейтронов веществом открывает новые возможности для получения дополнительной информации о спектре возбуждений, т.е. о динамике вещества, и для ряда водородосодержащих веществ (предельные, непредельные и ароматические углеводороды) получение такой информации имеет большое практическое и теоретическое значение. До последнего времени динамика указанных веществ исследовалась, главным образом, как по измерению температурной зависимости их теплоемкости, так и спектров поглощения инфракрасного излучения и спектров комбинационного рассеяния. Однако, как известно, данные по температурной зависимости теплоемкости не позволяют проводить однозначное восстановление спектра колебаний бозе-системы, а в оптических измерениях исследованию и интерпретации подвергаются, главным образом, высокоэнергетические переходы, отвечающие внутри молекулярным движениям. Изучение низкоэнергетических переходов, отвечающих межмолекулярным движениям, оптическими методами затруднено, причем это связано как с аппаратурными, так и принципиально физическими причинами. Поэтому исследование неупругого рассеяния нейтронов на водородосодержащих веществах представляет большой интерес, особенно в области малых энергий.

При этом следует отметить особенности информации, которую несет спектр нейтронов, рассеянных неупруго на углеводородных соединениях. Поскольку в состав рассматриваемых соединений входят атомы Н и С, сильно различающиеся по массе и амплитудам рассеяния нейтронов, то казалось бы, информация об оптической части спектра колебаний должна быть более достоверной, так как сечение взаимодействия с водородом больше, чем с углеродом, и водород принимает участие в основном в оптических колебаниях. В противоположном направлении действует фактор заселенности уровней (фактор Больцмана), который приводит к тому, что больше возбуждены, например, акустические колебания и, следовательно, сечение неупругого взаимодействия с ними выше. Кроме того, необходимо отметить, что использование экспериментальных результатов для решения обратной задачи восстановления спектра колебаний по спектру неупруго рассеянных нейтронов для углеводородов невозможно. Оно невозможно из-за незнания а priori соотношения между векторами поляризации  $ar{l}_{lpha}(ar{r})$  для различных колебаний, входящих в общее выражение для сечения неупругого рассеяния [1] :

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}\epsilon} \sim \mathrm{e}^{-2w} \sum_{\alpha} \int \frac{\mathrm{d}^{3}f}{\mathrm{e}^{\frac{\pi}{\hbar}\omega_{\alpha}(f)/k\,T} - 1} \frac{|\kappa\,I_{\alpha}\left(f\right)|^{2}}{\omega_{\alpha}\left(f\right)} \,\delta\left[\vec{\epsilon} - \hbar\omega_{\alpha}(\vec{f})\right].$$

Поскольку на векторы поляризации наложено единственное ограничение  $\sum | \bar{I}_{\alpha}(\bar{f}) |^2 = 1$ . Следовательно, для установления спектра

колебаний из нейтронного эксперимента необходимо привлечение модельных представлений о динамике углеводородов. Поэтому анализ экспериментальных данных по неупругому рассеянию холодных нейтронов на бензоле, дифениле и облученном и необлученном полиэтилене будет ограничен качественным сравнением с результатами оптических исследований и результатами теоретических работ.

## 2. ПРОВЕДЕНИЕ ЭКСПЕРИМЕНТА И ВВЕДЕНИЕ ПОПРАВОК

Измерения неупругого рассеяния холодных нейтронов на образцах бензола, дифенила, необлученного и облученного полиэтилена было выполнено в ИАЭ им. И.В. Курчатова на установке, смонтированной на реакторе ИРТ-1000 [2]. Первичная линия холодных нейтронов выделялась с помощью фильтра из поликристаллического Ве, анализ рассеянных нейтронов проводился под углом 90° к падающему пучку по времени пролета с помощью механического прерывателя и 128-канального временного анализатора. Образцы с

толщиной 0,1 см устанавливались под углом 45° к падающему пучку, их температура составляла 20°С. Для обеспечения максимального

разрешения нейтронного спектрометра  $\frac{\Delta \epsilon}{\epsilon} = 6 + 7\%$  весь исследован-

ный интервал энергий рассеянных нейтронов от  $5 \cdot 10^{-3}$  до  $2 \cdot 10^{-2}$  эв разбивался на 5 участков, каждый из которых изучался при соответствующих скоростях вращения механического прерывателя, временных задержках на магнитострикционных линиях, ширинах каналов временного анализатора и т. д. После учета искажений, вносимых функцией пропускания механического прерывателя, данные по отдельным сериям измерений на основании показаний мониторов "сшивались"друг с другом. Затем в полученные результаты вводились поправки на отклонение эффективности детектора от закона 1/v и на ослабление рассеянных нейтронов воздухом, находящемся между прерывателем и детектором. Поправка на деформацию образцом спектра падающих и рассеянных нейтронов не вводилась, так как для углеводородов она мала. Действительно, выражение для измеряемого спектра после интегрирования по толщине образца имеет вид:

$$I(\lambda_{0}, \lambda) = I_{0}(\lambda_{0}) \frac{d^{2}\sigma(\lambda_{0}, \lambda)}{d\Omega d\lambda} - \frac{1 - \exp\left\{-\sqrt{2} N\left[\sigma_{t}(\lambda_{0}) + \sigma_{a}(\lambda)\right] d\right\}}{\sqrt{2} N\left[\sigma_{t}(\lambda_{0}) + \sigma_{a}(\lambda)\right]}$$

где  $J_0(\lambda_0)$  - спектральная линия холодных нейтронов;

 $\frac{d^2\sigma(\lambda_0,\lambda)}{d\Omega d\lambda}$  - сечение неупругого рассеяния;

 $\sigma_t(\lambda_0)$  - полное сечение для холодных нейтронов;

$\sigma_a(\lambda)$	- сечение поглощения для рассеянных нейтронов;
N	- плотность ядер;
đ	- толщина образца.

При предположении, что  $J_0(\lambda_0) = \delta(\lambda_0 - \lambda cp)$  и толщине образца ~ 0,1 см, поправкой можно пренебречь, так как  $\sigma_t(\lambda_0) \gg \sigma_a(\lambda)$  и 1 » exp  $\{-\sqrt{2} N [\sigma_t(\lambda_0) + \sigma_a(\lambda)]d\}$ .

## 3. РЕЗУЛЬТАТЫ ИЗМЕРЕНИЙ И ОБСУЖДЕНИЕ

a) Бензол. Молекула бензола является одной из простейших многоатомных циклических молекул, и поэтому ее спектр как в конденсированном состоянии, так и в парах подробно исследовался

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теоретически и экспериментально. Эта молекула принадлежит к точечной группе D<sub>64</sub>, для которой справедлив альтернативный запрет, т.е. частоты, проявляющиеся в комбинационном спектре, должны отсутствовать в инфракрасном спектре и наоборот. Известно, что для центросимметричных молекул могут существовать переходы, запрещенные как в инфракрасном спектре, так и в комбинационном. В случае молекулы бензола рассчитано девять таких неактивных основных частот, полученных из симметрии молекулы, которые однако в эксперименте непосредственно не наблюдались. В связи с этим следует ожидать, что нейтронноскопические исследования спектра бензола должны обнаружить такие запрещенные энергетические переходы.



Рис.1

#### Спектр нейтронов, рассеянных на жидком бензоле.

На рис.1 представлен спектр нейтронов, рассеянных на образце жидкого бензола при температуре 20°С, полученный в течение ~ 180 часов работы установки. Интенсивность отложена в зависимости от длины волны рассеянного нейтрона; разрешение спектрометра по времени пролета указано треугольниками, стрелками отмечено положение линий, полученных в спектрах комбинационного рассеяния и спектрах поглощения инфракрасного излучения [3,4,5].

Прежде всего следует отметить, что максимум при  $\lambda_{H} \simeq 4$  Å ( $\lambda_{H} = 3,952$  Å), соответствующий упругому рассеянию первичной линии колодных нейтронов, проявляется в спектре слабо, причем по интенсивности сравнивается со слабым максимумом в первичной линии (рис.2), соответствующим системе плоскостей Be(111).

Такое изменение в спектре, очевидно, объясняется тем, что в жидком бензоле в области малых энергий имеется большая плотность уровней, связанная как с квазифононным спектром, так и с вращательными состояниями молекул, а также с наличием сильного



Спектральная линия нейтронов, фильтрованных поликристаллическим бериллием.

диффузионного движения. Поэтому сечение неупругого рассеяния холодных нейтронов оказывается сравнимым с сечением упругого рассеяния, а это приводит к размытию пика упругого рассеяния.

Далее из сравнения результатов оптических исследований со спектром неупруго рассеянных нейтронов следует, что все уровни, проявляющиеся в оптическом спектре бензола, проявились и в нейтронном. Отличие заключается лишь в том, что линии с частотами 63 и 63 см<sup>-1</sup> ( $\lambda_{\rm H}$  = 2,68 и 2,60 Å), соответствующие вращательным колебаниям вокруг плоскостной оси и оси цестого порядка, не разрешены, а линия v = 405 см<sup>-1</sup> ( $\lambda_{\rm H}$  = 1,23 Å), обычно слабо проявляющаяся в оптике, в нейтроном спектре проявилась отчетливо. Остальные запрещенные частоты (538, 1008, 1160, 1190, 1145, 1520 и 1854 см<sup>1</sup>) наблюдать не удалось из-за недостаточного разрешения установки и малой статистической точности экспериментальных результатов.

Но наряду с максимумами спектра неупруго рассеянных нейтронов, которые совпадают по положению с линиями оптических спектров, наблюдается 2 Максимума, не обнаруженные ранее оптическими методами. Это максимум при  $\lambda_{\rm H} = 1,30$  Å ( $v \simeq 360$  см<sup>-1</sup>) и очень широкий максимум при  $\lambda_{\rm H} = 2,90$  Å ( $v \simeq 50$  см<sup>-1</sup>), расположенный между уровнями вращательных колебаний вокруг плоскостных осей и оси шестого порядка.

б) Дифенил. Экспериментальный спектр неупруго рассеянных нейтронов на образце поликристаллического дифенила представлен на рис.З. Как и в случае бензола, результаты оптических исследований спектра дифенила, главным образом по деполяризации линий комбинационного рассеяния [3], указаны на рисунке стрелками. В противоположность бензолу, в нейтронном спектре дифенила резко выражена область упругого рассеяния нейтронов первичной линии



Рис.3

Спектр нейтронов, рассеянных на поликристаллическом дифениле.

 $(\lambda_{\rm H} = 3,64$  Å и 4 Å). Наклон переднего фронта основного максимума упругого рассеяния при  $\lambda_{\rm H} \simeq 4$  Å определяется только разрешением нейтронного спектрометра, и, следовательно, при температуре эксперимента, которая на 50° ниже температуры плавления дифенила диффузионное движение в дифениле практически отсутствует. Из соотношения ординат максимумов упругого рассеяния при  $\lambda_{\mu} = 3,64$  Å и  $\lambda_{\rm H} \simeq 4$  Å, которое не сильно отличается от соотношения ординат в первичной линии, можно сделать заключение, что плотность уровней в твердом дифениле в области малых энергий вблизи 10<sup>-3</sup> эв незначительна. Так же, как и в случае бензола, в спектре неупруго рассеянных на дифениле нейтронов наряду с линиями, проявляющимися в оптических спектрах, наблюдаются линии, которые в оптических спектрах отсутствуют. В спектре дифенила эти линии расположены при  $\lambda_{\rm H} = 2,23$  Å ( $\nu \simeq 104 \text{ см}^{-1}$ ) и  $\lambda_{\rm H} = 3,25$  Å ( $\nu \simeq 34 \text{ см}^{-1}$ ). На рис.З эти линии указаны стрелками со знаком (?) Хотя природа этих максимумов еще не установлена, однако, необходимо отметить, что и в оптическом и в нейтронном спектрах бензола проявляются максимумы при указанных длинах волн.

в) Необлученный и облученный полиэтилен. В качестве образцов был использован пленочный полиэтилен низкого давления со средним молекулярным весом ~60%. Один из образцов полиэтилена был облучен в реакторе интегральной дозой около 500 Мрад, что соответствует образованию > 10% спивок между цепочками полимера. Экспериментальные результаты по исмерению спектров неупруго рассеянных нейтронов на образцах полиэтилена представлены на рис.4 и на рис.5. Для удобства сравнения спектры нормированы на одинаковую интенсивность в максимуме упругого рассеяния при  $\lambda_{\rm H} \simeq 4$  и весь исследованный интервал длин волн рассеянных нейтронов разбит на две части: область от 0,7 до 1,2 Å (рис.4) и область от 1,2 до



Рис.4

Спектр нейтронов, рассеянных на облученном и необлученном полиэтилене в интервале длин волн от 0,7А до 1,2А.





Спектр нейтронов, рассеянных на облученном и необлученном полиэтилене в интервале длин волн от 1,2Å до 4,5Å.

4,5 Å (рис.5). Как и прежде, стрелками указаны положения линий, обнаруженных в оптических спектрах полиэтилена [6,7,8]. Из сравнения результатов оптических исследований со спектром неупруго рассеянных нейтронов (рис.4) можно заключить, что спектр неупруго рассеянных нейтронов в значительной степени повторяет оптический спектр, т.е. линиям поглощения инфракрасного излучения и линиям спектра комбинационного рассеяния соответствуют совпадающие в пределах разрешения максимумы нейтронного спектра.

При этом в нейтронном спектре проявляются линии, которые в оптическом спектре классифицируются как очень слабые, а для ряда близко расположенных линий оптического спектра ( $\lambda_{\mu}$  = 0, 145 + 0,780Å) из-за недостаточности разрешения нейтронный спектр дает огибарщую. Как видно из рис.4 в интервале длин волн рассеянных нейтронов от 0,7 до 1,2 Å не наблюдается заметного различия между спектрами необлученного и облученного полиэтилена и нейтронного спектра с оптическим. Такое отличие проявляется в области больших длин волн рассеянных нейтронов с  $\lambda_{\mu}$  > 1,2Å (рис.5). В этой области обращает на себя внимание переход от упругого рассеяния (максимумы при  $\lambda_{\rm H} = 4$  и 3.64 Å) к неупругому рассеянию. Отношение интенсивностей упругого рассеяния к неупругому составляет 3:1. Такое соотношение говорит о том, что как в облученном, так и в необлученном полиэтилене имеется значительная плотность уровней в области малых энергий, связанных возможно с вращением сегментов полимерных цепей. Этот результат находится в согласии с результатами исследования линий ядерного магнитного резонанса на полиэтилене, где для объяснения малой ширины экспериментально наблюдаемых линий приходится предполагать наличие в полиэтилене системы низкоэнергетических уровней [9].

В упоминавшихся работах по исследованию оптических спектров полиэтилена имеются указания на обнаружения слабых линий с частотами ~150 см<sup>-1</sup> и ~200 см<sup>-1</sup> (соответствующие  $\lambda_{\rm H} = 1,94$  и 1,71Å). Как видно из рис.5, в нейтронном спектре необлученного и облученного полиэтилена проявляются два максимума, которые можно считать совпадающими в пределах разрешения с результатами оптических исследований. Это линии при  $\lambda_{\rm H}=2,04$  Å и  $\lambda_{\rm H}=1,78$  Å (оптические частоты v ≈ 135 и v ≈ 184 см<sup>-1</sup>. Однако структура нейтронных спектров более сложная. В этой связи представлялось бы желательным провести сравнение результатов нейтронного исследования спектра полиэтилена в рассматриваемой области длин волн с теоретическими работами по динамике высокоанизотропных цепочечных материалов, которые используются для объяснения температурной зависимости теплоемкости [10,11]. Однако, модель полиэтилена, положенная в основу теоретического анализа работы [10], в которой истинная структура кристаллических областей полиэтилена приближается тетрагональной решеткой, не учитывается наличие аморфной фазы и решения динамической матрицы неустойчивы по отношению к выбору силовых постоянных, далека от действительности. Следовательно, сравнение данных нейтронного эксперимента с этой теорией не представляется убедительным.

В спектре неупруго рассеянных нейтронов при  $\lambda_{\rm H} > 1,2$  наряду с линиями при  $\lambda_{\rm H} = 2,04$  и  $\lambda_{\rm H} = 1,78$  Å проявляется еще ряд максимумов: отчетливый максимум при  $\lambda_{\rm H} = 1,51 \, {\rm \AA} \, (v \simeq 264 \, {\rm cm}^{-1})$  и в облученном и в необлученном полиэтилене, и максимумы при λн = 2,20 и λ<sub>н</sub> = 2,94Å, которые более отчетливо проявляются в спектре необлученного полиэтилена. В спектре облученного полиэтилена проявляется также слабый максимум при 2,63 Å (v = 64 см<sup>-1</sup>). В какой степени указанные максимумы связаны с особенностями (сингулярностями) фононного спектра полиэтилена по результатам данного эксперимента, судить трудно. Что же касается различия в спектре неупруго рассеянных нейтронов на необлученном и облученном полиэтилене, то как видно из рис.4 и 5, значительного различия в этих спектрах нет. Наблюдаются лишь слабые расхождения между спектрами, которые проявляются лишь в длинноволновой части спектра и требуют, по-видимому, более детального исследования.

## ЗАКЛЮЧЕНИЕ

В результате исследования спектров неупруго рассеянных нейтронов на образцах бензола, дифенила, необлученного и облученного полиэтилена при температуре 20°С, установлено наличие в нейтронных спектрах указанных веществ ряда особенностей, не проявляющихся в их оптических спектрах. Уточнение энергетического положения этих особенностей и установление их природы требуют, с одной стороны, увеличения разрешения нейтронного спектрометра по времени пролета и значительного сужения первичной спектральной линии холодных нейтронов, с другой стороны, проведения измерения спектра неупруго рассеянных нейтронов при различных температурах выше и ниже температуры плавления и температуры Т<sub>л</sub>.

Авторы выражают признательность М.И. Певзнеру за постоянный интерес к работе и участие в обсуждении результатов, Шавкутенко Г.Ф., Комарову М.А. и Игнашеву А.С. за помощь в проведении эксперимента.

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## DISCUSSION

D. T. GOLDMAN : Your results on polyethylene were very interesting, mainly because so little detailed work on neutron scattering has been done on this substance. You have concentrated on the acoustical energy region, and this is actually the most important one from the chemical point of view because it has been shown that the specific heat as a function of temperature is most sensitive to the acoustical vibrations for a good portion of the range, whereas the optical vibrations do not make a contribution until you get to rather high temperatures, or at least to room temperatures and above. It would therefore be very interesting if these measurements could also be performed at higher energies where the neutron scattering would give information on the optical scattering and verify the very few optical measurements now being made.

N. A. TCHERNOPLEKOV: I do not quite agree with you. On the assumption that polyethylene can be considered as a crystal, we have indeed made measurements with regard to the optical mode - I am referring here to the optical range of atomic vibrations - and the results have been included in our curves. However, I do not think it is worthwhile using neutrons for the study of this region because they cannot compete with the old and reliable optical methods. I agree with you, of course, that the study of this lower part, where neutrons are most advantageous, is very interesting, but unfortunately the amount of information we have received in this way is as yet small. We shall have to improve our methods of study considerably.

# INELASTIC SCATTERING OF THERMAL NEUTRONS FROM DOWTHERM "A"

## W. GLÄSER

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### Abstract — Résumé — Аннотация — Resumen

INELASTIC SCATTERING OF THERMAL NEUTRONS FROM DOWTHERM "A". The angular and energy distributions of neutrons scattered from room temperature samples of Dowtherm "A" have been measured using a few different initial neutron energies in the range from  $10^{-2}$  to  $10^{-1}$  eV.

The experiment has been performed with a rotating crystal spectrometer as pulsed monoenergetic beam source and a  $16 \times 256$  - channel time analyser for timing of the scattered neutrons. With this arrangement data for several angles have been taken simultaneously.

Results are represented in the form of differential cross-sections and also in the "Scattering Law" form. Physical interpretation with the aid of the space-time correlation function of Van Hove is discussed.

DIFFUSION INÉLASTIQUE DE NEUTRONS THERMIQUES PAR LE DOWTHERM "A". L'auteur a mesuré la distribution angulaire et le spectre d'énergie de neutrons diffusés par des échantillons de Dowtherm "A" à la température ambiante, en employant des neutrons dont l'énergie incidente variait de  $10^{-2}$  à  $10^{-1}$  eV.

L'expérience a été faite à l'aide d'un spectromètre à cristal toumant, employé comme source monoénergétique pulsée, et d'un analyseur en temps de  $16 \times 256$  canaux. Ce dispositif a permis de recueillir simultanément des données pour différents angles.

Les résultats sont présentés sous la forme de sections efficaces différentielles et aussi sous la forme d'une loi de diffusion. L'auteur discute l'interprétation physique de ces résultats à l'aide de la fonction de corrélation spatiotemporelle de Van Hove.

НЕУПРУГОЕ РАССЕЯНИЕ ТЕПЛОВЫХ НЕЙТРОНОВ ДОУТЭРМОМ "А". Угловые и энергетические распределения нейтронов, рассеянных образцами доутэрма "А" при комнатной температуре, были измерены при различных исходных энергиях нейтронов в пределах от 10<sup>-2</sup> до 10<sup>-1</sup> эв.

Опыт приводился на спектрометре с вращающимся кристаллом, который представляет собой источник пульсирующего монознергетического пучка и временной многоканальный анализатор 16 х 256 для определения времени пролета рассеянных нейтронов. Одновременно с этим были получены данные для нескольких углов рассеяния.

Результать представлены в виде дифференциальных сечений, а также в виде "закона рассеяния". Обсуждается их физическая сущность и согласование с пространственной временной функцией Ван Гофа.

DISPERSIÓN INELÁSTICA DE NEUTRONES TÉRMICOS POR EL DOWTHERM "A". El autor ha medido la distribución angular y energética de neutrones dispersados por muestras de Dowtherm "A" a temperatura ambiente, para una serie de energías iniciales de los neutrones comprendidas entre 10<sup>-2</sup> y 10<sup>-1</sup> eV.

El experimento se ha realizado con un espectrómetro de cristal rotativo, que se ha utilizado como fuente pulsada de haz monoenergético, y un analizador de tiempo de 16 × 256 canales para el cronometraje de los neutrones dispersados. Con este dispositivo, se han obtenido simultáneamente datos correspondientes a diferentes ángulos.

El autor expone los resultados en forma de secciones eficaces diferenciales y también en forma de "ley de dispersión". Estudia la interpretación física del fenómeno con ayuda de la función de correlación espaciotiempo de Van Hove.

## I. INTRODUCTION

In the past few years considerable effort has been spent on measuring the influence of chemical binding on the scattering of slow neutrons. In this

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way much information about many-particle systems such as solids, liquids and gases has become available.

The information about scattering behaviour is of primary interest for reactor physics because the binding effects determine the slowing down of neutrons in the energy region where the spectrum shape is most important. Data of moderators like  $H_2O$ ,  $D_2O$ , graphite, beryllium and terphenyl have been measured with the phased-rotor systems at Chalk River and Idaho Falls [1, 2].

Of similar interest for organic moderated and cooled reactors are the chemical compounds diphenyl, diphenyloxyd and the eutectic mixture of both called Dowtherm "A".

In continuing the series of experiments with moderators several samples of Dowtherm "A" and diphenyl have been studied using a rotating crystal time-of-flight spectrometer. The selected materials have the advantage of easy handling and of being primarily incoherent scatterers.

A few incident neutron energies, 0.019, 0.032 and 0.079 eV have been used. For each energy the scattered intensities were taken simultaneously at several angles. Usually the seven detector angles 20°, 40°, 60°, 70°, 80°, 100° and 120° were realized. Examples of results are presented as raw data and in the converted form as differential scattering cross-section per solid angle and time-of-flight. Results as far as now available are also represented in the well known scattering law form  $S(\alpha, \beta)$ .  $S(\alpha, \beta)$  [3] is different from the function  $S(\kappa, \omega)$  defined by VAN HOVE [4]. Energy change is measured in units of  $K_BT$ ,  $\beta = \hbar\omega/K_BT$ , where  $\hbar\omega$  is the energy change and  $K_BT$  is the temperature of the sample in energy units. Momentum transfer is represented by  $\alpha = \hbar^2 \kappa^2 / 2M K_B T$ , where  $\kappa = \kappa - \kappa_0$  is the difference of initial and final wave vector of the neutron and M is the mass of the principal scattering nucleus. Furthermore the detailed balance factor is extracted with the consequence that  $S(\alpha, \beta)$  is even in  $\beta$ .

The determination of the generalized frequency distribution  $p(\beta)$  proposed by EGELSTAFF [5] was tried.

#### II. EXPERIMENTAL ARRANGEMENT

#### Apparatus

Bursts of monoenergetic neutrons have been producted with a rotating crystal using a neutron beam from the reactor Diorit at Würenlingen. A preliminary description of the spectrometer has been given earlier [6]. The general layout is shown in Fig.1. The rotating single crystal fulfills two tasks. Firstly, due to the Bragg reflection at the planes of the crystal it produces monoenergetic neutrons in a selected direction and secondly, due to its spinning, it chops the beam and delivers short pulses for the timeof-flight measurements. The present measurements are done with a copper crystal usually spinning at 14 200 rpm, using two (111) reflections per revolution. The advantages of this device are its simplicity, the fact that there is almost no time-dependent background and the possibility of using several incident energies simultaneously. Principally the last feature allows to take all information needed for scattering law calculations in one single run.





Schematic diagram of the rotating crystal spectrometer at the reactor Diorit, Würenlingen, Switzerland.

In scattering experiments the sample position was 2.65 m behind the crystal. For a primary energy of 0.032 eV the pulse width at this position was  $22\,\mu\text{s}$  and the intensity about  $1.5\cdot10^3$  n/cm<sup>2</sup>s. The performance of the machine was tested continuously with two BF<sub>3</sub> monitors in the monochromatic beam. One was a short distance in front of the sample and the other 2 m behind it. With these monitors energy, resolution and intensity of the incoming neutrons could also be measured.

The scattered neutrons are detected with a set of 5 in diam. scintillation counters positioned at a distance of 2 m from the sample and at angles of  $20^{\circ}$ ,  $40^{\circ}$ ,  $60^{\circ}$ ,  $70^{\circ}$ ,  $80^{\circ}$ ,  $100^{\circ}$  and  $120^{\circ}$  with respect to the monoenergetic beam. The signals of each detector were fed into a group of 256 channels of a 4096-channel magnetic core time sorter, using  $8 \mu s$  channel width. The detector efficiencies have been determined by scattering from vanadium.

## Scattering samples

For liquid Dowtherm "A" sample containers consisting of an aluminum frame 0.06 cm thick covered with 0.03 cm thick windows of aluminum have

been made. The surface of the sample was 5 cm broad and 15 cm high, so that the full beam cross-section could be used. The transmissions of our samples varied between 90 and 75% for different incident energies and different horizontal inclinations to the beam. Diphenyl which is solid at room temperature was heated slightly above melting point and cast in a similar frame.

## **III. MEASUREMENTS AND RESULTS**

Before scattering runs were started, a flux map at the sample position was taken and the detector efficiencies were determined. Usually 20-h runs, 10 h for sample in and 10 h for background, were made. Fig.2 shows the results of a typical sample and background run.



Raw scattering curves for an incident energy of 0.079 eV and seven scattering angles. These data were obtained in 20 h. 10 h for sample in and 1 h for background.



The principal steps in conversion of the experimental data.

Memory content of the time analyser was punched on paper tape. This tape was fed directly into a computer. A computer programme has been written with which the data were normalized for equal initial intensity and, if necessary, also for equal background at small and large neutron velocities. Then data were converted to differential scattering cross-sections and finally to the scattering law form  $S(\alpha, \beta)$ . These steps are demonstrated in Fig.3 for the results at an angle of 70° and an energy of 0.032 eV. No smoothing of the statistics and no corrections for the finite energy resolution have been done. The S-values as far as now available are shown in Fig.4 and 5. In these diagrams the results of two incident energies and seven different scattering angles are plotted for fixed  $\beta$ -values as parameters. This kind of plot is a good check of the reliability of the data.


Scattering law for Dowtherm "A" at room temperature represented per molecule.

## IV. DISCUSSION AND CONCLUSIONS

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No significant differences between the room temperature scattering data for Dowtherm "A" and diphenyl have been observed. The diphenyl crosssections are somewhat higher for  $\beta = 0$  and decrease more rapidly with increasing  $\beta$ -s for small  $\beta$ -s. Also there is no clear indication of resonance bands in the data.

The exact way to determine the space-time self-correlation function  $G_s(\mathbf{r}, t)$  of Van Hove is to make double Fourier transformations of the measured differential scattering cross-sections. Because we have measured only a limited range of energy and momentum transfers the results of such transformations would be doubtful. Instead we have tried the method of Egelstaff



Scattering law for diphenyl at room temperature.

to extrapolate  $S/\alpha$  to  $\alpha = 0$  for different fixed  $\beta$ . Multiplication of the limit  $[S/\alpha]_{\alpha=0}$  with  $\beta^2$  yields a generalized frequency distribution  $p(\beta)$  which is directly related to the velocity correlation function of the system. There is a fair agreement between solid and liquid data. The curves also show two peaks. In the region of the last peak several infra-red absorption bands have been found. But at present the uncertainties of the most points are too large as to draw more serious conclusions.

Measurements at other initial energies are in progress and measurements with higher temperatures are planned.

## ACKNOWLEDGEMENTS

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## DISCUSSION

W. KLEY: I do not quite understand your technique of obtaining background data by removing the scattering sample from the impinging beam. We have found that if the sample is taken out of the beam the fast neutron background is also removed and therefore cannot be detected.

W. GLASER: I can only say that this is the usual technique for measuring background in other time-of-flight experiments as well. In background measurements account must of course be taken of the empty sample container in the beam. The monochromatic beam is a very pure one, so there is only a very small fast neutron background. We have made corrections for differences in sample background in the beam and outside it.

B. N. BROCKHOUSE: One of the attractive features of the rotating crystal spectrometer used by Dr. Gläser is that the fast neutron background is time-independent, so that a variety of ways are available for dealing with it.

W. KLEY: Yes, but with the technique described by Dr. Gläser you not only produce thermal-neutron pulsed beams but you also get a continuous background of fast neutrons. When you put the sample in the pulsed beams, you have the continuous background of fast neutrons which is then seen by the detector as long as the sample is in the beam. When you take the sample out, you remove the fast neutron background.

W. GLÄSER: That is true, but there will be a difference between these two sorts of background and since the background is not time-dependent you can make a very good correction for these effects. The results would be somewhat better than with a fast-chopper system for example.

P.K. IYENGAR: I think Dr. Kley's point is that you could have cut the beam, say with a cadmium shield, and then have taken the background, which would include the fast neutron effects.

B. N. BROCKHOUSE: I think it would be appropriate at this point to present a brief report on work which has been done by my colleague L. N. Becka on rotational transition in cyclohexane.

A number of "globular" organic compounds\*, which undergo phase changes that are believed to be of rotational nature, have been studied using the rotating crystal spectrometer\*\* at the NRU reactor at Chalk River. The

<sup>\*</sup> TIMMERMANS, J. phys. and chem. Solids, 18, (1961) 1.

<sup>\*\*\*</sup> BROCKHOUSE, B. N. "Inelastic Scattering of Neutrons in Solids and Liquids", IAEA, Vienna (1961)113.

results for cyclohexane are shown in the figure below. At 115°K, below the transition at 186°K, the patterns show strong elastic peaks and at least two inelastic peaks (at 6.2 and 10 meV). The fact that the elastic peaks for the



Fig.1

Wavelength distributions for cyclohexane at two angles and at temperatures above and below the transition.

two angles are not greatly different shows that the Debye-Waller factor is normal, and therefore that the molecule is not in rotation. At 215°K the Debye-Waller factor is greatly reduced, especially at the larger angle. Thus the proton motion is very great and the molecule is presumably in rotation. Since the two peaks also disappear, they must represent rotational levels.

Other substances studied were 2-2-dimethylbutane and 1-4-diazobicyclo-(2.2.2)-octane, with differing but interesting results. A full report is being submitted to J. chem. Phys.

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# A STUDY OF THE DIFFUSIVE ATOMIC MOTIONS IN GLYCEROL AND OF THE VIBRATORY MOTIONS IN GLYCEROL AND LIGHT AND HEAVY WATER BY COLD NEUTRON SCATTERING

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### Abstract — Résumé — Аннотация — Resumen

A STUDY OF THE DIFFUSIVE ATOMIC MOTIONS IN GLYCEROL AND OF THE VIBRATORY MOTIONS IN GLYCEROL AND LIGHT AND HEAVY WATER BY COLD NEUTRON SCATTERING. The cold neutron scattering studies of the vibrational and diffusive properties of light and heavy water have been continued at the Stockholm reactor. Vibrational "frequency spectra" have been derived from observations on heavy water up to 350°C. The damping of the molecular vibrations and rotations is very strong at the higher temperatures.

A study has been performed on the quasi-elastic and inelastic scattering from glycerine, a hydrogenous liquid showing a strong variation of its viscosity with temperature. The diffusion constants that may be deduced from the experiment are several powers of ten larger than those calculated from the Einstein - Stoke or from the Eyring formulas using the measured viscosity. The variation of line width with temperature shows a tendency opposite of that for water, which indicates that for glycerine jump diffusion might be the most important process. The broad inelastically-scattered spectrum from glycerine shows similarities to the spectra derived from the measurements on light and heavy water.

ÉTUDE DES MOUVEMENTS ATOMIQUES DE DIFFUSION DANS LE GLYCÉROL ET DES MOUVEMENTS DE VIBRATION DANS LE GLYCÉROL, L'EAU LOURDE ET L'EAU LÉGÈRE DU FAIT DE LA DIFFUSION DES NEU-TRONS FROIDS. Les auteurs ont continué les recherches entreprises au réacteur de Stockholm par la méthode de diffusion des neutrons froids sur les propriétés de diffusion et de vibration des eaux lourdes et légères. Ils ont déterminé le spectre de fréquence des vibrations à partir d'observations faites sur l'eau lourde, pour des températures allant jusqu'à 350°C. L'amortissement des vibrations et des rotations moléculaires est très intense pour les températures élevées.

Une étude a été faite sur la diffusion quasi-élastique et inélastique dans la glycérine; la viscosité de ce liquide hydrogéné varie beaucoup en fonction de la température. Les constantes de diffusion que l'on peut déduire des expériences sont de plusieurs puissances de 10 supérieures à celles que l'on obtient en employant la mesure de la viscosité dans les formules de Einstein-Stokes ou de Eyring. La variation de la largeur de la raie en fonction de la température accuse une tendance opposée à celle que l'on observe pour l'eau : elle montre que pour la glycérine, la diffusion par sauts pourrait bien être le processus le plus important. Le large spectre de diffusion inélastique dans la glycérine présente des similitudes avec les spectres découlant des mesures faites dans l'eau lourde et dans l'eau légère.

ИЗУЧЕНИЕ ДИФФУЗИОННЫХ ДВИЖЕНИЙ АТОМОВ В ГЛИЦЕРИНЕ И КОЛЕБАТЕЛЬНЫХ ДВИЖЕНИЙ В ГЛИЦЕРИНЕ И ЛЕГКОЙ И ТЯЖЕЛОЙ ВОДЕ ПРИ ПОМОЩИ РАССЕЯНИЯ ХОЛОДНЫХ НЕЙТРОНОВ. На стокгольмском реакторе были продолжены исследования вибрационных и диффузионных свойств обычной и тяжелой воды методом рассеяния холодных нейтронов. Из наблюдения над тяжелой водой при температурах до 350°С были выведены вибрационные "спектры частот". Очень онльное гашение модекудярных колебаний и вращений наблюдается при более высоких температурах.

Исследования квазиупругого и неупругого рассеяния были произведены на глицерине, т.е. содержащей водород жидкости, вязкость которой сильно изменяется в зависимости от температуры. Козффициенты диффузии, которые могут быть получены из этих экспериментов, превышают на несколько

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порядков значения, подсчитанные по формулам Эйнштейна-Стоука или Эйринга при помощи измерения вязкости. Измерения ширины спектральной линии в зависимости от температуры выявляют тенденцию, противоположную тенденции для воды, что указывает на то, что наиболее важным процессом для глицерина может быть диффузия скачками. Спектр неупругого рассеяния для глицерина несколько сходен со спектрами, полученными из опытов с дегкой и тяжелой водой.

ESTUDIO POR DISPERSIÓN DE NEUTRONES FRÍOS, DE LOS MOVIMIENTOS ATÓMICOS DE DIFUSIÓN EN GLICERINA Y DE LOS MOVIMIENTOS DE VIBRACIÓN EN GLICERINA Y AGUA LIGERA Y PESADA. Han seguido en el reactor de Estocolmo los estudios sobre las propiedades de vibración y difusión del agua ligera y pesada por dispersión de neutrones fríos. Se han determinado los "espectros de frecuencia" vibratorios basándose en las observaciones realizadas con agua pesada hasta 350°, llegándose a la conclusión de que el amortiguamiento de los movimientos vibratorios y rotatorios moleculares es muy acusado a temperaturas elevadas.

Se ha realizado un estudio sobre la dispersión cuasi elástica e inelástica por glicerina. Ifquido que contiene hidrógeno y cuya viscosidad varía considerablemente con la temperatura. Las constantes de difusión que se han podido deducir experimentalmente superan en varias potencias de diez a las calculadas según las fórmulas de Einstein-Stoke o de Eyring, utilizando la viscosidad medida. La variación de la anchura de la raya en función de la temperatura presenta une tendencia opuesta a la del agua, lo que indica que en el caso de la glicerina el proceso más importante consiste probablemente en una difusión discontinua. El espectro ensanchado de dispersión inelástica correspondiente a la glicerina presenta analogías con los espectros deducidos de las mediciones realizadas con agua ligera y pesada.

#### INTRODUCTION

Recently a considerable effort has been devoted to the study of the neutron spectrum scattered from light and heavy water. Various techniques involving the crystal spectrometer [1], the mechanical monochromator [2] and cold neutron techniques [3] have been used to collect experimental data. The reason why these two liquids have been studied experimentally in so much detail are their importance as moderators in reactors and the hope that the complete understanding of the fundamental atomic motions in these liquids would make it possible to calculate the thermal and near thermal equilibrium neutron spectrum in a reactor [4, 5]. The observed differential neutron cross-sections have, however, proved to be very complex and difficult to understand in full detail [6, 7, 8a b c]. On the time scale of about  $10^{-12}$  s within which the slow neutrons perform their interaction with the atomic motions, different kinds of either atomic or molecular motions in a hydrogenous scatterer may contribute to the scattering with different statistical weights. To elucidate these phenomena it was thought to be of great interest to investigate a hydrogenous liquid, the viscosity of which should vary very strongly with temperature. A good substance is glycerol for which the viscosity varies from 15 poise at room temperature to a few centipoise at 130°C. Accordingly the self diffusion coefficient should vary greatly over this temperature region, if the simple type of random walk formulae, like the Stoke-Einstein or the Eyring formulae, were to be valid for this case. As such a variation of the diffusive motions in an incoherently scattering liquid is advantageously studied by the neutron scattering technique an extensive study of the cold neutron scattering from glycerol was undertaken at the Stockholm reactor.

Earlier [9] a series of neutron scattering measurements on light water in a temperature range from  $-10^{\circ}$ C to  $+92^{\circ}$ C, and on heavy water from  $-10^{\circ}$ C to  $+300^{\circ}$ C, have been undertaken. These results will also be shortly discussed in this report.

## I. TECHNIQUE OF MEASUREMENT AND INTERPRETATION OF DATA

In all the measurements to be discussed here a beryllium-filtered neutron beam was used as ingoing spectrum with the idea that the sharp edge at 3.95 Å should operate as the monochromatic "line" in the study of the diffusive motions in the scatterer and the whole cold neutron spectrum as an approximation to the monochromatic beam in the study of the oscillatory motions in the scatterer. If accurate results are to be obtained in the study of line widths a careful examination of the shape of the line measured in straight transmission has to be carried out [10, 11] (compare detailed discussion on this subject carried out in the pp. 58-62 of [10], and in pp. 372-374 of [11]. Such a measurement gives all the details about the instrumental effects. As all the line width data to be discussed later to a large degree depend upon the accurate and careful interpretation of instrumental effects, a detailed discussion of the line shape studies will be given. Similarly the possible effects of the wide ingoing spectrum on the interpretation of the inelastically-scattered spectrum will be given careful attention.

### (a) Width of the quasi-elastic line

Many measurements [1, 12, 13] have shown that the effect of the diffusive motions on the ingoing neutron line is to broaden it. For many liquids like water, glycerol and liquid helium in their respective lower temperature regions this broadening is very small. The interpretation of the experimental line as a folding of two functions, the resolution and the very small natural width, depends therefore critically on the shape of the ingoing neutron line. At the other temperature end, high temperatures, the natural line width is much larger than the resolution width and the main problem here is to separate the diffusive line from the intense inelastically-scattered spectrum. Particularly for the small natural line width region it is desirable to have a high resolution.

The slow chopper time-of-flight apparatus used at the Stockholm reactor has been described in detail earlier [3]. The resolution has, however, been increased considerably by changing the detector. The detector formerly consisted of a BF<sub>3</sub> detector battery of an effective thickness of 6.5 cm. By using much thinner  $BF_3$  counters filled to twice the pressure, 1150 mm Hg, the thickness of the detector battery, now consisting of 41 counters with an effective area of  $19 \times 20$  cm<sup>2</sup> at the end of a 3 m flight path, is only 3.1 cm. The percentage time resolution dt/t, due to flight time through the detector is thus decreased from 2% to 1%. The overall resolution of the instrument is at present 20  $\mu$ s/m or 2% at 4 A. In earlier work with this apparatus the corresponding figure was  $30-40 \,\mu s/m$ . The effect of this increase of resolution is illustrated in Fig. 1a. The sharp beryllium cut-off at 3.95 Å is replaced by two, one at 3.95 Å rising to 70% of full intensity and another at about 4.05 Å corresponding to the combined crystalline cut-off's of aluminium and iron in the beam. This aluminium and iron scatters out about 30% of the neutrons from the beam in the region between 4.05 and 3.95 Å as indicated in the figure. In Fig. 1b, is given an example of the scattering picture from glycerol at 96°C and 60° angle of observation still showing the dip in the intensity at about 4 Å. Obviously only the part of the break corresponding



(a) The shape of the break region of the cold neutron spectrum observed in straight transmission. Also given is the spectrum expected for infinitely good resolution.

(b) The shape of the break region as observed in quasi-elastic scattering from glycerol at +96°C and 60° angle of observation. The definition of the observed width value is shown as the time difference between A and B.

to the 3.95 A beryllium break should be used in the interpretation of the line width. The following procedure of analysis was therefore adopted:

Each neutron energy in the theoretical neutron spectrum,  $f(E) \sim E dE$ , indicated in Fig. 1a is supposed to be broadened according to a Lorentz function,



The result of the folding of this Lorentz function and the spectrum E dE including the step at 4.05Å is a broadened break similar to the one given in Fig. 1a or b. This broadened spectrum is converted to time-of-flight scale and again folded with a resolution function assumed to be Gaussian,

$$\exp\left[-\left(\frac{t-t_0}{\Delta t_1}\right)^2\right].$$

This of course again broadens the break and again tends to smear out the step between 3.95 Å and 4.05 Å. Using an electronic computing machine a great number of theoretical line shapes were calculated for a constant resolution width  $\Delta t$  but for various values of the width  $\Delta E$  of the Lorentz function. Finally the natural line width  $2\Delta E$  could be plotted as a function of the full width of the different lines. This full width includes the widths of the  $\overline{two}$  breaks at 3.95 and 4.05 Å and is readily found from a plot of the calculated line. With the calibration curve of  $2\Delta E$  as a function of full line width the only procedure that is necessary to do in order to get the natural line width  $2\Delta E$ , from an observation like the one given in Fig.1b is to draw the tangent to the 3.952 Å part of the break and extrapolate the top part of the curve until it intersects the tangent which determine the top point (A) of the tangent. Then the inelastically-scattered spectrum is extrapolated in under the quasi-elastic "line" until this extrapolated spectrum part intersects the tangent, which determines the bottom point (B) of the tangent. At higher sample temperatures when the quasi-elastic spectrum merges into the inelastic spectrum over a wide energy region this separation becomes very difficult and puts a limit to the method of separating the inelastic and quasielastic spectra. The time distance between the top and bottom points read along the time-of-flight axis gives the full line width. Using the calibration curve,  $2\Delta E$  is then found directly. In this way a correction has been made for other scattering materials than beryllium in the beam. The remaining weak point is that a Lorentz shape is assumed for the natural line broadening.

## (b) Interpretation of the inelastically-scattered neutron spectrum

As shown by many scattering experiments on hydrogenous liquids neutrons are scattered into energy regions far from the ingoing one. An example is given in Fig. 2 where the complete scattering pictures from glycerol at temperatures of  $20^{\circ}$ C and  $130^{\circ}$ C for an angle of observation of  $60^{\circ}$  are given. The observed neutron energy gains ranges from 0 to 100 mV. Obviously the shape of the inelastically-scattered spectrum in an energy range up to about 20 mV might be affected by the width of the ingoing spectrum ranging from 0 to 5 mV with a width of about 2 mV. Above 20 mV the observed spectrum should correspond closely to the spectrum observed if all the primary neutrons were concentrated in a line at the centre of gravity of the cold neutron spectrum. To investigate the effect of the width of the primary spectrum on the shape of the inelastically-scattered spectrum one has to fall back on some model for the scattering process and calculate the scattered spectrum for different ingoing energies. As the stochastic model of a liquid developed



Fig.	2
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The complete neutron spectra scattered from glycerol at 20°C and 130°C and an angle of observation of 60°.

by RAHMAN, SINGWI and SJÖLANDER [8c] had a certain success in explaining the cold neutron scattering results on water, this model was used for the present investigation. The energy region within which this model seemed to be so relatively successful just happens to be the energy region of interest here, i.e. from 5 to 20 mV. The reason for this is that the Debye temperature of many liquids falls in the range of 0-15 mV. There is also another reason why this model is preferred for this discussion namely that it includes so many features typical of a solid. As is alredy known, and will be shown again in this paper, liquids show many properties typical of a solid when studied on a time scale of  $10^{-13}$  to  $10^{-11}$  s. To investigate what the effect of the broad ingoing spectrum might be on the shape of the inelastic spectrum in the energy transfer region 0-20 mV, this spectrum was calculated using the equation

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = a_{\mathrm{inc}}^{2}\frac{k}{k_{0}}e^{\frac{\hbar\omega}{2k_{\mathrm{B}}T}}\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{-i\omega t}e^{-\kappa^{2}}\rho(t)_{\mathrm{d}t}$$
(1)

where  $\underline{k}$ ,  $\underline{k}_0$  are the scattered and ingoing wave vectors,  $\hbar\omega$  is the energy transfer,  $\underline{\mathbf{k}} = \underline{\mathbf{k}} - \underline{\mathbf{k}}_0$ , T is the sample temperature and  $\rho(t)$  is the width function of the self correlation function. The form chosen for  $\rho(t)$  is one in which both diffusive and vibratory modes of atomic motion are represented [8c]. Effectively three constants enter into the theory for  $\rho(t)$ , namely a Debye temperature of frequency,  $\omega_{\rm D}$ , a frequency  $\omega'$  below which no vibratory modes occur and a damping factor  $\Gamma$ , which describes how fast the vibratory energy in a mode is dissipated. This same model has also been used to calculate line widths for comparison with the present experimental data on glycerol. In this way the values for the three constants  $\omega_{\rm D}$ ,  $\omega^{\rm I}$  and  $\Gamma$ , which corresponds to the best fit to the line width data, were also used to calculate the inelastically-scattered spectrum. In this theory  $\omega^{\dagger}/\omega_{D}$  is the factor which mainly determines the line width, while  $\Gamma$  determines the shape of the inelastic spectrum. For this reason computations were made for two values of  $\Gamma$  namely  $\Gamma$  = 2.0 (strong damping) and  $\Gamma$  = 0.5 (somewhat weaker damping). The values used for  $\omega_{\rm D} = 2.0 \cdot 10^{13}$  and  $\omega^{*} = 0.2 \cdot 10^{13}$  rad/s (compare the line width data to be presented later in this paper). Computations were made for three cases:

- (a) All the ingoing neutrons assumed concentrated in a line at  $\lambda = 4$  Å;
- (b) All the ingoing neutrons assumed concentrated in a line at the centre of gravity of the cold neutron spectrum  $\lambda = 4.7 \text{ Å}$ , and
- (c) The ingoing energies divided into a large number of lines in the cold neutron range and each energy weighted properly according to the shape of the ingoing cold neutron spectrum. All the contributions at a given mark on the energy transfer scale are then added.

The scattered spectra were calculated for  $30^{\circ}$ ,  $90^{\circ}$  and  $120^{\circ}$  angle of observation.

The results of this computation are given in Fig. 3. The interesting conclusion of this computation is that it does not matter if a whole cold neutron spectrum or a neutron line at the centre of gravity at 4.7 Å is used as ingoing spectrum. Another way of stating this result is, that the average value of the cross-section  $\overline{\sigma} (E \rightarrow E^{\dagger})$  for energy transfer from E to E<sup>t</sup>, where E is in the cold neutron region and E<sup>t</sup> is a fix energy in the inelastic scattering region, is to a good approximation proportional to the cross-section  $\sigma(\overline{E}\rightarrow E^{\dagger})$  for energy transfer from the average energy,  $\overline{E}$ , in the cold neutron spectrum to E<sup>t</sup>. It is, of course, impossible to say something about the range of validity of this result. On the other hand, if all the neutrons were concentrated at 4Å the inelastically-scattered spectrum would have a different shape. In the analysis of the inelastically-scattered spectrum is concentrated at 4.7 Å.

As the measurements show that both glycerol and water have many properties in common with solids as seen by cold neutrons, the inelasticallyscattered neutron spectra are used to derive frequency spectra for the atomic vibrations on the basis of some simple solid state model. The model we have been using connecting the neutron cross-section and the frequency spectrum is the phonon expansion model. The cross-section for inelastic neutron scattering is then given by [14]



Calculated inclastically-scattered neutron spectra from a substance of the glycerol type for three different assumptions about the ingoing neutron spectra, showing that the calculated spectra agree almost exactly at three angles of observation if either the ingoing wave length is 4.7 Å or if the whole cold spectrum is used as ingoing with the appropriate weighting.

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = a_{\mathrm{inc}}^2 \frac{k}{k_0} \exp\left(-\frac{\hbar\omega}{2\,k_B^{\,\mathrm{T}}} - 2W\right) \sum_{n=1}^{\infty} \frac{(2\,W)^n}{n} \overline{G}_n(\omega) \tag{2}$$

where several symbols have the same meaning as in Eq.(1). 2W is the Debye-Waller factor, and the  $\overline{G}_n$  are certain functions of the energy transfer  $\hbar\omega$ . In the series of terms the first, the one phonon term, might be written:

$$2 \operatorname{W} \overline{G}_{1} = \frac{h \kappa^{2} \cdot f(\omega)}{2M \cdot 2\omega \cdot \sinh \frac{h\omega}{2k_{B}T}} = \frac{\alpha f(\omega)}{2\beta \sinh \frac{\beta}{2}}$$
(3)

where  $\alpha = \hbar K^2 / 2Mk_B T$  with M = the mass of the scattering atom and  $\beta = \hbar \omega / k_B T$ f( $\omega$ ) is the frequency spectrum, which is the object of the study. As follows from (2) and (3) the frequency spectrum is obtained from the measured energy distribution I( $\varphi$ ) at the angle of observation  $\varphi$  from;

$$I(\varphi) \quad \frac{k_0}{k} \frac{\beta(e^{\beta} - 1)}{\alpha} \sim f(\omega) \cdot e^{-2W} + \alpha \cdot \psi(\beta, \alpha).$$
(2a)

As 2 W contains a factor proportional to  $\alpha$ , it is seen that  $f(\omega)$  is obtained from  $I(\varphi)$  only in the limit  $\alpha \rightarrow 0$ . All the multiphonon terms included in  $\psi(\beta, \alpha)$ disappear in the limit of observation in the forward direction. This factwas discussed earlier for instance by EGELSTAFF [15].

As shown by Fig. 2 the observed neutron spectra ranges out to energies of 100 mV, i.e. much higher than what would correspond to the observed Debye temperatures corresponding to 10-15 mV. Therefore the correction for multiphonon terms as well as the effect of the Debye-Waller factor should cover only the low part of the spectra, i.e. the energy range 5-20 mV. If the form (2a) is used over the higher energy transfer region, 20-100 mV, the multiphonon terms must tend towards zero because of the high apparent Debye temperature which must be associated with these high frequency modes. Therefore, if the observations are made at a small angle, say 30°, and if the ingoing energies are small, the  $\kappa$ -values and therefore the  $\alpha$ values become small in the low energy transfer region, and as a first approximation to the frequency spectrum we use

$$f(\omega) \sim I(\varphi)(k_0/k)(\omega/k^2)[\exp(\hbar\omega/k_BT) - 1]$$
(4)

No correction has yet been made for possible coherence effects.

#### **II. OBSERVATIONS ON GLYCEROL**

### (a) Measurements

With the improved time-of-flight instrument at the Stockholm reactor R1 a series of observations were made on the neutron spectra scattered from glycerol at angles of observation,  $\varphi$ , of 30, 60, 90 and 130°. A wide temperature range was also covered in that the observations were made at -7, +20, +61, +96 and +130°C. As the viscosity of glycerol is very sensitive to any water content, a chemical analysis of its water concentration was made before and after measurements and found to be 0.25%. The sample holder consisted of an aluminium container with 1 mm thick walls giving a sample size of  $7 \times 10$  cm<sup>2</sup> and a sample thickness of 0.2 mm corresponding to about 90% transmission. Round the thick outer rim of the container could be wrapped either a heating coil or thin pipes through which cooling liquids could be circulated (alcohol by dry ice or liquid nitrogen). The whole sample container was installed in a vacuum vessel with aluminium walls. The tem-

perature was measured by thermocouples and electronically controlled. The runs made at  $-7^{\circ}$ C require a particular explanation.

It is known that glycerol has a freezing point of -89°C, where it goes over into a glassy state. If it is heated up very slowly it is maintained in this crystalline state up to +17°C, where a melting point is found [16]. Therefore it is possible to study glycerol both in the solid and the highly viscous liquid state at one and the same temperature. We made this measurement as follows. First the liquid was cooled down to -7°C by alcohol-cooling and runs were made at 30, 60 and 90° angle of observation. The sample was then cooled down to -120°C by circulating liquid nitrogen round the sample holder. Then it was allowed to heat up from -120°C to -7°C in about 30 h. It was then maintained at -7°C by circulation of cold alcohol and runs were made at the same angles of observation as mentioned above. From previous laboratory experiments we had found out what speed of heating up was allowed to really maintain the crystalline state. Series of runs were always made with and without sample to find the background corrections. The data corrected for (a) background were further corrected for detector efficiency (b) and chopper transmission (c). The only instrumental effects left are then the effect of the time resolution and the ingoing spectrum width, which were discussed in Section I. A typical example of primary data corrected for the instrumental effects, a, b and c is given in Fig. 2.

### (b) Line width data - diffusive motions

The primary data thus obtained naturally divide into the quasi-elastic part and the inelastic part as shown by Fig. 2. The quasi-elastic part was treated as described in Section Ia. The experimentally observed line widths are all collected in Fig. 4, where the observed values of  $2\Delta E$ , are plotted as a function of  $\kappa^2$ . As is well known the value of the line width tends towards the value  $2hD\kappa^2$ , when  $\kappa$  tends to zero. Thus the slope of the tangents to the curve at the origin, equal to 2hD, gives values for the diffusion constant at the different temperatures. These values are plotted <u>versus</u> 1/Tin Fig. 5. Two important facts are noticed:

(1) The value of D measured in this way is 100 times larger than predicted by the Eyring formula

$$D = \frac{k_{\rm B}T}{2r\eta} \tag{5}$$

in a temperature region near room temperature. In formula (5) r is the radius of the molecule, 4Å, and  $\eta$  is the viscosity, 15 poise at room temperature. At 130°C the calculated value and the measured are about equal, if one uses a value of 4 centipoise for  $\eta$ . The latter value of  $\eta$  is an extrapolation of measured data [17]. This would indicate that the neutron does not only observe the motion of the whole molecule but also - and perhaps mainly - the individual motion of the scatterer, the hydrogen nucleus, at room temperature. Another and still stronger indication in the same direction is that the width of the quasi-elastic peak observed at -7°C is the same in the liquid and in the crystalline states. The curve at 266°K of Fig. 4



Fig.4

The experimentally-determined natural line width of the quasi-elastically-scattered neutron spectrum from glycerol at various temperatures. Error bars include estimated systematic error sources.



Fig.5

Self diffusion constant of glycerol as derived from the slope at the origin of the tangent to the line width curves of the previous figure.

is identical in the solid and liquid phases. This can only happen, if the neutron mainly observes the proton motion, because the molecular motions must be rather different in the solid and liquid cases.

(2) As shown by Fig. 5 the temperature variation of D may be described by a function  $D(T) = 62 \cdot 10^{-5} \exp(E_0/k_BT) \operatorname{cm}^2/\mathrm{s}$  with  $E_0 = 0.13$  eV. This corresponds to an activation energy of 3000 calories/mol. The value observed at 130°C seems, however, to deviate from this law, indicating a more rapid variation of the observed D at higher temperatures. This seems to be in conformity with the idea that at 130°C and higher temperatures the neutron is observing the motion of the molecule as an entirety, because then the observed temperature variation of D should be described by Eq. (5).

The temperature variation [17] of  $\eta$  is very strong as  $\ln \eta$  varies approximately as T<sup>-3</sup>.

Lately several models [8, 18] for the diffusive motions in liquids have been proposed and worked out. One of these models is the stochastic one developed by Rahman, Singwi and Sjölander. The cross-section in this model is described by Eq. (1). The important magnitude is the width function  $\rho(t)$ describing the square of the deviation of an atom from the origin, where it was at time zero. In the present theory it is assumed that the atoms perform vibrations and that these vibrations have a Debye distribution with a characteristic Debye frequency,  $\omega_{\rm D}$ . Below a certain frequency,  $\omega'$ , all of the modes go into diffusion. By this artifice the condition found experimentally, that only a fraction of all the degrees of freedom are used up in diffusion, is automatically fullfilled. In the wave picture it also agrees with the observation that no low frequency transverse modes can be propagated through a liquid. All the motions are damped and the damping is characterized by the damping constant  $\Gamma.$  One of the variables,  $\omega_D,$  was determined directly by measurement of the angular distribution of quasi-elastically-scattered neutrons from room temperature glycerol using a three axis crystal spectrometer. The result was  $\omega_D = 2.0 \cdot 10^{13}$  rad/s corresponding to an apparent Debye temperature,  $\theta_D$ , of 150°K, and this value was used in computations using Eq. (1). As it is assumed that the damping is strong and a certain saturation of the parameter  $\Gamma$  has occurred if  $\Gamma = 2$ , this value was used. The value of  $\Gamma$  has a very small influence on the line width. The determining factor is  $\omega^{J}$ . A series of computations was made of the cross-section. The full width of the calculated curve was then found on two extreme assumptions regarding the mass, M, of the scattering unit namely M = 92 which is the molecular mass of glycerol  $C_3H_5$  (OH)<sub>3</sub> and M = 1, the proton mass. The best fits are shown in Fig. 6. It will be seen in Fig. 6a that a good fit is found with  $\omega^{\dagger}$  - 0.45 rad/s at 96°C and with  $\omega^{\dagger}$  = 0.2 rad/s at 20°C for M = 92. The result of the computation with M = 1 is seen in Fig. 6b. The parameter  $\omega^{\dagger}$ now takes the values 0.10 rad/s at 96°C and 0.04 rad/s at room temperature. According to the conclusions from the values of the diffusion constant, it would be most logic to use a low mass value at 20°C and mass 92 at 96°C. However, the ratio of the calculated quasi-elastic to inelastic cross-sections for M = 1 does not agree with experiment, while the same ratio for M = 92 seems to be in better agreement with the observations. On the whole it does not seem that the theory used here is able to explain the observed facts.



Fig.6

Examples of calculated line width curves of the quasi-elastic neutron peak of glycerol based on the Rahman-Singwi-Sjölander theory at two temperatures, 20°C and 96°C. Experimental values taken from the present investigation

- are also shown.
- (a) Computation for mass 92.
- (b) Computation for mass 1.

An interesting quantity in this connection to study is  $\rho(t)$ . In Fig. 7  $\rho(t)$  is given for two of the cases considered. It is to be noticed that with the assumption of mass 92 the amplitude of the thermal cloud is small,  $\rho(t)$  being about  $0.017 \cdot 10^{-16}$  cm<sup>2</sup> corresponding to an amplitude of 0.13 Å at room temperature. At a mass value of 1 the same amplitude should be of the order of  $\sqrt{2}$  i.e. 1.4 Å according to Fig. 6b. A direct measurement of the angular distribution of quasi-elastically scattered neutrons from glycerol at room temperature gave a value for this amplitude of 0.15 - 0.20 Å. Because of the difficulties to separate true quasi-elastically from inelastically-scattered neutron intensity there is a relatively large uncertainty in this value. The amplitude of 0.15 Å is to be considered as a lower limit. Thus a mass value intermediate between 1 and 92 ought to give the best agreement with observation. This should be equivalent to the statement that a complex motion consisting in both free proton or radical motion and motion of the whole molecule should agree best with the observation.



The width function  $\rho(t)$ , which is a measure of the mean square displacement of an atom, for glycerol corresponding to the values of the parameters  $\omega_D \omega'$  and  $\Gamma$  giving the best fit with the experimentally observed line widths.

(a) Computation for mass 92.

(b) Computation for mass 1.

In this connection it is to be remembered that the ultrasonic relaxation time measurements [17] on glycerol give results of the order of  $10^{-9}$  s in the temperature region  $-7^{\circ}$ C to  $+20^{\circ}$ C. This is a time much too long to be observed with the neutron technique, which again supports the idea that the neutron only observes the motion of some lighter parts of the heavy molecule.

Another way of discussing the line width data has been proposed by EGELSTAFF [19]. In this representation  $2\Delta E$  is plotted as a function of  $\kappa^2 D$ . This is shown in Fig. 8. As shown by Egelstaff the line widths would vary with temperature in two different ways if the diffusive motion should be of the type free diffusion involving a continuous motion of the molecules, or if it should be of the jump diffusion type. If the latter should be the case



Fig.8

The experimentally observed line widths for glycerol plotted as a function of  $\kappa^2 D$ .

the deviation of the line width curves from the line  $\Delta E = 2\hbar D\kappa^2$  should decrease with increasing temperature at a constant value of  $D\kappa^2$ . If the opposite was true, i.e. if free diffusion was the dominating process the line width curves should deviate more and more from the line  $\Delta E = 2\hbar D\kappa^2$  with rising temperature. As seen from Fig. 8 it appears that the jump diffusion process is dominating at lower temperatures and that perhaps the free diffusion process could take over the role as the main process at the higher temperatures, >130°C. This conclusion is a very good agreement with the picture that at lower temperature only the jumping motion of the protons is observed by the neutron, while at the higher temperatures the motion of the large molecule as an entirety is observed.

It is worth noticing that if the jump diffusion is the dominating process the limiting value of the line width for large  $\kappa$ -values is  $2h/\tau_0$ , where  $\tau_0$  is the cycle time or period of the random walk-like diffusion process:

$$\tau_0 = \frac{\ell^2}{6D} \tag{6}$$

For the lowest temperatures studied here,  $-7^{\circ}$ C and  $+20^{\circ}$ C, it is possible to derive these time values from the line width curves of Fig. 4. At  $-7^{\circ}$ C one finds  $\tau_0 = 1.8 \cdot 10^{-11}$  s and at  $+22^{\circ}$ C the result is  $\tau_0 = 0.9 \cdot 10^{-11}$  s. Combining these experimentally determined  $\tau_0$ -values with the D values from Fig. 5, which are D =  $2 \cdot 10^{-6}$  cm<sup>2</sup>/s at  $-7^{\circ}$ C and D =  $4 \cdot 10^{-6}$  cm<sup>2</sup>/s at  $+20^{\circ}$ C, one finds in both cases for the distance 1 covered in the time  $\tau_0$  the value 1.5 Å which happens to be almost exactly half the measured hydrogen bond distance in glycerol [19]. At these low temperatures most of the mean time  $\tau_{\theta}$  might be considered as a residence time. The gradual change of the shape of the curves might indicate that the importance of the transit time,  $\tau_1$ ,

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from one vibratory position to the next one gets an increasing importance. This conclusion is in conformity with the idea that at lower temperatures mainly the proton motions are observed, while at the higher temperatures the motion of the whole molecule is observed.

## (c) Inelastic spectrum - vibratory motions

On the theoretical basis discussed in Section Ib frequency spectra, f(E), for the vibratory motions of the scattering units were derived from the broad inelastically-scattered neutron spectra of which Fig. 2 gives two examples. Formula (4) used to derive f(E) of course corresponds to a first approximation. Fig. 9 gives examples of such spectra derived from observations on liquid glycerol at temperatures of -7, +61 and  $+130^{\circ}$ C. The angle of observation was  $30^{\circ}$ . The spectra derived from other angles do not differ appreciably from the  $30^{\circ}$  observations. As will be seen from the figure there is a tendency of structure in the low energy region, E < 0.04 eV, while the spectrum of higher vibrational energies is very flat. The structure at lower energies gets more and more smeared out with increasing temperature, again in agreement with the idea, that at higher temperatures the diffusive molecular motion is superimposed on the motion of some lighter parts of the molecule. This idea gets further support from the frequency spectra derived from the observations on glycerol made at  $30^{\circ}$  angle of observation





Frequency spectra derived from inelastically-scattered neutron spectra obtained from liquid glycerol at temperatures of -7, +61 and +130°C. Angle of observation is 30°.

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Fig. 10

Frequency spectra of glycerol in solid and liquid phase derived from measurements at  $-7^{\circ}$ C at an angle of observation of 30°.

and at -7°C in the solid and liquid phases. These spectra are shown in Fig. 10. The spectrum derived from the crystalline state observation shows a rich structure with peaks at 6, 15, 19 and 27 mV. These peaks are effectively lost in the liquid phase. A tendency of peaks shifted towards lower energies is noted. The corresponding two spectra derived from observations at 90° angle do not show such a large difference between the solid and liquid state spectra in that the crystalline state spectrum is more similar to the liquid state spectrum. This could mean that some of the peaks in the 30° spectrum have coherence origin because the  $\kappa$ -values are small just in the energy region where the peaks occur [15].

## III. OBSERVATIONS ON LIGHT AND HEAVY WATER

A series of observations [9] on the scattered neutron spectra from light water in a temperature range from  $-9^{\circ}$ C to  $+92^{\circ}$ C and on heavy water from  $-9^{\circ}$ C to  $+300^{\circ}$ C has been performed at angles of observation of  $30^{\circ}$  and  $90^{\circ}$ . Samples of 90% transmission were used, i.e. 0.2 mm samples of H<sub>2</sub>O and 2.0 mm samples of D<sub>2</sub>O. In the high temperature range for D<sub>2</sub>O a sample container consisting of 23 hypodermic needles of an outer diameter of 2.9 mm made of stainless steel and with a wall thickness of 0.2 mm was used. Its construction is shown in Fig. 11. Because of difficult background problems with the sample container of stainless steel, giving Bragg reflections as





Sample container for the scattering experiments on D<sub>2</sub>O at high temperatures.

- (a) artists' view of sample container
- (b) cross-section of the container
- (1) hypodermic needle,
- (2) framework of stainless steel,
- (3) weldings,
- (4) stainless steel filling lines for  $D_2O_2$ .

well as incoherent scattering within the cold neutron region near 4 Å, the quasi-elastic scattering could not be studied with confidence. Therefore only vibratory properties derived from the inelastically-scattered neutron spectra will be discussed here.

Examples of neutron spectra scattered from  $D_2O$  at 20°C, 155°C and 300°C at 90° angle of observation are given in Fig. 12. The extremely high observed intensity in the cold neutron range, 0-5 mV, particularly at room temperature, depends upon the fact that the structure factor happens to have a peak in the corresponding region of  $\kappa$ -values as indicated by the top part of the figure. In all spectra of this kind only the part found above 6 mV was used to calculate frequency spectra according to Eq. (4).

A series of examples of frequency spectra derived from the measurements on light water at 30° angle of observation are given in Figs 13 and 14. In Fig. 13 is given the resulting frequency spectra derived from runs on H<sub>2</sub>O at -3 and +2°C, i.e. just below and just above the melting point. As shown the two spectra coincide. This is taken as an indication that at least near the melting point the vibratory motions in water closely resemble the motions in ice. In itself this observation is a justification for the use of the simple phonon formula (4). As the temperature is raised, the peak of the high energy vibratory modes, hindered rotations, is shifted towards lower energies (Fig. 14). Empirically it is found that in the temperature range 0 - 100°C the product  $E_{max} \times T^{3/2}$  = constant = 34, where  $E_{max}$  is the





Primary neutron spectra obtained from  $D_2O$  at 20°, 155° and 300°C and at 90° angle of observation.



Frequency spectra derived from neutron spectra observed in  $H_2O$  at  $+2^{\circ}C$ and ice at  $-3^{\circ}C$  showing an exact coincidence. Angle of observation 30°.

energy of the peak in electron volts and T is the temperature in °K. The low lying part of the spectrum, E < 0.04, is smeared out when the temperature rises (compare the results on glycerol) but its structure seems to be left unchanged as the peaks do not shift. The observations on D<sub>2</sub>O are very similar as shown by Fig. 15. It is interesting to note that even in this case the hindered rotation peak is shifted towards lower energies as the temperature is increased. The product  $E_{max} \times T^{3/2}$  is again found constant and = 26. If the ratio is taken one observes that  $(E_{max})_{H_2O}/(E_{max})_{D_2O}= 1.34$ , which is not far from  $\sqrt{2}$  as it should be, if the H and D nuclei were the scattering centra and the motion was simple harmonic vibration.

As to the low frequency part of the spectra, E < 0.04 eV, it could be distorted by two effects:

(1) The width of the incoming cold neutron spectrum,

(2) Coherence effects.







The change of shape of the derived frequency spectra for  $H_2O$  at +2°C and ice at -3°C showing an exact coincidence. Angle of observation 30°.

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Frequency spectra for D<sub>2</sub>O at the temperature 155°C and 300°C at angles of observation of 30° and 90°.

Concerning the first point it was shown in Section Ib that if 4.7 Å is taken as the ingoing neutron energy in the evaluation of f(E), there are probably not any serious errors produced in the low energy part of f(E). Concerning the coherence effects it is more difficult to say anything definitely. If, however, the results on  $H_2O$  and  $D_2O$ , presented in Figs14 and 15, are compared it seems improbable that the peak at 7 mV in the case of  $H_2O$  could be produced by some coherence effects as the coherent scattering in  $H_2O$ is about 4% and in  $D_2O$  about 80%. The peak in  $D_2O$  should then appear much higher than in H<sub>2</sub>O which is not the case. The same argument might be used for the energy band round 20 mV. To further elucidate the situation in this

low lying energy region examples of frequency spectra derived from D<sub>2</sub>O runs at 155°C and 300°C are given in Fig. 16. As will be seen the spectra derived from 30° and 90° angle of observation do not agree in the energy range, E < 0.035 eV. In the phonon model, which is of course doubtful at these high temperatures, it is quite clear that the observations should not coincide until this spectrum part has been corrected for multiphonon terms and the Debye-Waller factor. From the intensity distribution in the quasielastically-scattered peak in  $D_2O$  at 90° angle of observation (Fig. 12) and the assumption that  $D_0O$  and  $H_0O$  have the same Debye temperature at room temperature, namely [12]  $\theta_{\rm D}$  = 135°K, one may estimate that the Debye temperature of D<sub>2</sub>O at 300°C is about  $\theta_D = 75$ °K. This is a very low value compared to the sample temperature, 573°K, why a very large effect of multiphonon terms should arise. A correction for these terms would decrease the spectrum part between 6 and 15 mV, but the peak at 7 mV would not disappear. It should be noted, that the instrumental resolution in the energy range, 0-40 mV, is as good as 2-4%.



Low energy part of observed frequency spectra for  $H_2O$  at -3°C and +2°C compared with the calculated dispersion relations for ice.

Finally it is of interest to compare the low energy part of the frequency distribution observed at the temperatures of  $-3^{\circ}$ C and  $+2^{\circ}$ C in H<sub>2</sub>O with calculations of the dispersion relations in ice by FORSLIND [21]. Using the elastic constants of ice he finds dispersion relations (Fig. 17) with resulting

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concentrations of acoustic vibrations in an energy range round 7 mV and a concentration of optical vibrations round 20-25 mV. These regions exactly coincide with the observed peaks at 7 mV and 25 mV on ice at  $-3^{\circ}$ C and water at  $+2^{\circ}$ C, which again strengthens the idea of resembling a liquid of this kind to a solid. As shown by Fig. 14 the frequency spectrum of water, rich in detail near the crystallization point, is quickly smeared out, so that already at room temperature this smearing has reached a sort of saturation nature. This would mean that in water with its low viscosity the motions of the molecules are so vivid already at  $+20^{\circ}$ C that the more distinct protonic motions are masked by the chaotic diffusive motions of the molecules as entireties. The same type of conclusion was drawn from the study of the diffusive motions in glycerol, where, because of the high viscosity values, the gradual inset of the molecular motions is spread over a larger temperature region.

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## DISCUSSION

W. KLEY: With regard to the latter part of your paper, I think it is extremely interesting that the "frequency distribution" of light and heavy water should show such a similarity. However, in the case of  $D_2O$  the

measurement may not give the true frequency distribution, since it is impossible to reach all q values in reciprocal space by means of the coldneutron technique. Should this fact have only a small effect on the frequency distribution, the technique might be used for any powder sample that scattered neutrons coherently.

K.E. LARSSON: I quite agree with your statement. The spectra in light and heavy water really do look similar and some contribution may well be made by coherence effects. However, in this early stage of experiment and theory in the field of coherent inelastic scattering of neutrons, at least as far as scattering from liquids is concerned, all we can do is make a guess and hope that the result is correct to zero order.

P. EGELSTAFF: I think that the multiphonon effect might be of suffificient importance to distort your frequency distribution in the neighbourhood of the broad hindered-rotation peak. It might have the effect of moving the mean energy to somewhat higher value. I would be interested in your comments on this. I would also like to ask for further details on how you evaluated the Debye-Waller factor when deducing the frequency spectrum from the one-phonon formula, since it is important to take the correct vibrational contribution to this factor.

K.E. LARSSON: According to measurements which were reported at the previous Symposium in Vienna\*, we found a Debye temperature of 130°K for water at room temperature. Only the low-frequency motions in the water spectrum ( $\hbar\omega$  > 30 meV) could have contributed to building up this Debye-Waller factor of  $\Theta_{D}$  = 130°K. However, the measurements of the frequency spectra in ice and water  $(-2^{\circ}C \text{ and } +3^{\circ}C)$  show that the spectrum naturally divides into two parts, one for  $\hbar\omega < 30-40$  meV and another for  $\hbar\omega > 30-40$  meV. The lower one, describing the acoustical and perhaps the optical modes of motion, is corrected for the Debye-Waller factor and multiphonon effects. The upper part, corresponding to the hindered rotation band, is not corrected at all since this part would have a  $\Theta_{ID}$  of about 1200°K in the Debye model. At this high Debye temperature the multiphonon terms and the Debye-Waller factor are small and therefore no correction is made. For this region  $T < < \Theta_D$ . The curves on  $D_2\,O$  at +155° and +300°C show that only the  $\hbar\omega < 30-40$  meV region needs a correction. Of course, I am fully aware that my procedure is only a zero-order approximation. The curves presented are not fully corrected or final ones. They are intended solely to give an idea of the main features involved.

P. SCHOFIELD: I do not think that there is any contradiction between the statements of Dr. Larsson and Dr. Egelstaff. The multiphonon contribution increases as you go up in energy and this has the very effect described by Dr. Egelstaff. It tends to produce greater intensity further down in the spectrum, hence the effect of shifting the peak downwards in Dr. Larsson's observations.

S. COCKING: For the benefit of the experimentalists, I would like to comment that the technique involving the use of highly pressured samples and a large number of narrow tubes is very valuable. It opens up the possibility of measurements at high temperatures and pressures, e.g. at the

\* <u>Op. cit.</u>, p. 329

critical point for many materials. At Harwell we have completed tests on several tube sizes. In our design, a continuous tube is wrapped back on itself to cover a large sample area. The containing tube, being of light gauge, is used as its own heater element.

K.E. LARSSON: I would like to point out, however, that in using this hypodermic-needle type of stainless steel container, you often run into trouble with Bragg reflections in the region of the incoming energies. This is the reason, for example, why we did not study the quasi-elastic scattering at higher temperatures.

P. SCHOFIELD: Have nuclear magnetic resonance measurements been made on glycerol in the solid and liquid phases at the same temperature? It would be interesting to see if such measurements support the hypothesis of the protons hopping.

K.E. LARSSON: No such measurements have been made, as far as I know.

K.S. SINGWI: I think there is enough evidence about what Dr. Schofield was asking because the spin lattice relaxation time has been observed in glycerine in great detail under various conditions of temperature and I think the value you get from Dr. Larsson's data for the cycle time  $\tau_0$  comes out nearly the same as the correlation time which you get in the formula for the spin lattice relaxation time in glycerine in nuclear magnetic resonant experiments.

K.E. LARSSON: Yes, this cycle time is about  $1.9 \ge 10^{-11}$  s.

# THE MOTION OF HYDROGEN IN WATER\*

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#### Abstract — Résumé — Аннотация — Resumen

THE MOTION OF HYDROGEN IN WATER. Recent measurements of neutron scattering by water are combined with our previously published work, and analysed in terms of a generalized frequency function  $p(\beta)$ , and "non-Gaussian" components. The theoretical calculations are performed with the LEAP programme using the methods of Egelstaff and Schofield. Diffusive, rotational and vibrational components can be seen in the frequency distribution and the change of the first two with temperature observed.

MOUVEMENT DE L'HYDROGÈNE DANS L'EAU. Les auteurs font la synthèse de mesures faites récemment sur la diffusion des neutrons par l'eau et de résultats précédents et ils en font l'analyse sous forme d'une fonction de fréquence généralisée  $p(\beta)$  et de composants non gaussiens. Ils font les calculs théoriques au moyen du programme LEAP fondé sur les méthodes de Egelstaff et Schofield. Il est possible de séparer les composantes de diffusion, de rotation et de vibration dans la distribution de fréquences ainsi que les variations des deux premières composantes en fonction de la température.

ДВИЖЕНИЕ ВОДОРОДА В ВОДЕ. Последние измерения рассеяния нейтронов водой объединены с нашей предыдущей опубликованной работой и анализируются с точки эрения обобщенной функции частоты р (В) и "негауссовскими" компонентами. Теоретические расчеты выполнены с помощью программы LEAP с использованием методов Игельстафа и Скофильда. В распределении частот наблюдаются диффузионные, вращательные и колебательные компоненты, и найдеко, что первые два изменяются в зависимости от температуры.

EL MOVIMIENTO DEL HIDRÓGENO EN EL AGUA. Los autores combinan los resultados de mediciones recientemente efectuadas con los datos contenidos en un trabajo anterior y los analizan expresándolos como función de frecuencia generalizada  $p(\beta)$  y como componentes "no gaussianos". Los cálculos teóricos se han realizado según el programa LEAP aplicando los métodos de Egelstaff y Schofield.

En la distribución de frecuencias, es posible observar componentes de difusión, rotación y vibración, así como la variación de las dos últimas en función de la temperatura.

#### INTRODUCTION

The thermal neutron scattering cross-sections of water have been measured over a wide range of neutron energies and angles of scatter by EGELSTAFF et al. [1] and HAYWOOD and THORSON [2]. Although the aim of these measurements was to provide input date for neutron spectrum calculations in light water reactor systems, nevertheless it is of interest to analyse these data to see what information about molecular dynamics is contained therein.

This discussion will be divided into three parts. First the technique of analysis and its application to room temperature light water. Secondly the behaviour of water at 150°C compared to room temperature, and thirdly

<sup>\*</sup> Joint project between AECL, Chalk River and AERE, Harwell.

the comparison of light and heavy water. It will be concluded that the hindered rotation level previously stated [3] to be at ~ 0.06 eV, is very broad and asymmetric and extends to ~ 0.15 eV, probably mixing with the vibrational level at ~ 0.2 eV and making the application of the KRIEGER and NELKIN [4] approximation rather unsatisfactory. The position in energy of this level decreases with increase of temperature or mass. A level at an energy of ~ 0.015 eV is observed which is due to the motion of a group of molecules. An initial estimate of the frequency distribution for proton motions in water is derived for water at room temperature and 150° C.

## ANALYTICAL TECHNIQUE

It is not expected that the diffusive motions in water will seriously effect the other motions discussed above because of the time scale for diffusion is much longer than that for rotation. This can be demonstrated conveniently by reference to the generalized frequency distribution of EGELSTAFF [5] In this distribution the diffusive motion appears as a sharp peak near the origin, the width of which may be discussed theoretically [6] in terms of the time for diffusion. On a simple model the peaks due to other motions would be broadened by folding the diffusive peak with them. Reference to Fig. 3a shows that this extra broadening would be a small effect.

Nevertheless, the interactions between molecules will be strong and this will lead to broadening of the peaks in the frequency distribution corres, ponding to particular motions, as seen in Fig. 3a. These same interactions should lead to anharmonic contributions to the motions of atoms and molecules in water. Thus the effect of interactions can be observed in two ways, first through the shape of features in the frequency distribution and secondly through terms in the cross-section in addition to those obtained from an harmonic approximation calculation.

Treatment of the problem along these lines requires a reliable method of deriving the frequency distribution from the data. This is true even when the iterative procedure suggested by EGELSTAFF et al. [1] is used, because the rapid convergence of the iterations depends upon a good initial estimate of this distribution. In the original method of EGELSTAFF [5, 1] the cross-sections were converted to a scattering law per unit of squared momentum transfer (S/ $\alpha$ ), A linear plot of this quantity against momentum transfer squared ( $\alpha$ ) for a given energy transfer ( $\beta$ ) was extrapolated to zero momentum transfer. The intercept on this axis gave the first approximation to the value of the frequency distribution at that value of the energy transfer. One difficulty with this method is that for water the function  $S/\alpha$  is not linear over the experimental range of  $\alpha$ . However, for a reasonable range of  $\beta$  values it is roughly exponential, as shown in a companion paper (EGELSTAFF [7]). Thus extrapolations of log S/ $\alpha$  versus  $\alpha$  will be used here, and some typical examples are shown at Fig. 1 compared to a theoretical calculation described later. (Further details of the analysis of the data are given in an Appendix.)

At the low values of  $\beta$  and  $\alpha$  where the diffusion term is important, this method of extrapolation is unsatisfactory. Also at higher values of  $\beta$  where more than one type of atomic motion may be important the plots will be simi-



EXTRAPOLATIONS OF S TO a=0

Fig.1

Examples of extrapolation of water data to zero momentum transfer. The curves have been displaced from one another for the sake of clarity. The solid lines are the "best" curves through the experimental points, while the dotted lines have been calculated from an initial estimate of  $p(\beta)$  and are used for guidance in drawing the solid line. Curves are for water at 150°C.

lar to the upper curve of Fig. 1b. In this case the extrapolation is strongly dependent upon the theoretical model used. However, rough calculations show that the  $\beta$ -range considered here is sufficiently below the region of the vibrational levels (which is the most important region for this effect) so that this effect is not large. Thus all the data will be treated as at Fig. 1.

The magnitude of the vibrational levels will affect the slope of the curves of Fig. 1. As shown later the variation of the ratio of areas in the rotational to vibrational sections of the frequency distribution alters the slope of these curves. Thus in effect, the Debye-Waller factor for the vibrational states is determined by measuring the amplitude of the rotational term as a function of momentum transfer.

The calculations of S as a function of  $\alpha$  can be made through the use of the harmonic approximation in the way described by EGELSTAFF and SCHOFIELD [8]. Over the entire range of  $\beta$  the anharmonic terms average to zero, but over the range of  $\beta$  being considered here they may give a purely positive or negative contribution to the value of S. In addition since they depend strongly on momentum transfer the slope of the lines in Fig. 1 may be modified by these terms. An approach will be adopted in which an attempt is made to fit the data using the harmonic approximation only, and if a fit is not obtained the difference between calculation and experiment will be attributed to anharmonic effects.

At low values of  $\alpha$ , several effects combine to distort the result. These effects may be listed as follows:

- (1) Interference term in scattering law,
- (2) Experimental resolution,
- (3) Multiple scattering in sample,
- (4) Anharmonic terms as discussed above.

The first three of these effects are of the same sign and produce a sharp rise in the value of  $S/\alpha$  at low  $\alpha$  which can be easily distinguished empirically. It is probable that the anharmonic terms would have their maximum effect at low values of  $\alpha$  and  $\beta$  because this corresponds to a range of atomic movements over which the harmonic approximation breaks down), but this is not certain for a complicated molecule like water. In any case a sharp rise of  $S/\alpha$  at low values of  $\alpha$  will be disregarded.

## INTERPRETATION OF ROOM TEMPERATURE WATER DATA

The first question to be considered in interpreting these data is the ratio between the low energy (rotational) and the high energy (vibrational) parts of the frequency spectrum. If water were composed of free molecules  $(H_2O)$  in which the rotations took place about an axis nearly passing through the position of the oxygen atom, then this ratio would be almost unity. This is assumed in the NELKIN model of water [9]. On the other hand if water is considered as a crystalline hydride with similar structure to a metal hydride, then the ratio would be nearly zero. Probably the structure of water lies between these two extremes and the observed ratio will depend upon the nature of the intermolecular bonds.

The validity of the harmonic approximation will be assumed to show how this step in the analysis is made. Write:

$$S(\alpha, \beta) = \int e^{i\beta t} \exp(-\alpha \cdot w(t)) dt.$$
 (1)

where w(t) is a width function as used by VINEYARD [10]. This function may be divided into components due to rotation and vibration (denoted by R and V respectively) as follows:

$$w(t) = w_{R}(t) + w_{V}(t)$$
  
= w<sub>R</sub>(t) + A<sub>V</sub> - U<sub>V</sub>(t) (2)

where  $A_V$  is the Debye-Waller constant for vibrational modes, and  $U_V(t)$  contains the time dependance of the width function. Thus a "phonon" expansion of the vibrational term gives:

$$S(\alpha, \beta) = e^{-\alpha A_V} \left[ S_R(\alpha, \beta) + O(\alpha B) \right]$$
(3)

where B is the value of  $1/\beta^2$  averaged over the vibrational spectrum, and  $S_R$  is the scattering law for the rotational part of the frequency spectrum.

Now if the two parts of the frequency spectrum are fairly well separated then there will be a range of  $\alpha$  and  $\beta$  for which  $S_R$  is nearly independent of the shape of the rotational spectrum and the terms  $O(\alpha \beta)$  are not very important. In this situation the variation of  $S(\alpha, \beta)$  with  $\alpha$  will be determined by  $\exp(-\alpha A_V)$ , and hence can be used to give the value of  $A_V$ . This will be related to the ratio (G) of low to high energy parts of the frequency spectrum if the vibrational spectrum is confined to narrow ranges of frequency and can be represented as a set of  $\delta$ -functions of pre-determined position and relative size. In this case:

$$A = \frac{1}{1+G} \sum_{n=1}^{\infty} \frac{a_n}{\beta_n} \operatorname{Coth} \beta_n / 2.$$
(4)

where  $a_n$  is the relative amplitude and  $\beta_n$  is the position of the nth vibrational level.



Frequency spectra for various cases,

At Fig. 2 these points are illustrated by numerical computations. Fig. 2a shows the several types of frequency distributions used; Fig. 2b shows the relative shapes obtained with the four  $\delta$ -function (Nelkin) model of water compared to a model in which  $\delta$ -functions for the vibrations are combined with the observed curve for rotations, and Fig. 2c shows the shapes obtained with observed rotational curve when combined with  $\delta$ -function or rectangular vibrations. It can be seen that for the range of  $\beta$  covered and for the parameter  $\alpha$  between 4 and 16 the detailed shapes of the rotational and vibrational spectra are not very important. However the slope of the lines in 2c is less than that of 2b due to the ratio G being changed from 1 to 0.42 between the two calculations. Fig. 2d shows the experimental data of EGELSTAFF








Fig.2c

Comparison of scattering laws for different shaped vibrational components. The ratio between the rotational and vibrational components is 1 for (b) and 0.42 for (c).



11g.20

Comparison of calculated curves for G = 1 and 0.42 with the experimental data.

<u>et al.</u> [1] compared to the calculations for these two ratios. Considering only the region between  $\alpha = 4$  and 16, the ratio G = 0.42 gives a better fit to the data. This is confirmed by a similar test at values of  $\beta$  other than those shown. Thus the intermolecular bonding in the water is intermediate between the two limits quoted above.

An initial estimate of the frequency spectrum of water can be obtained by the extrapolation method using the data of HAYWOOD and THORSON [2], as explained in an appendix. These data are given in Fig. 3a and the values of  $(S/\alpha)$  calculated from them are given in Fig. 3b (in these calculations a value of G = 0.42 was used). In both Figs. 2d and 3b the rise near the origin of  $\alpha$  can be seen clearly and is discarded for the reasons given above. However, for  $\alpha > 2$  the calculated curves are in reasonable agreement with the experimental ones. Some discrepancies clearly exist however which may be reduced by further iterations, but it seems probable that differences of about 20% in the cross-sections could remain unexplained and must be attributed to anharmonic or non-symmetrical terms in the potential.

The frequency spectrum of Fig. 3a shows several interesting features. One is the existence of a clearly distinct diffusion peak near the origin. The value at  $\beta = 0$  is determined by the diffusion constant, and the line has been drawn up to the calculated  $\beta = 0$  value from the last experimental point. Another feature is the existence of a peak at  $\beta = 0.6$  so far unexplained. The peak at  $\beta \simeq 3.5$  is now seen to be quite broad and extends to  $\beta = 6$ ; possibly it merges with the vibrational peak expected from infra-red experiments





Comparison of calculation with experiment for spectrum of Fig. 3a.

to be at  $\beta = 8$ . If the distribution is divided into the two regions  $\beta > 9$  (which covers the major vibration peaks at  $\beta \sim 20$ ) and  $\beta < 9$ , the ratio of these two parts is  $\approx 1$  for a value of G = 0.42 (as previously defined). This result suggests that the peak at  $\beta \approx 3.5$  previously ascribed to the hindered rotation of single molecules, is due to a more complicated motion probably involving several molecules. It is possible that the hindered rotation of a single molecules to the  $\beta = 8$  vibration which corresponds to the expansion and contraction of the angle between the hydrogen bonds.

Alternatively the vibrational part of the spectrum could have an amplitude corresponding to G = 0.42, if the lower part of the spectrum ( $\beta < 7$ ) corresponded to acoustical vibrations as in a crystalline lattice. The broad peak might then be a vibration of the tetrahedral unit proposed by BERNAL and FOWLER [11], and the ratio G = 0.42 would be explained by appropriate bond strengths within the tetrahedron. If this explanation were correct the suspected phase transition at 42°C would be worth investigation by neutron techniques.

## COMPARISON OF FREQUENCY DISTRIBUTIONS OF WATER AT ROOM TEMPERATURE AND 150° C

The extrapolation technique has also been employed for the data of HAYWOOD and THORSON [2] on water at 150°C with a frequency spectrum as given in Fig. 4. Initial calculations using the LEAP computer programme and this distribution show agreement with the experimental data about as





Frequency spectrum of water at 150°C via extrapolation technique. The inset shows a comparison of calculation with experiment for  $S/\alpha$  as a function of a for  $\beta = 1.0$ .

good as in Fig. 3b provided a value of G = 1 is used. An example is given in the inset to Fig. 4.

If further calculations confirm that  $G \approx 1$  at 150°C, it would indicate that the molecule is more free to rotate at this temperature than at room temperature as expected from the density difference. Again it is possible that the lowest vibrational level (which occurs for  $\beta \sim 5$ ) is coupled with the rotational states. These facts suggest that the peak for  $_{\beta}\beta \sim 2$  is due to rotation of a single molecule.

It is interesting to note that for the same intermolecular forces the rotational peak should move to higher energy as the temperature is raised. Comparison of Figs.3b and 4 shows that the value of  $\beta$ kt corresponding to the main peak is approximately independent of temperature. This shows either that different motions are involved or that the intermolecular forces have weakened considerably. Both possibilities may occur since water expands considerably over this temperature range. An alternative explanation on a crystal model leads to the same effect due to expansion of the lattice. The peak at  $\beta \sim 8.5$  in Fig. 4 is at a value of  $\beta$ kT similar to that of the corresponding peak in Fig. 3b.

Finally the diffusion peak near the  $\beta$  origin has increased with temperature due to the sharp increase of the diffusion constant, but it still represents only a small fraction of the area of the frequency spectrum, (it should be noted that EGELSTAFF et al. [1] in Fig. 4b of their paper, plot the wrong value of the diffusion constant for 150°C water; if the correct value of the diffusion constant is used a sharp peak at the origin can be inferred from their data too). This means that the "effective mass" for diffusion is equal to the mass of many molecules at this temperature, as at room temperature.

## ANALYSIS OF D2O SCATTERING LAW AT ROOM TEMPERATURE

The interference terms in the scattering law for  $D_2O$  can be evaluated empirically from the sharp rise of log  $(S/\alpha)$  near  $\alpha \rightarrow 0$ . After selecting a region of  $\alpha$  over which the interference terms are negligible the data for  $H_2O$  and  $B_2O$  can be compared. This comparison demonstrates that the scattering law for  $D_2O$  at  $\beta \lesssim 1$  is significantly larger than that for  $H_2O$ . The difference is not observed at values of  $\beta \sim 3$ .

This affect can be explained by assuming that the frequency distribution for oxygen in heavy water is concentrated at low values of  $\beta$  compared to the range of  $\beta$  for the deuterium frequency distribution. BUTLFR [12] has developed a model for D<sub>2</sub>O similar to Nelkin's model for H<sub>2</sub>O but assumes in addition that the oxygen can be represented as a nearly perfect gas. BUTLER's [12] calculated scattering law is in reasonable accord with the measured values of EGELSTAFF et al. [1] (see Discussion).

Thus over the measured range of  $\alpha$  and  $\beta$  the D<sub>2</sub>O data involves two different frequency distributions and hence cannot be interpreted without further assumptions. In this paper only the higher  $\beta$  region will be considered where the oxygen contribution is small, and thus a part of the frequency distribution for deuterium may be obtained from the data. This region includes a broad peak at  $\beta \approx 2.5$  or  $\beta kT \approx 0.06eV$ , compared to 0.09 eV in H<sub>2</sub>O. The ratio of these values is  $\simeq \sqrt{2}$  as would be expected either for the votation of a single molecule or for the optical modes in a crystal.

The analysis of the peak at  $\beta \simeq 0.06$  in the  $D_2O$  data is complicated by the influence of the oxygen frequency distribution. However if this peak is due to the rotation of groups of molecules the distributions for oxygen and deuterium would be similar. If the metal hydride type of model is considered the frequency distribution for oxygen would be mainly confined to  $low\beta$  values, and would be similar to the deuterium distribution in this region (since this is the region of acoustical modes). Thus both models suggest similar assumptions which could form the basis of further calculations.

## COMPARISON WITH OTHER DATA

LARSSON and DAHLBORG [13] have evaluated a frequency distribution for water at several temperatures from results of their experiments on the scattering of beryllium-filtered slow neutrons. These results cover a section of the scattering law taken along a line in energy-momentum space in which the energy change was almost proportional to the square of the mo-



Comparison of spectrum of Fig. 3b with that of LARSSON and DAHLBORG[13]. The arrows show the position of peaks seen in infra-red spectra [15].

mentum change. The frequency distribution was derived from these results by assuming that water is a solid and using a formula mentioned by PLACZEK [14]. While this frequency distribution has some similarities with those derived by EGELSTAFF et al. [1] and HAYWOOD and THORSON [2] there are significant differences. A comparison between Fig. 3a and the results of Larsson et al. is shown in Fig. 5. The latter results have been renormalized to give the best agreement with the absolute scale of Fig. 3a in the region  $\beta = 1$  to  $\beta = 2.5$ .

From Fig. 5a we can see that the position of the peak of the distribution is at  $\beta \simeq 3.5$  or  $\beta$ kT = 0.09 eV, while Fig. 5b peaks at  $\beta \approx 2.5 \beta$ kT = 0.065 eV. Raman spectrum measurements [15] attribute a broad level centred about 0.07 eV to a hindered rotation of a single water molecule and this fits in equally well with either set of results. A broad energy level attributed to "hindered translation" of a water molecule at 0.02 eV is also seen in optical absorption spectra and this agrees with the weak level at  $\beta = 0.9$  found by Larsson et al. better than with the peak centred around  $\beta = 0.6$  found by Haywood et al. The level in H<sub>2</sub>O at 0.0066 eV found by Larsson may correspond to a very weak level at 0.0075 eV reported by BOLLA [16] but not mentioned by other workers [15, 17]. It would be expected that such a strong level in the neutron scattering would be seen in the Raman spectrum unless the motions involve a symmetrical group of molecules.

The discrepancies between the two frequency distributions found by neutron scattering may be due to the different methods of evaluation of  $p(\beta)$ used. Compared to the method used here, Larsson <u>et al.</u> make more assumptions and take data over a much smaller range of momentum transfer. However even allowing for the difficulties in both experiments it is not easy to account for the discrepancies. The difference may be due to the difference in the anharmonic terms in the cross-sections but work is still needed to clarify these questions.

## CONCLUSION

The experimental data analysed here differ from optical data on water (and also from other neutron experiments [3, 13]) in providing, for each value of the energy transfer, a wide range of momentum transfers. In principle this enables anharmonic or non-symmetrical terms in the potential to be studied, but in practice due to the smallness of these effects their study is rather complicated. In addition to precise and extensive measurements it is necessary to have an elaborate set of computed data to compare with these measurements. The discussion in this paper has indicated how this can be done and that the above effects produce  $\leq 20\%$  changes in the cross-section of water over most of the range studied.

Measurements over a wide range of momentum transfer also allow the generalized frequency function to be determined with reasonable accuracy. In this paper only the main features of this function have been considered and how they vary with temperature and isotopic composition.

This discussion suggested that room temperature water was part way between a free molecular system and a crystalline hydride, whereas at 150°C it was nearer to the free system. Interpretation of the data as a relatively free molecular system seems to be only about as successful as an interpretation of water as a (relatively) bound molecular crystalline system. New calculations are required which are based on these models and give definite predictions of the shape and magnitude of the frequency distribution. Comparison of such predictions with the measured values would be very useful.

Analysis of neutron energy loss data (which mainly determines the peak in Fig. 3a) has given a higher energy to the hindered rotation of the water molecule than the energy gain data [3, 13]. This difficulty is not yet explained.

The work reported here has indicated the value of these techniques and the data which may be obtained by their use. A considerable extension of this work is needed to utilize them properly and also to understand the results.

## APPENDIX

## METHOD OF ANALYSIS OF SCATTERING LAW DATA

The early work on the scattering law described by EGELSTAFF [1] was analysed in the following manner; individual values of S were plotted on an S versus time-channel or S versus energy transfer plot and a smooth curve drawn through the points. From this curve values of S at fixed  $\beta$  may be picked off and after being divided by the approximate  $\alpha$  are plotted as (S/ $\alpha$ ) or log (S/ $\alpha$ ) versus  $\alpha$  and extrapolated to  $\alpha = 0$ . From these values of  $\lim_{\alpha \to 0} s/\alpha$ , curves of p( $\beta$ ) can be drawn up. This method was also used by HAYWOOD and THORSON [2]. The above method suffers from the disadvantage that in drawing the smoothed curve small effects which are present at the same value of energy transfer at each angle of scatter may be averaged out. In the present



Fig.6

#### Values of $(S/\alpha)_0$ for D<sub>2</sub>O at 22°C, obtained at two incident energies.

method the raw data at each time channel (i.e. at fixed energy-transfer values) are plotted in the form log  $(S/\alpha)$  versus  $\alpha$  and extrapolated to  $\alpha = 0$ . These individual values of Lim  $S/\alpha$  are converted to  $p(\beta)$ .

The results of HAYWOOD et al. [2] have been reanalysed by this method and new values of  $p(\beta)$  evaluated. Results for positive and negative values of  $\beta$  and for various incident energies are compared on a graph of  $(S/\alpha)_0$  versus  $\beta$ , and an example for room temperature  $D_2O$  is given at Fig. 6. Figs. 3a and 4 are simplified versions of these plots in which representative points are shown superimposed on a smooth line through data for the type shown at Fig. 6. As can be seen by a comparison of Fig. 3a of this paper and Fig. 10 of [2] better resolution is obtained in interesting regions of  $\beta$  by the present method.

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## DISCUSSION

P.A. EGELSTAFF: I would like to present the figure below which compares our data for  $D_2O$  with some recent calculations by Butler (see





Comparison of calculation and experiment for room temperature D,O at  $\beta = 1$ .

Ref. [12] ). Butler used a model in which the molecules were assumed to be free and it can be seen that the result of his calculation agrees with experiment. This is in contrast to the result described by Thorson for  $H_2$  O. One possibility is that, owing to the smaller amplitude of the D's, a  $D_2$  O molecule appears to be free in a situation where the larger amplitude of a hydrogen atom vibration would cause the binding effects to show up.

# THE SCATTERING LAW FOR ROOM TEMPERATURE LIGHT WATER\*

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## Abstract — Résumé — Аннотация — Resumen

THE SCATTERING LAW FOR ROOM TEMPERATURE LIGHT WATER. The Hanford triple-axis crystal spectrometer has been used to measure the Egelstaff scattering law for light water at  $22^{\circ}$ C for neutron wave vector changes up to  $14^{\circ}$ Å<sup>-1</sup> and energy transfers in the range 0.05 to 0.25 eV. The values of initial neutron energy were 0.15, 0.20, 0.30, and 0.40 eV, and scattering angles ranged from 4° to 72°. Scattering by a vanadium sample at 77K served to establish the spectrometer resolution and efficiency functions.

The scattering law  $S(\alpha, \beta)$  and the generalized frequency distribution  $p(\beta)$  derived from it are in substantial agreement in the overlap region with results obtained by Haywood and Thorson at Chalk River. The function  $p(\beta)$  has been extended to  $\beta \approx 10$  to include the region occupied by the lowest molecular vibration level near  $\beta = 8$ . In this region the measured  $p(\beta)$  has a low sloping plateau, indicating that the vibrational peak has been smeared out by broad instrumental resolution. The normalization integral of the measured  $p(\beta)$  is higher than its theoretical value.

LOI DE DIFFUSION DANS L'EAU LÉGÈRE A LA TEMPÉRATURE AMBIANTE. Les auteurs ont employé le spectromètre à cristal triaxial de Hanford pour mesurer la loi de diffusion d'Egelstaff dans l'eau légère à la température de 22°, pour un vecteur d'ondes neutroniques pouvant atteindre 14 Å<sup>-1</sup> et pour des transferts d'énergie compris entre 0,05 et 0,25 eV. L'énergie neutronique initiale était de 0,15, 0,20, 0,30 et 0,40 eV et les angles de diffusion étaient compris entre 4° et 72°. La diffusion par un échantillon de vanadium à 77K a permis d'établir la résolution du spectromètre ainsi que les fonctions d'efficacité.

La loi de diffusion  $S(\alpha, \beta)$  et la distribution des fréquences généralisée  $p(\beta)$  qui en dérive concordent bieu dans la région de recouvrement avec les résultats obtenus par Haywood et Thorson, à Chalk River. La fonction  $p(\beta)$  a été étendue à  $\beta \approx 10$  de manière à englober la région occupée par le plus bas niveau de vibrations moléculaires, qui se trouve dans le voisinage de  $\beta = 8$ . Dans cette région, la distribution  $p(\beta)$  mesurée comporte un domaine à pente douce, ce qui indique que le pic de vibrations a été effacé à cause de la résolution large des instruments. L'intégrale de normalisation de la distribution  $p(\beta)$  mesurée est plus élevée que sa valeur théorique.

ЗАКОН РАССЕЯНИЯ НЕЙТРОНОВ ЛЕГКОЙ ВОДОЙ КОМНАТНОЙ ТЕМПЕРАТУРЫ. Хэнфордский трехосный кристаллический спектрометр использовался для измерения с целью определения закона рассеяния Эгельптаффа для легкой воды при температуре 22°С при изменениях волнового вектора нейтрона до 14 Å<sup>-1</sup> и переносах энергии в пределах от 0,05 до 0,25 эв. Величины первоначальной энергии нейтроков были: 0.15; 0,20; 0,30 и 0,40 эв, а углы рассеяния менялись от 4 до 72°. Рассеяние образцом ванадия дало возможность установить разрешалиую способность спектрометра и эффективные функции.

Закон рассеяния S ( $\alpha,\beta$ ) и обобщенное распределение частоты p ( $\beta$ ), выведенные в результате этого опыта, находятся в существенном соответствии в районе перекрытия с результатами, полученными Хейвудом и Торсоном в Чок Ривер. Функция p ( $\beta$ ) расширена до  $\beta^{2}$ 10 и олвативает область, соответствующую самому низкому уровню молекулярной вибрации приблизительно  $\beta = 8$ . В этой области измеренная p ( $\beta$ ) имеет наклонное плато, показывая, что вибрацииный пик размазывается ввиду плохой разрешающей способности прибора. Интеграл нормализации измеренной p ( $\beta$ ) выше теоретической величины.

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LEY DE DISPERSIÓN DEL AGUA LIGERA A TEMPERATURA AMBIENTE. Los autores han utilizado el espectrómetro de cristal triaxial de Hanford para determinar la ley de dispersión de Egelstaff en el caso del agua ligera a 22°C, con variación del vector de onda neutrónica hasta  $14 \text{ Å}^{-1}$  y transferencias de energía del orden de 0,05 a 0,25 eV. Los valores de la energía neutrónica inicial fueron 0,15, 0,20, 0,30 y 0,40 eV, y los angulos de dispersión variaron de 4° a 72°. La dispersión por una muestra de vanadio a 77K (25°C) haservido para determinar el poder de resolución del espectrómetro y las funciones de rendimiento.

La ley de dispersión  $S(\alpha, \beta)$  y la distribución de frecuencia generalizada  $p(\beta)$  derivada de la misma concuerdan esencialmente en la región de superposición con los resultados obtenidos por Haywood y Thorson en Chalk River. La función  $p(\beta)$  se ha ampliado hasta  $\beta \approx 10$  a fin de incluir la región ocupada por los niveles de vibración molecular más bajos, en las proximidades de  $\beta = 8$ . En este intervalo, la distribución  $p(\beta)$  medida presenta un rellano de pendiente poco acusada que indica que los picos de vibración han sido difuminados por el escaso poder de resolución del instrumento. La integral de normalización de los valores medidos de  $p(\beta)$ es superior a su valor teórico.

## I. INTRODUCTION

Slow-neutron scattering measurements on light water provide significant information in two distinct areas. One is the area of nuclear reactor design, in which a knowledge of the slow-neutron differential (in angle and energy) scattering cross-section of important moderator and coolant materials is required for accurate calculation of neutron-thermalization effects. The second area is the physics of liquids, for which the same scattering crosssection provides detailed information on the motions of the hydrogen atoms present [1].

A number of workers have reported inelastic differential scattering experiments on water, in which relative scattered intensities were obtained [2, 3, 4, 5]. More recently, absolute cross-sections have been measured for water and other materials [6, 7, 8]. The present paper contains the results of work of the latter type, in which are covered larger energy transfers than hitherto reported.

#### **II. THEORY**

VAN HOVE [1], SCHOFIELD [9] and EGELSTAFF [10] have shown that the scattering cross-section for an isotropic material may be written

$$\frac{d^{2} \sigma (E_{1} \rightarrow E_{2}, \varphi)}{d\Omega dE} = \frac{\sigma_{b}}{4\pi kT} \left( \frac{E_{2}}{E_{1}} \right)^{\frac{1}{2}} e^{-\beta/2} S(\alpha, |\beta|)$$

$$\alpha = \frac{(\Delta p)^{2}}{2MkT} = \frac{m(E_{1} + E_{2} - 2[E_{1} E_{2}]^{\frac{1}{2}} \cos \varphi)}{MkT}$$
(1)
$$\beta = \frac{E_{2} - E_{1}}{kT}$$

where  $E_1$  = initial neutron energy,  $E_2$  = final neutron energy,  $\varphi$  = scattering angle,  $\sigma_b$  = bound cross-section of principal scattering atom, k = Boltzmann's constant, T = absolute temperature of sample, m = mass of neutron, M = mass of principal scattering atom and  $\Delta p$  = momentum transfer. The quantity  $S(\alpha, \beta)$ , the so-called "scattering law", in general depends only on the arrangement and motion of the atoms in the scatterer. Because scattering by protons with randomly oriented spins is almost completely incoherent, S for water is sensitive only to the motion of individual hydrogen atoms.  $\alpha$  and  $\beta$  are dimensionless variables proportional to the square of momentum transfer and the energy transfer, respectively [10]. They are scaled to similar relevant physical quantities of atoms in the scatterer and thus have magnitudes of order unity. The present cross-section results will be given in terms of S( $\alpha$ ,  $\beta$ ) because of its convenience and also to facilitate comparison with previous work.

Valuable information about the motions of the atoms in the scattering **system** is contained in the generalized frequency spectrum  $p(\beta)$ , introduced by EGELSTAFF [11].

$$p(\beta) = \beta^2 \lim_{\alpha \to 0} \left[ \frac{S(\alpha, \beta)}{\alpha} \right].$$
 (2)

The function  $p(\beta)$  is the Fourier transform of the velocity correlation function of the atoms of the scattering system and is very closely related to the phonon frequency spectrum in the case of a solid scatterer. By extension to fluid scatterers,  $p(\beta)$  provides a rough picture of the frequency spectrum associated with translational and rotational motions as well as the vibrational ones. The limiting value of  $S/\alpha$  required in Eq. (2) may be obtained by extrapolation of plotted curves of ln  $(S/\alpha)$  versus  $\alpha$  [8]. A check on the accuracy of  $p(\beta)$  is furnished by the PLACZEK first moment theorem [12], which gives

$$2\int_{\beta}^{\infty} \frac{\mathbf{p}(\beta) \sinh(\beta/2)}{\beta} d\beta = 1.$$
 (3)

## **III. APPARATUS**

The basic instrument is a triple-axis crystal spectrometer (Fig. 1). The first axis is heavily shielded and has an available range of approximately  $-15^{\circ}$  to  $+30^{\circ}$  Bragg angle. The Bragg angle for the crystal at this axis is changed manually by a shaft which penetrates the shielding blocks? The second rotation axis (sample axis) mounted on and outside of the rotating shielding allows a rotation of about  $80^{\circ}$ . The analysing spectrometer rotates about the second axis and can reach Bragg angles of approximately  $45^{\circ}$  in either direction. Vertical-axis crystal rotations are performed by commercial precision rotary tables, upon which are mounted interchangeable precision goniometers which provide for manual orientation and positioning of the crystals. All angular settings can be made to within a few 0.01°, a much greater precision than required for the low resolution experiments reported here.

The spectrometer is equipped for automatic programming of arm angles by selected angular increments between two preselected angles. It can be operated by means of a selector switch in either of two modes of operation: (1) at a given scattering angle the analysing spectrometer moves through a sequence of Bragg angles to record an energy distribution, or (2) at a



Fig. 1 Schematic diagram of the Hanford triple-axis crystal spectrometer.

given Bragg angle of the analysing spectrometer an angular distribution about the scattering sample is taken. Automatic recording of the spectrometer arm angles, neutron counting data, and elapsed counting time of each counting interval is done by an electric typewriter.

The monoenergetic beam of neutrons incident on the scattering sample passes through a thin boron chamber to monitor the incident flux. The boron is a very thin and uniform layer cathodically sputtered on aluminium foil and has a detection efficiency of  $5 \times 10^{-5}$  at 0.1 eV. Thus it has a very good 1/v efficiency at all energies of present interest. The detector for the analysing spectrometer is a bank of three BF<sub>3</sub> counters in borated paraffin shielding. These detectors have a calculated efficiency of 25% at 0.15 eV.

The water sample holders have 0.001-in brass windows stretched over knife edges. They were intended to produce a uniform sample of known thickness. However, subsequent thickness measurements using an electrically contacting micrometer have shown that the nominal 0.030-in thick sample bulges to 0.037 in (averaged over the neutron beam), and the nominal 0.013-in sample bulges to 0.020 in.

## IV. EXPERIMENTAL PROCEDURE AND DETAILS

Beryllium monochromating crystals were used at both the first and third rotation axes of the spectrometer. The (0002) planes were used in the analysing crystal for all of the runs and in the monochromating crystal for most of the runs. However, because of the presence of appreciable half-order contamination in the 0.4 eV incident beam, additional runs were made using the (1120) planes in the monochromating crystals. The energy scales of the spectrometer were determined from narrow quasi-elastic scattering peaks observed in both first and second order in the analysing spectrometer, as shown in Fig. 2.



Energy distributions of scattered neutron intensity for water for initial energy of 0.20 eV and scattering angles of  $10^{\circ}$  and  $50^{\circ}$ . The peak at 0.05 eV is due to 2nd order reflection by the analysing crystal. The points represent raw data uncorrected for non-Bragg background in the analysing spectrometer and for scattering from the empty sample holder and environs, which are shown separately by solid and dashed lines, respectively.

Except for a few isolated points, the scattering law results to be presented below are based on angular distribution data taken for selected initial and final energies. However, in order to take angular distribution data for which energy resolution effects can be ignored, it is necessary to make preliminary energy distribution runs at fixed scattering angles in order to locate the energy regions strongly influenced by the quasi-elastic scattering peaks. These peaks are shown in Fig. 2, from which it can be seen that, for an initial energy of 0.2 eV, the range of final energies permissible without energy resolution corrections is 0.075 to 0.15 eV. For higher initial energies the permissible range is smaller, because the quasi-elastic peaks are observed with poorer resolution in both orders.

The water scattering runs were made for initial energies 0.15, 0.20, 0.30, and 0.40 eV and for scattering angles ranging from 4° to 72°. Wave vector changes up to  $14 \text{ A}^{-1}$  ( $\alpha \approx 16$ ) and energy transfers up to 0.25 eV ( $|\beta| \approx 10$ ) were covered. The sample temperature was  $22^{\circ} \pm 2^{\circ}$  C.

All of the present results on water were obtained with the 0.037-in thick sample mounted perpendicular to the incident beam. A few runs were made with the 0.020-in sample, and shape differences of the order of 5 to 15% were indicated. However, these differences were not very significant statistically and no attempt was made to use data from the thinner sample for multiple scattering corrections. At the energies used in the present experiments the thick-sample transmission ranged from 77 to 85%.

The resolution of the monochromating spectrometer and the resolution and sensitivity of the analysing spectrometer were obtained by a series of energy distribution and angular distribution measurements of the scattering from a vanadium sample 0.253-in thick. The vanadium was cooled to the temperature of liquid nitrogen to reduce one-phonon scattering to only a few percent of the elastic scattering even for the largest energy and scattering angle employed. Furthermore, the spectrometer energy resolution was broad enough to include a substantial fraction of the one-phonon scattering together with the elastic scattering. Thus the angular distribution for coldvanadium elastic scattering should be isotopic for a very thin sample. The measured angular distributions, when corrected for absorption and multiple scattering are substantially isotropic, as shown in Fig. 3 for the case of



Fig.3

Angular distribution of elastic scattering of 0.15 eV neutrons from 0.25 in vanadium sample at 77 K. Observed and corrected data points are shown. The curved line relative to the horizontal line gives the multiple scattering and absorption correction factors computed with a neutron transport code.

0.15 eV. In the figure, the observed scattering (corrected for background) and the observed scattering corrected for multiple scattering and absorption are plotted for each scattering angle. The straight line is fitted to the average of the corrected points, and the curved line in relationship to the straight line shows the magnitude and angle dependence of the correction factor. This result also establishes that the analysing spectrometer sensitivity is independent of scattering angle. These correction factors for absorption and multiple scattering for vanadium were computed by means of an  $S_n$  transport theory code [13],

The scheme used for determining the scattering cross-section of water relative to the known scattering cross-section of vanadium is based on the following assumptions:

- (1) The resolution functions for the monochromating and analysing spectrometers are Gaussian;
- (2) The thin boron monitor has 1/v sensitivity;
- (3) The water cross-sections being measured and the detector efficiencies are slowly varying functions within instrumental energy and angular resolution;
- (4) The cold-vanadium scattering cross-section is perfectly elastic, isotropic, and independent of energy.

Under these assumptions it is a straightforward matter to derive the following expression for the scattering law

$$S(\alpha, \beta) = F(E_2) e^{\beta/2} C_{\mu}(E_1 \rightarrow E_2, \varphi)$$
(4)

where the sensitivity factor  $F(E_2)$  is given by

$$\mathbf{F}(\mathbf{E}_{2}) = \frac{\mathbf{k} \mathbf{T} \sigma_{\mathbf{v}} \mathbf{n}_{\mathbf{v}}}{\sqrt{2\pi} \sigma_{\mathbf{Hb}} \mathbf{n}_{\mathbf{H}}} \times \frac{1}{\mathbf{C}_{\mathbf{v}}(\mathbf{E}_{2}) \Delta(\mathbf{E}_{2})}$$
(5)

and where  $C_{H}(E_1 \rightarrow E_2, \varphi) =$  normalized water scattering counts,  $\sigma_v =$  total scattering cross-section of vanadium,  $\sigma_{Hb}$  = bound total scattering cross-section of hydrogen,  $n_y$  = area density of vanadium atoms in sample,  $n_H$  = area density of protons in water sample,  $C_v(E_2)$  = normalized vanadium scattering counts, and  $\Delta(E_2)$  = energy width (standard deviation) of the vanadium elastic peak.  $C_{H}(E_1 \rightarrow E_2, \varphi)$  and  $C_{v}(E_2)$  are each the number of accumulated scattered counts normalized to a fixed standard number of accumulated incident beam monitor counts. This normalization is done primarily for convenience in data handling, but it also has the further advantage that the factor  $(E_2/E_1)^{1/2}$  in Eq. (1) is cancelled because of the 1/v monitor efficiency. To determine  $F(E_2)$  it is necessary only to obtain an energy distribution of the vanadium elastic peak and measure its height and width. In Fig. 4 the energy distribution corrected for background is shown for the case of  $E_1 = 0.15$  eV and scattering angle  $\varphi = 16^\circ$ . The energy widths  $\Delta(E_2)$  are obtained from such curves. The peak values, however, are obtained from corrected angular distribution curves, as in Fig. 3, to get better averaging. It is not necessary to know the individual energy resolutions of the monochromating and analysing spectrometers, crystal reflectivities, or the sensitivity of the BF3 detectors. In this manner  $F(E_2)$  was measured at 0.05, 0.10, 0.15, 0.20, and 0.25 eV. A smooth curve was then drawn to obtain interpolated values (see Fig. 5). In calculating  $F(E_2)$ , values of 5.1 and 81b were used for  $\sigma_v$ and  $\sigma_{Hb}$ , respectively.

In order to find the resolution for  $E_1$  and  $E_2$  separately, additional measurements were made of vanadium elastic scattering, using high resolution in the analysing spectrometer to determine the resolution of the monochromating spectrometer. The resolution of the analysing spectrometer





Energy distribution at 16° scattering angle of 0.15 eV neutrons scattered from 0.25 in vanadium at 77°K.



Fig.5

The analysing spectrometer sensitivity function  $F(E_2)$  defined by Eq.(5) in the text. The size of the plotted dots indicates the statistical error of the measured values. The plotted curve is used for interpolation.

was then obtained by unfolding it from the overall resolution function obtained under conditions of standard resolution. The resulting full width at half maximum of the Bragg angle are 0.5° for the monochromating and 1.3° for the analysing spectrometer. For most of the energy region covered these Bragg-angle widths lead to values of 20 to 40% for  $\Delta\beta/\beta$  (full width at half maximum).

The dimensions of the collimator slits are such that except for very small scattering angles, the angular resolution for the scattering angle is  $2.0^{\circ}$ . The angular spread in the vertical plane is  $4.6^{\circ}$ . These are full widths at half maximum.

Cadmium and gadolinium filters were used to determine the amount of order contamination in the Bragg diffracted beams. Less than 2% of the monitor counts of the incident beam were due to high-order neutrons. Since the scattered beam may be expected to have even less than this, it was not checked for higher orders. Unfortunately the otherwise highly desirable beryllium (0002) planes are susceptible to half-order contamination when conditions for multiple Bragg scattering are satisfied [14]. Filter measurements of the incident and scattered beams indicated that only approximately 5 to 10% of the count in both beams were due to half-order neutrons when the initial energy was 0.15, 0.20, or 0.30 eV. However, at an initial energy of 0.4 eV about 53% of the monitor counts in the incident beam were due to 0.1 eV neutrons, while almost none appeared in the scattered beam. The net result of the order measurements was that, except for the runs at 0.4 eV, no order corrections were made since (a) the effects are small and (b) they partially cancel out due to the presence of contamination in both incident and scattered beams. At 0.4 eV incident energy, the full correction indicated by the filter measurements was done. In addition two check runs at 0.4 eV and one at 0.3 eV incident energy were made, using the beryllium (1120) planes of the monochromating crystal. These planes do not reflect half-order neutrons. The results obtained agree to within about 20% of the corrected results obtained with the (0002) planes.

Empty sample-holder runs were made for the water and cold-vanadium cases to correct for scattering by air and the sample holder windows. Throughout the series of experiments periodic measurements of the scattering from room-temperature vanadium were made to check the stability of the equipment. In most cases the duration of the run and the individual counting periods was arranged so that the spectrometer stepped through approximately three complete cycles of arm motion. Control of counting time was by preset monitor count. In each run background data were taken at each spectrometer step by automatically shifting the analysing crystal several degrees away from the Bragg position.

## V. RESULTS AND DISCUSSION

The water scattering data corrected for background, empty sample holder and order contamination (when necessary as discussed above) were then reduced by means of Eq. (4) to the scattering law  $S(\alpha,\beta)$ , which is plotted in Figs. 6 and 7 versus  $\alpha$  for various fixed values of  $\beta$ . For  $\beta$  = -2.1, -3.0, -6.9, -7.9. and -8.8 there is more than one independent determination of  $S(\alpha,\beta)$ . At  $\beta$  = -2.1 and -3.0, most of the results were obtained for  $E_1$  = 0.2 eV, but a few came from  $E_1 = 0.15$  eV. At  $\beta = -6.9$  results were obtained for  $E_1 = 0.3$  eV with beryllium (0002) planes and beryllium (1120) planes. At  $\beta$  = -7.9 three determinations were made: for E<sub>1</sub> = 0.3 eV with (0002) planes, for  $E_1 = 0.4 \text{ eV}$  (0002) planes which required a large order correction, and for  $E_1 = 0.4$  eV with (1120) planes At  $\beta = -8.8$  results were obtained for  $E_1 = 0.4$  eV with both types of crystal planes. The level of disagreement, which is approximately  $\pm 15\%$ , is a fair measure of the systematic errors due to multiple scattering, order contamination, possible structure in the analysing crystal reflectivity, energy resolution effects, variations in sample thickness, and variations in the stability of the counting electromics.

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The scattering law  $S(a, \beta)$  of water at 22°C as a function of a for various large values of  $\beta$ .

In order to obtain the generalized frequency distribution  $p(\beta)$  defined in Eq. (2), plots of  $\ln S/\alpha$  versus  $\alpha$  were extrapolated by eye to  $\alpha = 0$ . Sample curves are shown in Fig. 8. In the extrapolation greatest weight was given



Fig.8

Curves of S/a for various values of a, extrapolated to a = 0. Uncertainties in the extrapolation due to statistical and systematic errors are indicated by dashed lines.

to the points for intermediate values of  $\alpha$ , since the air scattering corrections are large for small  $\alpha$ . Crude error estimates including systematic effects have been made for the extrapolated values.

The spectrum  $p(\beta)$  obtained in the manner described above is plotted in Fig. 9 together with the results of HAYWOOD and THORSON [8]. In the region of overlap near the hindered rotation peak at  $\beta = 3$ , the agreement with their results appears to be quite satisfactory. The present results give a sloping plateau without structure near  $\beta = 8$ , which corresponds to the lowest molecular vibration level of 0.2 eV in water. Since the resolution in  $\beta$  is approximately 30%, no large amount of structure can be expected.

Despite the surprisingly good agreement between the two sets of results, the situation is not completely satisfactory. The trouble is that the normalization integral in Eq. (3) is too high by at least 46% when calculated from the  $p(\beta)$  curve plotted in Fig. 9. Three possible reasons for this difficulty can be suggested at once. The first is that the increasingly broad resolution in  $\beta$  as  $\beta$  increases may distort the broad hindered-rotation peak



The generalized frequency spectrum  $p(\beta)$  for water at 22°C. Present results are compared to those of HAYWOOD and THORSON [8]. The resolution in the present work is indicated by triangles.

centred near  $\beta = 3$ , and cause it to be partially shifted to higher values of  $\beta$  where it is giver much more weight in the integral. This it may not be valid to neglect energy resolution effects as was done in the present analysis. A second contributing cause may be multiple scattering. The present results have not been corrected for multiple scattering in the water sample. Crude estimates of this correction indicate that it may be as large as 15%. However, the correction cannot be adequately made experimentally with our sparse thin-sample data, and we have not yet had an opportunity to do the multigroup transport calculation necessary to make it theoretically. The third possible source of difficulty may be a systematic error in the S/ $\alpha$  extrapolation which leads to an overestimate of p( $\beta$ ). Unfortunately it is difficult to make an independent estimate of this kind of error.

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## QUASI-ELASTIC SCATTERING BY ROOM TEMPERATURE LIGHT WATER\*

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## Abstract — Résumé — Аннотация — Resumen

QUASI-ELASTIC SCATTERING BY ROOM TEMPERATURE LIGHT WATER. The energy width and integrated intensity of the quasi-elastic scattering peak of light water at 22°C have been measured on the Hanford triple-axis crystal spectrometer at a number of scattering angles for neutrons of energy 0.10, 0.15, and 0.25 eV. The energy resolution was 7, 11, and 10%, respectively. Wave-vector transfers ranged from 1 to  $7 \text{ Å}^{-1}$ .

The quasi-elastic peak was assumed to have a Lorentzian shape in correcting the observed peaks for resolution. When plotted versus the square of the wave-vector transfer, both the corrected line width and integrated intensity exhibit systematic differences correlated with the energy of the neutrons used. In general, the present widths are greater than those obtained with cold and thermal neutrons. Neither the simple classical model nor the Singwi-Sjölander model for self-diffusion in water give completely satisfactory agreement with the present results.

DIFFUSION QUASI-ÉLASTIQUE DANS L'EAU LÉGÈRE A LA TEMPÉRATURE DU LABORATOIRE. Les auteurs ont mesuré la largeur et la valeur intégrée du pic de diffusion quasi-élastique dans l'eau légère à 22°C, en employant le spectromètre triaxial à cristal, pour un certain nombre d'angles de diffusion et pour des neutrons ayant des énergies de 0,10, 0,15 et 0,25 eV. La résolution en énergie était de 7, 11 et 10% respectivement. Le vecteur d'onde variait entre 1 et 7 Å<sup>-1</sup>.

On a supposé que le pic de diffusion quasi élastique avait une forme lorentzienne lorsqu'on a corrigé les pics observés pour tenir compte de la résolution. Si l'on porte sur un diagramme les largeurs de raies corrigées et la valeur intégrée de l'intensité en ordonnée, et les tranferts du carté du vecteur en abscisse, on constate que les raies et l'intensité présentent des différences systématiques qui sont en corrélation avec l'énergie des neutrons utilisés. D'une manière générale, les largeurs de raies sont plus grandes que celles qu'on obtient avec des neutrons froids ou thermiques. Ni le modèle classique simple, ni le modèle de Singwi-Sjölander d'autodiffusion dans l'eau ne donnent une concordance entièrement satisfaisante avec les résultats indiqués dans le mémoire.

КВАЗИУПРУГОЕ РАССЕЯНИЕ НЕЙТРОНОВ В ЛЕГКОЙ ВОДЕ ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ. Энергетическая ширина и общая интенсивность в пике квазиупругого рассеяния нейтронов легкой водой при 22°С измерялись на хэнфордском трехосном кристаллическом спектрометре при нескольких углах рассеяния нейтронов с энергией 0,10; 0,15 и 0,25 эв. Энергетическая разрешающая способность составляла соответственно 7, 11 и 10%. Изменения волнового вектора кодебались в пределах от 1 до 7 Å<sup>-4</sup>.

Предполагалось, что квазиупругий пик имеет форму Лорентца, и это учитывалось при разрешении наблюдаемых пиков. При составлении графика в зависимости от квадрата волнового вектора как скорректированная ширина линии, так и общая интенсивность показывают систематические различия, которые связаны с энергией использованных нейтронов. В общем полученная ширина линий является значительно большей, чем ширина линий, полученная с помощью холодных и тепловых нейтронов. Ни простая классическая модель, ни модель Сингви-Сьеландера для самодиффузии в воде не дают полностью Удовлетворительного соответствия с настоящими результатами.

DISPERSIÓN CUASI ELÁSTICA POR AGUA LIGERA A TEMPERATURA AMBIENTE. Los autores han medido la amplitud energética y la intensidad integrada del pico de dispersión cuasi elástica del agua ligera a 22°C.

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utilizando el espectrométro de cristal triaxial de Hanford en varios ángulos de dispersión para energías neutrónicas de 0,10, 0,15 y 0,25 eV. El poder de resolución fue de 7, 11 y 10%, respectivamente. Los desplazamientos de los vectores de onda fueron del orden de 1 a 7 Å<sup>-1</sup>.

Al corregir los picos observados para tener en cuenta el poder de resolución de los instrumentos, se supuso que el pico cuasi elástico responde a una ecuación de Lorentz. Cuando se las representa en función del cuadrado del desplazamiento del vector de onda, tanto el ancho de línea corregido como la intensidad integrada presentan diferencias sistemáticas que guardan una relación con la energía de los neutrones empleados. En general, los anchos así obtenidos son superiores a los correspondientes a los neutrones fríos y térmicos. Ni el modelo clásico de dispersión simple ni el de Singwi-Sjölander de autodispersión en agua concuerdan de un modo completamente satisfactorio con los resultados obtenidos por los autores.

## I. INTRODUCTION

Inelastic differential scattering of slow neutrons in general provides detailed information about the structure and dynamics of the scattering material [1, 2]. Since scattering by light water is almost completely due to incoherent scattering by hydrogen, the inelastic differential cross-section is sensitive only to the motions of the constituent hydrogen atoms. Several years ago BROCKHOUSE found that the scattering cross-section for water as a function of final energy could be considered to consist of two overlapping components [3]. The first component covers a wide energy region and is attributable to a broad spectrum of fast atomic motions, such as rotations and vibrations. The second component is a rather narrow energy peak centred at the incident energy; it is attributable to a slow diffusive motion. In the present paper only the latter component, the quasi-elastic peak, is considered.

A number of experimental studies of the quasi-elastic scattering by light water have been reported [3, 4, 5, 6, 7, 8, 9]. Those studies were done with either thermal or cold neutrons and covered the region of small values of momentum transfer. The present paper reports on experiments performed with neutrons of somewhat higher energy and correspondingly larger values of momentum transfer.

## **II. THEORY**

5. 16.

The property of quasi-elastic scattering which has attracted most interest is its energy width. Theoretical considerations show that in general the width may be expected to be a function of the self-diffusion coefficient and of the square of the momentum transfer  $\hbar^2 Q^2$  [1,2]. A number of models for the diffusion process have been proposed [2,3,10,11]. Most of these models predict that the quasi-elastic peak broadens as the momentum transfer (or scattering angle) increases, particularly in the region of small values of momentum transfer. The simplest model [2,3], which corresponds to classical continuous diffusion, predicts that the line shape is Lorentzian with a full width at half maximum given by

$$\Delta E = 2 \hbar DQ^2. \tag{1}$$

A more complex model, in which a molecule oscillates for a mean time  $\tau_0$ and then diffuses by continuous motion for a mean time  $\tau_1$ , has been suggested by SINGWI and SJŌLANDER [10]. For  $\tau_1 \gg \tau_0$  the process reduces to continuous diffusion and the width is given by Eq. (1). For the other extreme case in which  $\tau_1 \ll \tau_0$  the line shape is again Lorentzian and the width is given by

$$\Delta \mathbf{E} = \frac{2\hbar}{\tau_0} \left( 1 - \frac{\mathbf{e}^{-2W}}{1 + \tau_0 \ \mathbf{D}\mathbf{Q}^2} \right)$$
(2)

where  $e^{-2W}$  is the Debye-Waller factor (defined immediately below).

The classical diffusion model starting with a Gaussian "cloud" of finite size [2] predicts that the angular dependence of the integrated quasi-elastic peak intensity is

$$I_{int} = I_0 e^{-2W} = I_0 e^{-Q^2 u^2}$$
(3)

where  $I_0$  is the integrated intensity in the forward direction and  $6u^2$  is the initial mean-square radius of the diffusing Gaussian cloud. The finite size of u is presumably due to vibrational and rotational motions which are very rapid on the diffusion time scale. The model of SINGWI and SJOLANDER[10] also gives an integrated intensity in accordance with Eq. (3) when  $\tau_1 \ll \tau_0$ .

## III. EXPERIMENTAL DETAILS

The experiments were performed with the Hanford triple-axis crystal spectrometer [12]. For an initial energy of 0.147 eV a series of energy distribution runs was made at scattering angles of 3°, 10°, 20°, 30°, 40° and 50°. A preliminary analysis of these experiments has been reported earlier [13]. In these runs beryllium (0002) planes were used in the monochromating spectrometer and aluminium (200) planes in the analysing spectrometer. The energy resolution was 11%. Subsequently, two brief series of runs were made at initial energies of 0.100 eV and 0.247 eV for scattering angles of 3°, 10°, 20° and 30° with resolutions 7% and 10% respectively. For these two series beryllium  $(11\overline{2}0)$  planes were used in the monochromator and beryllium  $(10\overline{13})$  planes were used in the analyser. In all of the runs listed above the water sample thickness was 1.7 mm; the thickness of each aluminium window of the sample holder was 0.03 mm. Finally, in order to check the effect of sample thickness, runs were made for an initial energy of 0.146 eV at scattering angles of 4° and 40°, using a water sample 0.9 mm thick between brass windows 0.03 mm thick. In these thin sample runs beryllium (1120) and 1013) planes were used with an energy resolution of 11%. The sample temperature was  $22 \pm 2^{\circ}C$ . The sample was mounted perpendicular to the incident beam.

A few energy distribution measurements of elastic scattering were also made employing a vanadium sample of 6.4 mm thickness to obtain the spectrometer resolution. However, it turned out that the resolution widths obtained with vanadium were very slightly larger than those obtained for water at small scattering angles, i.e. 3° or 4°. Perhaps the inelastic (phonon) scattering by vanadium broadened the elastic peak slightly. In any case the widths obtained from water scattering at small angles were used as resolution widths in the analysis of the data.

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An appropriate balance between intensity and resolution was obtained in the various series by varying the number of cadmium strips forming Sollertype slits in the analysing spectrometer. The incident beam was monitored with a thin boron chamber, while the scattered neutrons were detected with a bank of three  $BF_3$  tubes. Subsequent measurements with cadmium and gadolinium filters showed that order contamination effects amount to only a few percent at the energies used. Background was measured by automatically rotating the analysing crystal a few degrees away from the Bragg position. For water runs at small scattering angles using the sample holder with aluminium windows, air scattering was determined by removing the sample holder. For water runs using the brass windows, correction runs were made with an empty sample holder.

## IV. DATA AND ANALYSIS

In Fig. 1 are shown three typical energy distributions, which have been corrected for non-Bragg background and air scattering. Since the incident energy is well above thermal energy, the low inelastic plateau is located mainly at energies lower than the initial value. The usual broadening of width and decrease of peak intensity with increase in scattering angle observed in line studies of the quasi-elastic peak [3, 5, 6, 8] is evident here. The shape of the spectrometer resolution function, as given by the curve obtained at a scattering angle of  $3^{\circ}$ , is Gaussian.

The method of analysis of the quasi-elastic peak used here is the semiintuitive approach of BROCKHOUSE [3], who suggested that the peak may be isolated by subtracting off the inelastic component. In our first attempt the subtraction was carried out by drawing in a smooth interpolation of the inelastic component and fitting the remaining peak to a Gaussian function by means of a least-squares computer programme. However, this scheme failed because the wider peaks had tails too high to be well represented. This characteristic of the data, as well as theoretical considerations [3], suggested that the true shape of the quasi-elastic peak may be approximately Lorentzian. Thus the analysis of the present data is based on the assumption of a Lorentz line shape.

Since the convolution of a Gaussian and Lorentzian function was not found to be convenient for computation. the least-squares fitting programme was generalized to include several of the lowest-order Hermite functions as well as the Gaussian to represent the broadened quasi-elastic peak and a linear term to represent the inelastic component. The width of the peak determined by the Hermite functions is then tentatively taken as the measured width of the resolution-broadened quasi-elastic peak. From the ratio of this measured width to the resolution width, it is then possible to determine the ratio of the true (Lorentz) width to the resolution width. This operation is facilitated by appropriate graphs based on tables [14] of the function  $\Psi(\mathbf{x}, t)$ , the convolution of Lorentzian and Gaussian functions. The shape of the fitted peak in the wings is then checked for consistency with the shape of the convolution function determined by the tentative value for the measured width. If the shapes are not consistent, the linear function representing the inelastic component is adjusted (usually downward) graphically, and the widths are



Representative quasi-elastic peaks for 0.15 eV neutrons at scattering angles of 3°, 20° and 40°. Background subtractions have been made as well as corrections for air scattering for the 3° case. Each correction was approximately 40 to 50 units on the intensity scale shown. The plotted curves were fitted by a least-squares programme.

modified accordingly. In practice only one step of the iteration process is required to produce satisfactory agreement. When such an adjustment of the linear function is required, the statistical error estimates of the parameters of the peak produced by the programme are augmented manually to take into account the additional uncertainty introduced. These adjustments of the error estimates are quite generous, since the entire concept of subtracting the inelastic component is rather uncertain. For the narrow peaks found at small angles of scattering, the statistical error dominates, while for the broadened peaks found at larger angles, the uncertainty due to the position of the linear term dominates.

The area of each observed peak (omitting the linear function) is also computed by the programme as a measure of the integrated intensity in the quasi-elastic peak. In principle, this scheme gives the integrated intensity

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independent of any assumptions about the true line shape. However, it is subject to error when a substantial part of the area is in the tails and the data do not cover the tails completely. When the linear function requires manual adjustment to produce a consistent shape, the calculated area is modified accordingly. Here again rather generous allowance is made for uncertainty in the process of subtracting the inelastic component.

In the analysis of the data the true width and integrated intensity have not been corrected for multiple scattering. Despite the rather large thickness of the 1.7 mm sample (transmission  $\approx$  70%), rough estimates show that these corrections are only 3 to 5% for the cases covered. The effect on the peak width is small because a large fraction of the twice scattered neutrons are completely removed from the neighbourhood of the peak by broad inelastic scattering. The effect on the shape of the angular distribution of the integrated intensity is small because the difference in path length for neutrons at the various scattering angles is small. These conclusions are verified by the data taken at 0.15 eV using the 0.9-mm thick sample.

## TABLE I

QUASI-ELASTIC SCATTERING DATA AND RESULTS FOR WATER AT 22° The quantities tabulated are:  $E_0$  = neutron energy, t = sample thickness,  $\varphi$  = scattering angle,  $Q^2$  = square of wave vector transfer,  $(\Delta E)_0$  = directly observed width of quasi-elastic peak,  $I_p$  = observed intensity at peak maximum,  $\Delta E$  = true width of peak,  $I_{int}$  = integrated intensity of peak

				- 111			
E <sub>0</sub>	<b>t</b> -	φ	Q <sup>2</sup>	(∆E)₀	I <sub>p</sub>	∆E	I <sub>int</sub>
(eV)	(mm)	(deg)	(A-2)	(10-3 eV)	(arbitrary)	(10 ° eV)	(arbitrary)
0.1	1.7	3	0.13 ·	5.8 ± 0.1	270 ± 8		1.0 ± 0.03
		10	1.46	6.7±0.2	222 ± 5	1.7±0.4	0.94 ± 0.04
		20	5. 82	7.8 ± 0.4	165 ± 6	2.7 ± 0.7	0.82 ± 0.06
		30	12.9	11.1 ± 0.7	114 ± 8	8.0 ± 1.0	0.82 ± 0.17
		3	0,20	16.8 ± 0.3	690 ± 17		1.0 ± 0.024
0. 147	1,7	10	2.15	17.2 ± 0.3	650 ± 12	0.9 + 0.8 - 0.9	0.97 ± 0.02
		20	88.56	20.0±0.3	560 ± 10	5.8 + 0.8 - 1.0	0.98 ± 0.024
		<b>30</b> -	19.10	21.8 ± 0.9	320 ± 14	8.6 ± 1.5	0.64 ± 0.04
		40	33.2	25.3 ± 1.1	178 ± 10	14.1 ± 1.8	0.41 ± 0.03
		50	50.7	24.1 ± 3.3	95 ± 15	12.3 ± 5.3	<sup>1</sup> 0.21 ± 0.06
		• 4	0.35	16.3 ± 0.5	133 ± 4		1.0 ± 0.02
0.146	0.9	40	33.2	23.4 ± 2.2	72 ± 5	12.2 ± 3.3	0.46 ± 0.10
1.1		3	0.33	24.0±0.8	98 ± 3		1.0 ± 0.04
0.247	1.7	10	3.63	26.8 ± 1.2	104 ± 4	5.2 ± 2.4	1.18 ± 0.04
		20	14.3	31.0 ± 3.0	88 ± 5	12,0 ± 3,6	1.18 ± 0.12
		<b>3</b> 0	31.9	42.5 ± 5.6	50 ± 5	28.0 ± 8.0	0.74 ± 0.12

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## QUASI-ELASTIC SCATTERING BY LIGHT WATER

The results of the analysis are given in Table I, which also contains other pertinent experimental information, i.e. the initial energy, sample thickness, and scattering angle and the square of the wave vector transfer  $Q^2$  in Columns 1 through 4. In Columns 5 and 6 the observed width and peak intensity of each resolution-broadened peak are given. The derived values of true width and integrated intensity normalized to unity in the forward direction are given in Columns 7 and 8.

## V. RESULTS AND DISCUSSION

The integrated intensities and line widths obtained in the analysis described above are plotted as functions of  $Q^2$  in Fig. 2 and Fig. 3, respectively. It can be seen that the results obtained at 0.10 and 0.15 eV are in good agreement. However, the results obtained at 0.25 eV show a systematic deviation from the others, despite very large uncertainties. Furthermore it must be





Integrated intensity  $I_{int}$  of quasi-elastic peaks versus  $Q^2$  for 0.10, 0.15 and 0.25 eV neutrons. For each energy the intensity has been normalized to that obtained at a scattering angle of 3°. The plotted lines are given by  $I = I_0 e^{-Q^2 u^2}$  with the indicated values of u.

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The full width at half maximum  $\Delta E$  of quasi-elastic peak as a function of Q<sup>2</sup>. The solid line corresponds to the simple diffusion model with  $D = 3.7 \times 10^{-5} \text{ cm}^2/\text{s}$ . The dashed line corresponds to the Singwi-Sjölander formula with  $\tau_2 = 0.82 \times 10^{-13}$  s and  $D = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}$ .

noted that for small values of  $Q^2$  the widths obtained are approximately twice as large as those determined with cold neutrons and thermal neutrons [3, 4, 5, 6, 7, 8, 9]. Similarly the values found for the cloud size parameter u are about half as large as those obtained with slower neutrons [3, 7]. Thus the values of  $\Delta E$  and u appear to depend systematically on the energy of the neutrons used in the experiment. This suggests the possibility of appreciable systematic error in the experiments or the analysis scheme.

Temporarily ignoring this difficulty, one may reasonably treat the plotted results in two ways. The first is to give appropriate weight to all the plotted points in Fig. 3 and represent them in the simplest manner, i.e. with a straight line having the form of Eq. (1). Such a line has been drawn by eye in Fig.3. It corresponds to a classical diffusion coefficient  $D = 3.7 \times 10^{-5} \text{ cm}^2/\text{s}$ , a value which is 50% to 100% greater than those obtained in neutron scattering experiments [6, 7, 8] and in tracer and nuclear magnetic resonance experiments [15, 16, 17]. The second method of treatment is to ignore the discrepant results at 0.25 eV and to fit the concordant results at 0.10 eV and 0.15 eV. Since the width shows a tendency to saturate at large Q<sup>2</sup>, Eq. (2) is appropriate. As shown by the dashed line on the graph, a satisfactory fit is obtained for  $D = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $\tau_0 = 0.82 \times 10^{-13}$  s and u = 0.17 Å, the value of u having been obtained from the fitted line for 0.15 eV in Fig.2. While the indicated value of D is quite satisfactory, the value for  $\tau_0$  is ex-

tremely small compared to the characteristic times of various physical processes in water [10].

The preceding discussion shows that neither of the suggested alternative interpretations of the present results is completely satisfactory. This leads back to the possibility of systematic error in the experiment or analysis. It is clear that the line widths are unexpectedly large. Possible causes of overestimation of the line widths are multiple-scattering, an energy dependence of the spectrometer sensitivity which distorts the measured peak, a non-Lorentzian line shape, and incorrect estimates for the subtracted inelastic component.

There are, however, limits on the magnitude of the first three of the possible difficulties listed above. Each will be discussed in turn. First, multiple scattering has been shown experimentally to have a negligible effect. Second, there is no evidence for instrumental distortion, since the observed peaks have reasonably symmetrical shapes and are not displaced in position. Furthermore, similar results have been obtained with different monochromating crystals and different crystal planes. Third, an attempt has been made to evaluate the effect of line shape by trying a Gaussian in a few cases. However, this has given even greater line widths.

The fourth of the suggested causes of difficulty, i.e. incorrect estimates of the subtracted inelastic component, is hard to discuss quantitatively. Large allowances have already been made for uncertainty in the magnitude of the subtracted inelastic component on the assumption that it can be represented approximately by a linear function within the instrumental resolution. However, low-frequency vibratory motions corresponding to energy transfers of 0.006 to 0.010 eV [7] may give rise to a peak having a width comparable to the instrumental resolution. Such a peak would be almost inextricably superimposed on the true quasi-elastic peak due to diffusion and would cause overestimation of the diffusive peak width. It would also lead to a Debye-Waller factor corresponding to a small value of the cloud size parameter u, since the observed peaks would be sensitive to shorttime motions occurring prior to true diffusion. In view of this possible source of difficulty, a definite knowledge of the behaviour of the diffusive component of the quasi-elastic peak at large values of  $Q^2$  must await experiments at higher resolution.

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## DISCUSSION

## (on the previous two papers)

K. S. SINGWI: Since your incident neutron energy is so high, I would expect that all you were seeing was the gas-like behaviour of water molecules. In such a case there is no justification for analysing the quasi-elastic scattering in terms of diffusion, which is a form of long-term molecular behaviour. Were you trying to make a guess?

D. A. KOTTWITZ: I agree, but it is tempting to attempt this analysis, even though it is hard to know what kind of mass to use in the gas model. I am sure it would be greater than 1 and less than 18, but it would be difficult to give an exact figure.

K.E. LARSSON: What are the transmissions of your samples?

D. A. KOTTWITZ: About 70%. However, we did work with a much thinner sample and the result on the widths were precisely the same. The reason is that most of the high removal in the thick sample is due to removal from the peak. We are dealing with something exactly like an absorption cross-section. There is very little probability of its reappearing in the peak upon second scattering. Owing to the thickness of the sample, there is very little broadening. This has been checked experimentally and by calculation.

D. T. GOLDMAN: I think Dr. Singwi would agree that, in principle, it is possible to perform this experiment to get the diffusive motion but that the high energy makes it very hard to get the necessary energy resolution.

D. A. KOTTWITZ: That's right, if we could do it at a higher resolution, it would be quite feasible.

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## КВАЗИУПРУГОЕ РАССЕЯНИЕ ХОЛОДНЫХ НЕЙТРОНОВ НА ВОДЕ

## А. БАЙОРИК, В.В. ГОЛИКОВ, И. ЖУКОВСКАЯ, Ф.Л. ШАПИРО, А.ШКАТУЛА и Е.А. ЯНИК ОБЪЕДИНЕННЫЙ ИНСТИТУТ ЯДЕРНЫХ ИССЛЕДОВАНИЙ, ДУБНА СССР

## Abstract — Résumé — Аннотация — Resumen

QUASI-ELASTIC SCATTERING OF COLD NEUTRONS IN WATER. The authors discuss the results of investigations carried out with a cold-neutron spectrometer into the quasi-elastic scattering of cold neutrons in water. The neutron source was a pulsed fast reactor. Measurements were made with resolutions of up to 0.5% and an energy of 5 meV.

DIFFUSION QUASI-ÉLASTIQUE DES NEUTRONS THERMIQUES DANS L'EAU. Les auteurs exposent les résultats de leurs recherches sur la diffusion quasi-élastique des neutrons thermiques dans l'eau, qu'ils ont faites à l'aide d'un spectromètre à neutrons thermiques. Comme source de neutrons, ils ont utilisé un réacteur à flux pulsé de neutrons rapides. Le spectromètre avait un pouvoir de résolution de 0,5% et les neutrons avaient une énergie de 5 meV.

КВАЗИУПРУГОЕ РАССЕЯНИЕ ХОЛОДНЫХ НЕЙТРОНОВ НА ВОДЕ. В докладе излагаются результаты исследований квазиупругого рассеяния холодных нейтронов на воде, проведенных при помощи спектрометра холодных нейтронов. В качестве источника нейтронов использован импульсный быстрый реактор. Измерения выполнены с разрешением до 0,5% при энергии 5 миллизлектронвольт.

DISPERSIÓN CUASI ELÁSTICA DE NEUTRONES FRÍOS EN AGUA. Los autores exponen los resultados de sus investigaciones sobre la dispersión cuasi elástica de neutrones fríos en agua, efectuadas con ayuda de un espectrómetro de neutrones fríos. Como fuente de neutrones, utilizaron un reactor rápido pulsante. Las mediciones se efectuaron con un poder de resolución de 0,5%, como máximo, y una energía de 5 meV.

В последние годы было проведено несколько исследований нейтронных спектров, возникающих при рассеянии холодных нейтронов в воде [1-7]. В этих работах значительное внимание уделено квазиупругому рассеянию, т.е. рассеянию с передачей энергии, малой по сравнению с энергией падающего нейтрона. Теория [8,9] предсказывает, что при квазиупругом рассеянии моноэнергетических нейтронов в жидкости образуется спектр, имеющий лоренцову форму с полушириной

$$\Gamma = 2hx^2D, \qquad ($$

где  $h\vec{x}$  – изменение импульса при рассеянии, D – эффективный коэффициент автодиффузии. Классические методы дают для коэффициента диффузии молекул воды в воде значение D=1,85·10<sup>-5</sup> см<sup>2</sup>/сек.Анализируя квазиупругое рассеяние холодных нейтронов на воде, различные авторы приходят к несогласующимся выводам, получая значения D в пределах от D<0,1D<sub>0</sub> до D=D<sub>0</sub> [5]. Некоторые авторы усматривают также в спектрах рассеянных нейтронов пики, соответствующие передаче очень малых дискретных порций энергии (порядка 5·10<sup>-4</sup> эв) [1,2]; другие авторы не находят таких пиков [4-7].

В связи с отмеченными противоречиями представлялось интересным провести измерения спектров нейтронов, рассеянных на воде,

1)
с разрешением, заметно лучшим разрешения, достигнутого в работах [1-7]. В настоящем докладе сообщаются предварительные результати таких измерений, выполненых на импульсном быстром реакторе Объединенного института ядерных исследований. Использовавшаяся экспериментальная установка описана в докладе [10].

На слой воды толщиной около 0,3 мм направлялся импульсный пучок нейтронов, фильтрованных бериллием. Нейтроны, рассеянные на угол 75  $\pm$  10°, регистрировались детектором, установленным на расстоянии 17 или 45 м от образца. Для измерения спектра нейтронов, падающих на образец, использовалось упругое рассеяние на ванадии. Результаты измерений при температуре воды 25°С приведены на рис.1 и 2. Из кривых вычтен фон, для нахождения которого падающий на



Рис.1

Спектр нейтронов, рассеянных на ванадии (кривая 1)и воде (кривая 2). Расстояние от образца до детектора ~ 45 м.Ширина канала временного анализатора - 64 мксек. Пунктирные кривые проведены по экспериментальным точкам. Сплошные кривые проведены по точкам,исправленным на пропускание A1. образец пучок перекрывался кадмием. Фон был примерно в 4 раза меньше эффекта. В результате внесена также поправка на рассеяние алюминием (на пути рассеянного пучка находилась пластинка алюминия толщиной около 6 мм. Поправка расчитывалась по измерениям пропускания аналогичных алюминиевых листов, выполненным на базе 45 м(рис.3).

Как видно из кривой 1 (рис.1), полуширина наклона бериллиевого края составляет~120 мксекунд, что при расстоянии 45 м соответствует энергетическому разрешению 3·10<sup>-5</sup>эв для нейтронов с энергией в районе 5,2·10<sup>-3</sup> эв. Эту величину нужно сравнивать с предельным разрешением 2·10<sup>-4</sup> эв, использованным в предыдущих работах [4]. Сравнение кривых 1 и 2 (рис.2) показывает, вне всякого сомнения,





Спектр нейтронов, рассеянных слоем воды толщиной 0,3 мм. Кривая 2 снята на расстоянии от образца до детектора 45 м; кривая 3 - на расстоянии 17 м. Пунктирная кривая показывает форму спектра нейтронов, упруго рассеянных на ванадии на расстоянии 45 м.Все кривые исправлены на пропускание A1.

что при рассеянии на воде линия 5,2·10<sup>-3</sup> эв уширяется. Для количественной оценки нужно исходить из выражения для зависимости скорости счета N(t) рассеянных нейтронов от времени пролета t:

$$N(t)dt = dt \frac{dE}{dt} \int_{0}^{E_{0}} F(E^{\dagger})\sigma(E^{\prime})W(E^{\prime},E)dE^{\prime}, \qquad (2)$$

## где F(E')dE'- спектр падающего на образец потока;

о(Е') - сечение рассеяния на образце;

W(E',E)dE - спектр рассеянных нейтронов для первичной энергии E'. В теории квазиупругого рассеяния [8,9.] W (E',E) - лоренцова резонансная кривая с шириной на половине высоты Г [1]. Для определения Г можно воспользоваться расстоянием от середины бериллиевого края для ванадия до максимума распределения для воды. Это расстояние сложным образом зависит от Г и законов F(E) и σ(E). Поскольку последние в данной работе не изучались, этот путь казался нам неоднозначным, и мы предпочли опираться на значение логарифмической производной N'(t)/N(t) в центре бериллиевого края. Значение производной слабо зависит от спектра F(E')σ(E'); полагая F(E')σ(E')∞ E', нетрудно получить следующее выражение для Г, являющееся хорошим приближением:

$$\Gamma = 8E_0 / \pi \left[ \frac{N^{\dagger}(t_0)}{N(t_0)} t_0 + 5 \right]$$
(3)

Здесь  $E_0$ ,  $t_0$  - энергия и время пролета для бериллиего края; под  $N(t_0)$  следует понимать скорость счета при  $t = t_0$ , за вычетом подложки, не связанной с квазиупругим рассеянием. Оценка подложки не может быть проведена однозначно, так как неясно, является ли участок кривой в интервале 0,93 - 0,99 мсек "хвостом спектра" квазиупругого рассеяния, или здесь проявляются дискретные энергетические переходы. Если принять первое, а также пренебречь собственной шириной бериллиевого края (что для расстояния 45 м не будет плохим приближением), то получается значение:

$$\Gamma = (5 \pm 1) 10^{-4}$$
 эв.

Во втором предположении подложка выше, и

Можно принять  $\Gamma = (5 \pm 1) \cdot 10^{-4}$  эв, чему при угле рассеяния 75°  $(x^2 = 3, 7 \cdot A^{-2})$  соответствует  $D = 0, 5D_0$ .

Наш результат не отличается от последних данных Ларссона и Дальборга [7], получивших при комнатной температуре для  $x^2 = 3,7 \cdot A^{-2}$ значение  $\Gamma = (6 \pm 1) \cdot 10^{-4}$  эв.

В заключение остановимся на вопросе о малых дискретных передачах энергии. Во многих из проведенных нами двух - трех-дневных серий измерений в спектрах вблизи бериллиевого края проявились ступеньки соответствующие передачам энергии ~ 2,4 и 6.10<sup>-4</sup> эв. Высоты ступенек составляли несколько процентов от полной интенсивности при данном времени пролета. Положения и высоты ступенек в различных сериях измерений согласовывались, в том числе и в измерениях на базах 45 и 17 м (рис.2). При суммировании всех серий ступеньки, однако, сглаживались. Хотя это может объясняться дрейфами аппаратуры, в настоящее время вопрос о наличии или отсутствии ступенек остается открытым.

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Рис.3



Измерения рассеяния нейтронов на воде продолжаются - проводятся измерения при различных температурах жидкости, а также со льдом.





## А. БАЙОРИК и др.

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## DISCUSSION

A. SJÖLANDER: At what temperature was this experiment done?

J. JANIK: All the curves shown in the paper are for room temperature. I would merely point out that for lower temperatures the broadening is smaller.

K.S. SINGWI: Do you have any data for width as a function of scattering angle? With your high resolution such data would be valuable for a number of reasons.

J. JANIK: No, I do not. We could have changed the angles to  $30^{\circ}$  but we did not make any experiments along those lines. Our findings are for one angle (75°) only.

**P.A.** EGELSTAFF: I wonder if the theoreticians present would like to consider ways of constructing a model which would show the small steps on the side of the quasi-elastic peak. I raise this point because any simple model, e.g. one based on a Gaussian  $G_s(\underline{r}, t)$ , would lead to expressions in which the diffusive term is folded with the "phonon" terms. Consequently, small steps due to "phonon-like" energy levels would have the same width as the diffusion peak and would not be observed as steps.

I would also like to point out that at these Q values, a Lorentzian lineshape is probably a very poor assumption. If the line-shape turned out to be nearly Lorentzian for the Q value used in this experiment, it would indicate that more than one diffusive mode was being observed.

J. JANIK: Perhaps I should mention that since the theoretical quasielastic distribution (as shown in Fig. 4) fits the experimental data very well, the inelastic steps, if real, must have a very small intensity and appear as a "fine structure" only in the "quasi-elastic background".

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# CALCULATION OF THE INELASTIC SCATTERING OF NEUTRONS FROM POLYETHYLENE AND WATER

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#### Abstract — Résumé — Аннотация — Resumen

CALCULATION OF THE INELASTIC SCATTERING OF NEUTRONS FROM POLYETHYLENE AND WATER. A model for the calculation of the scattering of thermal neutrons from chemical system was proposed by Nelkin. This model considered the actual dynamics of the scattering system as composed of a set of oscillatory motions, each describable by a Hamiltonian which commuted with each of the others. It was then possible to express the differential scattering cross-section in closed form. This model has been used to calculate the. scattering of neutrons by water. Some care must be taken in performing the numerical integration over angle and energy. The scattering model has been extended to the calculation of neuron scattering from polyethylene  $C_nH_{2n}$ . Analogous levels of polyethylene can be noted at 0.089 eV, 0.182 eV, 0.354 eV, and 0.533 eV. The differential and total cross-sections have been calculated for the scattering and the latter has been seen to be in reasonable agreement with experiment at room temperature. Scattering kernels have been calculated for a number of temperatures and where possible the results have been compared with experiment. In addition, neutron flux spectra and diffusion lengths have been calculated using the equations of reactor physics. Comparison of these results with experimental data indicates that such integral measurements are indicative of at least the gross features of the scattering system and should be analysed in conjuction with the detailed differential cross-section results.

CALCUL DE LA DIFFUSION INÉLASTIQUE DES NEUTRONS PAR LE POLYÉTHYLÈNE ET L'EAU, Nelkin a proposé un modèle pour calculer la diffusion de neutrons thermiques dans des systèmes chimiques. Dans ce modèle on considère que la dynamique réelle du système de diffusion se compose d'un ensemble de mouvements oscillatoires, chaque mouvement pouvant être décrit par un hamiltonien commutant avec chacun des autres. Il est alors possible d'exprimer la section efficace différentielle de diffusion sous une forme fermée. Les auteurs ont employé ce modèle pour calculer la diffusion des neutrons par l'eau. Il faut prendre quelques précautions lorsque l'on fait l'intégration numérique par rapport aux angles et aux énergies. Le modèle de diffusion a été étendu aux calculs de la diffusion des neutrons par le polyéthylène $C_nH_{2n}$ . On note des niveaux analogues à 0,089 eV, 0,182 eV, 0,354 eV et 0,533 eV. Les auteurs ont calculé les sections efficaces différentielle et totale pour la diffusion et ils ont constaté que la seconde est en bon accord avec l'expérience à la température du laboratoire. Ils ont calculé des noyaux de diffusion pour un certain nombre de températures et, chaque fois qu'il était possible de le faire, ils ont comparé les résultats aux expériences. De plus, ils ont calculé les spectres de flux de neutrons et les longueurs de diffusion en se fondant sur les équations de la physique des réacteurs. En comparant ces résultats et les données expérimentales, on constate que ces mesures intégrales donnent au moins des indications générales sur les caractéristiques du système de diffusion et qu'il conviendrait de les analyser en tenant compte des résultats détaillés relatifs aux sections efficaces différentielles.

РАСЧЕТ НЕУПРУГОГО РАССЕЯНИЯ НЕЙТРОНОВ ПОЛИЭТИЛЕНОМ И ВОДОЙ. Модель для вичиодения рассеяния тепловых нейтронов химическими соединениями была предложена Нелькином. Эта модель рассчитивала действительную динамику рассеивающей системи, состоящей из набора колебательных движений, каждое из которых характеризуется Гамильтонианом и может быть заменено другим. После этого стало возможно определить дифференциальное сечение рассеяния в закрытых формах. Эта модель использовалась для того, чтобы подсчитать расссеяние нейтронов водой. Следует уделить некоторое внимание

\* Operated by the General Electric Company for the U.S. Atomic Energy Commission,

численному интегрированию по углам и энергиям. Модель рассеяния применялась к вычислению нейтрояного рассеяния полиэтиленом C<sub>n</sub>H<sub>2n</sub>. Можно отметить аналогичные уровни рассеяния полиэтиленом при 0,089; 0,182; 0,354 и 0,533 эв. Были высчитаны дифференциальные и общие сечения, и в последнем было обнаружено явное совпадение с опытом при комнатной температуре. Рассеизающиеся частицы были подсчитаны для целого ряда температур, и там, где это возможно, результаты были сравнены с опытными. Кроме того, спектры нейтронного потока и длины диффузии были высчитаны с помощью уравнений реакторной физики. Сравнение этих результатов с экспериментальными данными показывает, что такие интегральные измерения указывают, по крайней мере, на явные особенности рассеивающей системы и должны быть проанализированы в сочетании с подробными результатами дифференциального сечения.

CÁLCULO DE LA DISPERSIÓN INELÁSTICA DE NEUTRONES POR POLIETILENO Y AGUA. Nelkin propuso un modelo para calcular la dispersión de neutrones térmicos por sistemas quí micos. Con arreglo a este modelo, la dinámica real del sistema dispersante se consideraba compuesta por una serie de movimientos oscilatorios cada uno de los cuales podía describirse por un hamiltoniano que conmuta con los hamiltonianos de los otros movimientos oscilatorios. Ello permitiría expresar la sección eficaz diferencial de dispersión en forma cerrada. Los autores han utilizado este modelo para calcular la dispersión de neutrones por el agua. Debe procederse con cierto cuidado al efectuar la integración numérica respecto del ángulo y de la energía. El modelo se ha utilizado también para calcular la dispersión de neutrones por polietileno ( $C_{n}H_{2n}$ ). A 0,089 eV, 0,182 eV, 0,354 eV y 0,533 eV, se observan niveles analogos en el polietileno. Se ha calculado la sección eficaz diferencial y total de dispersión y la última parece concordar satisfactoriamente con los resultados de experimentos realizados a temperatura ambiente. Se han calculado los núcleos de dispersión para varias temperaturas y, cuando es posible, los resultados se comparan con los de los experimentos. Además se han calculado los espectros de flujo neutrónico y las longitudes de difusión utilizando para ello las ecuaciones de física de reactores. La comparación de estos resultados con los datos experimentales muestra que tales mediciones integrales constituyen por lo menos un índice de las características generales del sistema dispersante y deben analizarse conjuntamente con los resultados detallados relativos a les secciones eficaces diferenciales.

## I. INTRODUCTION

Theoretical methods for the calculation of the inelastic scattering of thermal energy neutrons by chemically bound systems have been proposed in the past few years. They are of special importance in predicting the properties of reactor systems where the interaction between the slowingdown neutron flux and the moderator must be known. Since the wave length of a neutron with an energy in the thermal range is of the order of molecular distances ( $\approx$  one Å), it is necessary to properly take into account the chemical binding effects of the scatterer. Furthermore it can be shown that except for a factor of the ratio of the square root of the final energy to the initial energy, the scattering cross-section is a function solely of the energy change and the momentum transferred. Thus from a knowledge of the inelastic scattering cross-section, it is possible to derive information about the chemical system. This can be seen from an examination of the four-dimensional Fourier transform,  $G(\mathbf{r}, t)$  of the differential crosssection,  $d^2\sigma/d\Omega dE$ , first introduced by VAN HOVE [1]

$$G(\underline{\mathbf{r}}, t) = \frac{1}{(2\pi)^{3}N} \int e^{i(\omega t - \underline{K} \cdot \underline{\mathbf{r}})} \frac{k_{0}}{k} \frac{d^{2}\sigma}{d\Omega dE} d\underline{K} d\omega$$
(1)

where

$$K = k - k_0$$
, the momentum transfer

and

$$\hbar E = (\hbar^2 k^2 / 2m) - (\hbar^2 k_0 / 2m)$$
, the energy change.

If we write the cross-section as made up of a "self" part, and a "distinct" part, and correspondingly,  $G(\underline{r},t) = G_s(\underline{r},t) + G_d(\underline{r},t)$ , Van Hove showed that in the limit as  $t \rightarrow 0$ ,

$$G_{s}(r, 0) = \delta(r), G_{d}(r, 0) = g(r)$$

where  $g(\underline{r})$  is the correlation function of the scatterer, which is customarily measured in X-ray diffraction experiments. For a wave length appropriate to molecular distances, the energy of the electromagnetic radiation is too large to be affected by the chemical binding effects of the scatterer, which corresponds to the  $t \rightarrow 0$  limit given above. Neutrons, on the other hand, have wave lengths and corresponding energies of just such a nature to be of use in determining the extended correlation function  $G(\underline{r}, t)$ . In this paper we shall be interested primarily in a calculation of the scattering process and then illustrate the necessity for using a proper model of scattering in calculation reactor fluxes.

In Section 2, a summary of the modified Nelkin water model is given together with some comparisons of predicted scattering cross-sections with experimental data. In Section 3 the polyethylene model is discussed. In Section 4 a method for the calculation of neutron fluxes is outlined and comparisons of theory and experiments presented. Section 5 consists of a brief discussion of diffusion lengths and suggestions for further endeavour.

### 2. WATER

Since water is one of the most common reactor materials, a large number of theoretical and experimental investigations of neutron scattering have used water as a target. In a purely theoretical sense this is somewhat unfortunate because the complicated nature of the liquid system makes precise analysis difficult.

As noted above, the neutron scattering is a function of the properties of the scattering system. NELKIN [2] replaced the complicated phonon spectrum of water [3] by the four distinct energy groups given in Table I, corresponding to an interaction Hamiltonian separable into four distinct com-

#### TABLE I

	Energy levels		
Nature of level	H <sub>2</sub> O	C <sub>n</sub> H <sub>2n</sub>	
Hindered rotational	0.06	0.089	
Vibrational	0. 205	0.187	
Vibrational	0. 474	0.354	
Vibrational	0.488	0. 533	

## ENERGY LEVELS OF WATER AND POLYETHYLENE

ponents, on hindered rotational and three vibrational. These correspond, respectively, to the circular motion of the H-O-H molecule about its centre of mass in the field of the other molecules, and to the three degrees of freedom of the H-O bond in the molecule. To these motions must be added the free movement of the entire water molecule. Since an exact treatment of the 0.06 eV hindered rotational level is quite lengthy, Nelkin replaces this by a vibrational level of different mass.

Nelkin approximated the intermediate scattering function introduced by ZEMACH and GLAUBER [4], X(R, t)

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k}{2\pi k_0} \int_{-\infty}^{\infty} dt e^{-i\omega t} X(\underline{K}, t)$$
(2)

by a product of the X's corresponding to the translation of the entire water molecule, the hindered rotational state and each of the vibrational states, separately averaged over initial states of the system. Since the approximation of harmonic motion for each of the degrees of freedom was made, using the formalism of ZEMACH and GLAUBER [4], similar functional forms for the intermediate scattering function result. For ease in calculation it was further proposed to treat only one mode oscillation exactly at a time, considering the other oscillations in either the high energy transfer or zero energy transfer limit. Thus for water there are three natural regions corresponding to energy transfers of  $\Delta E < 0.205 \le \Delta E < 0.481$ eV and  $0.481 \le \Delta E \le 0.8$  eV. Above an energy transfer of about 0.8 eV, the scattering is treated as that from a gas of free hydrogen atoms. Taking the time transform of the intermediate scattering function, the resulting equation for the differential cross-section is

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}E} = \frac{\sigma_0}{4\pi} \sqrt{\frac{\mathrm{E}}{\mathrm{E}_0}} \sqrt{\frac{\mathrm{m}}{2\pi E \mathrm{K}^2}} e^{-\mathrm{K}^2/2\mathrm{A}} \sum_{n^2 - \infty}^{\infty} e^{-n\omega/2\mathrm{T}}$$

$$\times \mathrm{I}_n \left(\frac{\mathrm{K}^2}{2\mathrm{B}}\right) e^{\frac{\mathrm{m}}{2\mathrm{E}\mathrm{K}^2} \left[(\mathrm{E} - \mathrm{E}_0 - n\omega + \frac{\mathrm{K}^2}{2\mathrm{m}})^2\right]}$$
(3)

where the undefined parameters are given in some detail by NELKIN  $[2]^*$ .

The total cross-section as a function of incident energy was computed by integrating the results obtained from the numerical evaluation of Eq. (3). Some care must be taken in choosing the integration scheme to avoid the problems associated with numerical evaluation of integrable singularities [5]. The results are shown in Fig. 1. To calculate the scattering from water, the individual hydrogen cross-sections were doubled and added to the oxygen cross-section (4 b). The agreement between experiment and theory for large incident energies was fixed by the choice of parameters but the comparison over the whole energy range shown is quite good. Also included is the calculated cross-section treating the scatterer as a system of a free gas of hydrogen atoms.

<sup>•</sup> In this original work Nelkin defined his regions corresponding to the incident neutron energy, rather than to the transfer energy.



Fig.1

Total cross-section for the scattering of neutrons by water.

A much more selective test of the quantitative accuracy of any scattering theory is the accuracy with which differential cross-sections are determined. A large body of such experimental data for water has been measured by EGELSTAFF [6] who reports his results in terms of the dimensionalless quantities

$$\alpha = \frac{\mathbf{E}_{i} + \mathbf{E}_{f} - 2\mu \sqrt{\mathbf{E}_{i} \mathbf{E}_{f}}}{T}$$
, the momentum transfer

 $\beta = \frac{E_f - E_i}{T}$ , the energy transfer (negative for an energy loss)

and the symmetric scattering law

$$S(\alpha, \beta) = \frac{d^2 \sigma (E_i \rightarrow E_f, \mu)}{d\Omega dE} T \sqrt{\frac{E_i}{E_f}} e^{\beta/2}$$

An example of such a comparison, albeit the most satisfactory we have determined thus far, is shown in Fig. 2.

Additional comparisons between theory and experiment using Egelstaff's representation directly were also undertaken. One such example is shown in Fig. 3. We see that the comparison looks reasonably close except for small  $\alpha$ . This is inevitable in any theory which uses the free translation approximation since for a free gas kernel,  $S/\alpha \rightarrow 0$  as  $\alpha \rightarrow 0$ . This is there-



Fig.2

The differential cross-section of water as a function of the cosine of the scattering angle for initial neutron energy of 0.14 eV and final energy of 0.06 eV.



Fig.3

The ratio S/a as a function of a for the scattering of neutrons by room temperature water.

fore visual evidence for the need for including diffusive effects which are apparent at small momentum and energy transfers.

The cross-section for the scattering from water at 150°C was then calculated in order to compare with some available data [7]. In Fig. 4 we see that the disagreement between theory and experiment is greatest for small  $\alpha$ .



The ratio S/a as a function of a for the scattering of neutrons by water at 150°C.

### 3. POLYETHYLENE

A study of the scattering from polyethylene was initiated since this substance is commonly used in reactor assemblies, due to the similarity in the chemical structure of each. This similarity has made it possible to extend the vibrational model of water to the case of polyethylene.

The chemical structure of the polyethylene is that of a long-chain organic molecule with the generic formula  $C_n H_{2n}$  [8]. Thus, it seemed possible to treat the individual component of the molecule, i.e. the H-C-H radical in a manner analogous to the representation of the water H-O-H molecule. To do this it was necessary to determine the frequency spectrum of the polyethylene molecule. We examined the data of NIELSEN and WOOLETT [9] for solid polyethylene and inferred the various energies of phonon excitation from their results. On the basis of their data, there appears to be reasonably well-separated energy levels at energies of 0.089 eV, 0.187 eV, 0.354 eV and 0.533 eV. These energies are given in Table I, and are listed alongside their possible analogous water levels. The total cross-section was then calculated assuming that each of the four levels corresponds to a normal mode of oscillation of the hydrogen atoms of the polyethylene molecule. This is an especially simple model and involves the selection of only one arbitrary parameter, chosen so that at high neutron energies ( $E_n \gtrsim 0.8 \text{ eV}$ ), the total cross-section be the same as that from a free proton gas. This takes the form of  $1 = 1/M + 1/m_v$  where M is the total mass of the CH<sub>2</sub> group (14) and  $m_v$  is the effective vibrator mass. There are now four regions, given by

Region I	$\Delta \mathrm{E} < 0.187 \ \mathrm{eV}$ ,
Region II	$0.187 \le \Delta E < 0.354 \text{ eV},$
Region III	$0.354 \le \Delta E \le 0.533 \text{ eV},$
Region IV	$0.533 \le \Delta E \le 0.8 \text{ eV}.$

In each region the translational motion is treated in the high energy limit

and one of the vibrational modes is treated exactly, in complete analogy to the method used for water-scattering. The differential cross-section is again given by Eq. (3) with the parameters defined by Table II.

The parameters listed in Table II have been used to calculate the neutron cross-sections. The total neutron cross-section calculated by the programme was compared with the experimental data of BACH <u>et al.</u> [10]. These results agree quite well with earlier data of RAINWATER <u>et al.</u> and have much smaller statistical errors associated with them. The comparison is shown in Fig. 5 where we have plotted the data of Bach <u>et al.</u> and the theoretical cross-section. It is apparent that calculated results are in quite good

### TABLE II

## PARAMETERS ENTERING INTO THE EQUATION FOR THE SCATTERING OF NEUTRONS BY POLYETHYLENE

Region I $\Delta E < 0.187 \text{ eV}$
m = M = 14
E = T = 0.0255 eV
$A^{-1} = \alpha_v^{-1} + (r m_v \omega_v \tanh \omega_0 / 2T)^{-1}$
$\alpha_{v}^{-1} = (4 m_{v})^{-1} (\omega_{1}^{-1} + \omega_{2}^{-1} + \omega_{3}^{-1})$
$\dot{A} = 0.195 \text{ eV}$
$B = 4 m_V \omega_0 / 2T$
= 1.06 eV
m <sub>v</sub> = 1.08
$\omega = \omega_0 = 0.089$
Region II 0.187 $eV \le E < 0.354 eV$
$1/m = 1/M + 1/4 m_v$
M = 3.294
M = 3.294 $\tilde{E} = 4 m_v T + M \tilde{E}_0 / M + 4 m_v  \tilde{E}_i = (1/e^{\omega_i / T_{-1}} + 1/2) \omega_i$
M = 3.294 $\tilde{E} = 4 m_v T + M \tilde{E}_0 / M + 4 m_v  \tilde{E}_i = (1 / e^{\omega_i / T - 1} + 1 / 2) \omega_i$ = 0.0422  eV
$M = 3.294$ $\tilde{E} = 4 m_v T + M \tilde{E}_0 / M + 4 m_v  \tilde{E}_i = (1 / e^{\omega_i t / T - 1} + 1 / 2) \omega_i$ $= 0.0422 \text{ eV}$ $A^{-1} = (4 m_v)^{-1} [\omega_2^{-1} + \omega_3^{-1} + (4 \omega_1 \tanh \omega_1 / 2T)^{-1}]$
$M = 3.294$ $\tilde{E} = 4 m_v T + M \tilde{E}_0 / M + 4 m_v  \tilde{E}_i = (1 / e^{\omega i / T - 1} + 1 / 2) \omega_i$ $= 0.0422 \text{ eV}$ $\cdot A^{-1} = (4 m_v)^{-1} [\omega_2^{-1} + \omega_3^{-1} + (4 \omega_1 \tanh \omega_1 / 2T)^{-1}]$ $A = 0.422 \text{ eV}$
$M = 3.294$ $\tilde{E} = 4 m_v T + M \tilde{E}_0 / M + 4 m_v  \tilde{E}_i = (1 / e^{\omega_i / T_{-1}} + 1/2) \omega_i$ $= 0.0422 eV$ $A^{-1} = (4 m_v)^{-1} [\omega_2^{-1} + \omega_3^{-1} + (4 \omega_1 \tanh \omega_1 / 2T)^{-1}]$ $A = 0.422 eV$ $B = 4 m_v \omega_1 \sinh \omega_i / 2T$
$M = 3.294$ $\vec{E} = 4 m_v T + M \vec{E}_0 / M + 4 m_v  \vec{E}_i = (1 / e^{\omega_i / T_{-1}} + 1/2) \omega_i$ $= 0.0422 eV$ $(A^{-1} = (4 m_v)^{-1} [\omega_2^{-1} + \omega_3^{-1} + (4 \omega_1 \tanh \omega_1 / 2T)^{-1}]$ $A = 0.422 eV$ $B = 4 m_v \omega_1 \sinh \omega_i / 2T$ $= 13.89 eV$

Region III 0.354 eV ≤ ΔE < 0.533 eV
$1/m = 1/M + 1/2m_v$
m = 1.868
$\tilde{E} = [(T/M) + (\tilde{E}_0 + \tilde{E}_1/4 m_v)] m$
= 0.0603 eV
$A^{-1} = (4 m_v)^{-1} [\omega_3^{-1} + (\omega_2 \tanh \omega_2 / 2T)^{-1}]$
A = 0.916 eV
B = $4 m_v \omega_2 \sinh \omega_2 / 2T$ = 787.6 eV
$\omega = \omega_2 = 0.354 \text{ eV}$
Region IV $0.533 \text{ eV} < E \leq 1 \text{ eV}$
$1/m = 1/M + 3/4 m_v$
m = 1.302
$\tilde{E} = T/M + 1/4 m_v (\tilde{E}_0 + \tilde{E}_1 + \tilde{E}_2) m$
= 0.0977 eV
A = $4 m_v \omega_3 \tanh \omega_3 / 2T$
= 2.296 eV
$B = 4 m_V \omega_3 \sinh \omega_3 / 2T$
$= 3.967 \times 10^4 \text{ eV}$
$\omega_3 = 0.533 \text{ eV}$

TABLE II (cont'd)

agreement with the experimentally-measured total cross-sections, a result not necessarily expected due to the naiveté of the model. The significance of these results is being investigated, but it would be of great benefit in this line to have available some differential cross-section measurements.

Fig. 6 presents an illustration of the various results for the ratio  $S(\alpha, \beta)/\alpha$  as a function of  $\alpha$  for  $\beta = 3.2$  using different theoretical forms of the scattering cross-section. For comparison we have indicated Egelstaff's experimental water results. The sensitivity of the calculations to the choice of the scattering kernel is evident.

## 4. FLUX SPECTRA

A critique of scattering models might be divided into two general categories, differential and integral portions. The details of the differential



Fig. 5

Total cross-section for the scattering of neutrons by polyethylene.



Calculated and experimental values of S/a as a function of a for  $\beta = 3.2$ .

considerations have been described in the previous two sections. The total cross-section, an integral quantity, has also been discussed. In this section the direct application of calculated scattering cross-sections to reactor flux spectra will be described. In this sense, the reactor itself performs an integral measurement of the cross-section. In performing calculations of flux spectra there arises the question of how well the reactor physicist is able to predict the observed behaviour of the reactor. This will not be discussed in this paper, except to say that infinite medium-thermal neutron spectra appear to be able to be predicted quite satisfactorily, and these calculations will be described in this section.

The infinite medium thermalization equation for energy E less than the energy of any source neutron is

$$[\Sigma_{a}(\mathbf{E}) + \Sigma_{s}(\mathbf{E})] \phi(\mathbf{E}) - \int_{0}^{\mathbf{E}_{c}} \Sigma(\mathbf{E}^{!} \to \mathbf{E}) \phi(\mathbf{E}^{!}) d\mathbf{E}^{!} = \mathbf{S}(\mathbf{E})$$
(4)

where  $\Sigma_a$  and  $\Sigma_s$  are the absorption and scattering cross-sections.  $\Sigma(E^{\dagger} \rightarrow E)$  is the cross-section for scattering from energy  $E^{\dagger}$  to the range dE about E

$$S(E) = \int_{E_{c}}^{\infty} \Sigma(E' \to E) \phi(E') dE'$$

is the source of neutrons scattered from energies above  $E_c$  to energies below  $E_c$ ,  $\phi(E)$  is the neutron flux, and  $E_c$  is a cut-off energy chosen so that



Infinite medium spectrum for material with 1/V absorption and  $\beta \gamma = 0.1$ .

the scattering from energies below  $E_c$  to energies above  $E_c$  can be neglected.  $E_c$  is also below the energy of any source neutron. If all quantities in (4) are evaluated at n values of  $E(=E_i)$ , and the integral replaced by a sum, the n equation

$$[\Sigma_{a}(\mathbf{E}_{i}) + \Sigma_{s}(\mathbf{E}_{i}) \phi(\mathbf{E}_{i})] - \sum_{j=i}^{n} \Sigma(\mathbf{E}_{j} \rightarrow \mathbf{E}_{j}) \phi(\mathbf{E}_{j}) \Delta_{j} = S(\mathbf{E}_{i})$$
(5)

are obtained. This represents a system of n linear equations in n unknowns (the  $\phi(\mathbf{E}_i)$ ) and can be solved by direct matrix inversion to obtain the flux spectrum  $\phi(\mathbf{E}_i)$ . Examples of flux spectra calculated with each of the kernels are shown in Figs. 7 and 8. Fig. 7 shows the infinite medium spectra



Fig.8

Infinite medium spectrum for material with 1/V absorption and  $\beta \gamma = 0.08$ .

for a region with only 1/V absorption and  $\beta\gamma = 0.1$ .  $\beta\gamma = \Sigma_a(kT)/\Sigma_s^H(\infty)$  is the ratio of the macroscopic absorption cross-section at kT to the asymptotic (high energy) macroscopic hydrogen scattering cross-section). Fig. 8 shows these spectra for a region with  $\beta\gamma = 0.8$ . It is apparent from these graphs that the use of the different kernels yields quite different results and therefore experimental comparisons are needed. This is further evidenced by the large differences in averages over these spectra of a unit 1/V cross-section. These figures are shown in Table III and can be seen to be quite different.

BEYSTER et al. [12] have measured infinite medium spectra in pure and poisoned water and polyethylene moderators. Fig. 9 shows Beyster's

## TABLE III

# AVERAGES OF UNIT 1/V CROSS-SECTION



Kernel	$\langle 1/V \rangle$ ; $\beta\gamma$ of $\phi = .1$	$\langle 1/V \rangle$ ; $\beta \gamma$ of $\phi = .8$	
Mass 1	.7826	.5217	
Water	.7593	.4901	
Polyethylene	. 7292	.4585	





## Calculated and experimental neutron spectra in boric acid.

experimental points as measured in various concentrations of boric acid. Also shown are the spectra as calculated on the basis of the free proton and bound water scattering models. All curves are normalized to the same 1/E high energy dependence. These curves show that the free proton kernel is not adequate to calculate spectra in water while the water kernel is much better able to predict these spectra. Furthermore, calculations of Beyster's experiment is borated polyethylene (see Figs. 10 and 11) show that the water



Calculated and experimental neutron spectra in borated polyethylene (5.74 b/H atom).



Calculated and experimental neutron spectra in borated polyethylene (10,45 b/H atom).

kernel should not be used to calculate polyethylene spectra, but that the model created specifically for polyethylene must be used.

Thus we see that infinite medium-thermal spectra are quite sensitive to the form of the scattering kernel. Kernels are available for the prediction of these spectra with reasonable precision.

## 5. DIFFUSION LENGTHS

We have seen that the water and polyethylene kernels described above yield good results when used to predict infinite medium spectra. This, however, is a test of only the  $P_0$  scattering kernel. In order to get some idea of the ability of these models to predict the angular distribution of the scattering law, some diffusion length calculations have been done. These serve as a test of the transport cross-sections.





Diffusion lengths of water and polyethylene as a function of temperature.

Following the methods of CALAME [13] diffusion lengths in water and polyethylene have been computed for a range of temperatures. In these calculations the water and polyethylene kernels as well as the mass 1, free gas kernels were used. For water and polyethylene, the transport crosssection was computed from:

$$\sigma_{tr} = (1 - \bar{\mu}) \sigma_s = \int \sigma_0 (\mathbf{E} \rightarrow \mathbf{E}) d\mathbf{E} - \int \sigma_1 (\mathbf{E} \rightarrow \mathbf{E}^{\dagger}) d\mathbf{E}^{\dagger} .$$

Results of these calculations are given in Fig. 12 where comparisons are given with the results of ROCKEY and SKOLNIK [14] and ESCH [15]. From these curves it is apparent that the water kernel is able to give a reasonable description of the temperature dependence of the diffusion length, but the polyethylene model does not seem adequate except at room temperature. This lack of agreement is probably due to the fact that the temperature increases, the structure of polyethylene changes and the room temperature phonon excitation frequencies are no longer valid. Since no data on these frequencies for hot polyethylene were available the room temperature values were used for the calculation of kernels at all temperatures. Thus the need for experiments on hot polyethylene is indicated to permit the calculation of improved scattering kernels.

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# SYSTEMATIC STUDY ON TOTAL NEUTRON SCATTERING CROSS-SECTIONS OF HYDROGEN CONTAINING MOLECULES

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#### Abstract — Résumé — Аннотация — Resumen

SYSTEMATIC STUDY ON TOTAL NEUTRON SCATTERING CROSS-SECTIONS OF HYDROGEN CON-TAINING MOLECULES. In addition to the previously reported results of total scattering cross-section measurements with hydrogen containing molecules ["Inelastic Scattering of Neutrons in Solids and Liquids", IAEA, Vienna (1961)] some new data for  $NH_3$ ,  $H_2S$  (gases) and  $CH_4$  (liquid) were obtained. The results for gases were compared with the theory of Krieger and Nelkin. The same comparison in the case of liquid  $CH_4$  led to the conclusion that  $CH_4$  molecules rotate freely in the liquid state.

New measurements of the scattering cross-sections of  $CH_3SH$  molecules in the gaseous and liquid state were also performed. The results do not confirm the previously reported data, i.e. they do not show any existance of peaks connected with the hindered internal rotation. However, a comparison with the theory of Krieger and Nelkin and the theory of Kolos gives evidence of inelastic transitions between successive energy levels of the hindered rotation.

ÉT UDE SYSTÉMATIQUE DES SECTIONS EFFICACES TOTALES DE DIFFUSION NEUTRONIQUE DANS LES MOLÉCULES HYDROGÉNÉES. Les auteurs ont obtenu quelques résultats complémentaires sur les mesures de sections efficaces totales de diffusion neutronique dans les molécules hydrogénées telles que  $NH_3$ ,  $H_2S$  (gaz) et  $CH_4$  liquide. Ils comparent les résultats relatifs au gaz aux prévisions de la théorie de Krieger et Nelkin. La même comparaison dans le cas de  $CH_4$  liquide permet de conclure que les molécules de  $CH_4$  tournent librement à l'état liquide.

Les auteurs ont aussi fait de nouvelles mesures des sections efficaces de diffusion dans les molécules de CH<sub>3</sub>SH à l'état gazeux et à l'état liquide. Leurs résultats ne confirment pas les données qu'ils avaient signalées antérieurement: ils ne révèlent pas la présence de pics liés à la rotation interne amortie. Toutefois, une comparaison avec la théorie de Krieger et Nelkin et avec la théorie de Kolos fournit la preuve de l'existence de transitions inélastiques entre les niveaux d'énergie successifs des états de rotation amortis.

СИСТЕМАТИЧЕСКОЕ ИЗУЧЕНИЕ ПОЛНЫХ ПОПЕРЕЧНЫХ СЕЧЕНИЙ РАССЕЯНИЯ НЕЙТРОНОВ ДЛЯ МОЛЕКУЛ, СОДЕРЖА-ШИХ ВОДОРОД. В дополнение к сообщенным ранее результатам измерений полного поперечного сечения рассеяния нейтронов для молекул, содержащих водород (труды Симпозиума по неупругому рассеянию нейтронов в твердых и жидких телах, Вена, 1960 год), были получены некоторые новые данные для NH<sub>3</sub>, H<sub>2</sub>S (в газообразном состоянии) и CH<sub>4</sub> в жидком состоянии). Результаты для газов были сопоставлены с теорией Кригера и Нелкина. Такое же сравнение для жидкого CH<sub>4</sub> приводит к заключению, что в жидком состоянии молекулы CH<sub>4</sub> вращаются свободно.

Были проведены также новые измерения поперечных сечений рассеяния молекул CH<sub>3</sub>SH в газообразном и жидком состояниях. Результать их не подтверждают сообщенных ранее данных, т.е. они не указывают на наличие пиков в связи с задержанным внутренним вращением. Тем не менее, сравнение с теорией Кригера и Нелкина и с теорией Колоса указывает на наличие неупругих переходов между последовательными уровнями энергии задержанного вращения.

ESTUDIO SISTEMÁTICO DE LAS SECCIONES EFICACES TOTALES DE DISPERSION NEUTRÓNICA DE MOLÉCULAS QUE CONTIENEN HIDRÓGENO. Además de los resultados referentes a la medición de las secciones eficaces totales de dispersión neutrónica de las moléculas que contienen hidrógeno dados a conocer anteriormente (Actas del Simposio sobre dispersión inelástica de los neutrones en los sólidos y los líquidos, Viena, 1961), los autores han obtenido algunos nuevos datos relativos al NH<sub>3</sub>, SH<sub>2</sub> (gases) y CH<sub>4</sub> (líquido). Han comparado los resultados referentes a los gases con los predichos por la teoría de Krieger y Nelkin. Esta misma comparación, efectuada en el caso de  $CH_4$  líquido, permite deducir que el movimiento de rotación de las moléculas de  $CH_4$  en estado líquido es libre.

Los autores han realizado nuevas mediciones de las secciones eficaces de dispersión de las moléculas de CH<sub>3</sub>SH en estado gaseoso y líquido. Los resultados no confirman los datos anteriormente comunicados, es decir, no muestran la existencia de picos asociados a la rotación interna restringida. Sin embargo, la comparación de la teoría de Krieger y Nelkin con la de Kolos revela la existencia de transiciones inelásticas entre los niveles energéticos sucesivos de la rotación restringida.

### INTRODUCTION

Continuing the measurements of total cross-sections for scattering of slow neutrons by molecules of gases and liquids [1, 2] some new data for gaseous and liquid NH<sub>3</sub>, gaseous and liquid H<sub>2</sub>S gaseous and liquid CH<sub>3</sub>SH, and liquid CH<sub>4</sub> were obtained. The results for gases were compared with the theory of KRIEGER and NELKIN[3]. The results for liquids led to some conclusions concerning the molecular rotation in the liquid state. The results for CH<sub>3</sub>SH molecules led to a revision of the formerly-reported data [1] and gave some suggestions as to the internal hindered rotation of the molecules. All experiments were performed by using a slow chopper and a time-of-flight technique applying a simple transmission method [4].

## RESULTS FOR GASEOUS NH<sub>3</sub> AND H<sub>2</sub>S

The purpose of the measurements was to prove the validity of the KRIEGER and NELKIN [3] theory for the scattering cross-section determination in the thermal energy region. The previously reported data do not give a definite answer to this problem. The experimental data of MELKONIAN [5] for gaseous  $CH_4$  fit very well the Krieger and Nelkin theory. A similarly good agreement obtains in the case of gaseous  $C_2 H_4$  [1]. The results of JANIK <u>et al.</u> [1, 6] for gaseous  $NH_3$  confirm also the validity of the Krieger and Nelkin theory. RUSH <u>et al.</u> [7], however, obtained a systematic deviation from the theory for these molecules. Finally the experimental points of HEINLOTH [8] for  $H_2O$  vapour deviate considerably from the Krieger and Nelkin theory.

Fig. 1 presents our new results obtained for gaseous  $NH_3$  molecules, which again well confirm the validity of the Krieger and Nelkin theory.

Fig. 2 shows our experimental results for gaseous  $H_2S$  molecules. The small but systematic deviation from the theory is in this case in the same direction as that obtained by Heinloth for  $H_2O$  vapour. It might be suspected that in view of the similarity of the geometrical structure of  $H_2O$  and  $H_2S$  molecules, the disagreement between theory and experiment has the same origin in the above two molecules, and may come from the approximative character of the Krieger and Nelkin theory.

## RESULTS FOR LIQUID CH4, NH3 AND H2S

It is well known that the neutron scattering cross-section for molecules of liquid  $H_2O$  is much higher than that determined from the Krieger and Nelkin theory and also much higher than the cross-section for gaseous  $H_2O$ .



Total neutron scattering cross-section per proton of NH, molecule versus neutron energy.







••• - experimental points for gas,

----- - K-N theory.



Fig.3

Total neutron scattering cross-section per proton of H<sub>2</sub>O molecule.

This situation is shown in Fig. 3. The increase of the cross-section at the transition from gas to liquid might in this case be explained as arising from a hindrance of molecular rotations in liquid caused by the association.

In view of the symmetry of the  $CH_4$  molecules, and in view of the lack of any association in liquid  $CH_4$  it might be suspected that the molecules rotate freely in this substance in the liquid state. Fig. 4 shows our results for liquid  $CH_4$  which are in perfect agreement with the Krieger and Nelkin theory for the gaseous substance, which confirms the above suggestion.

Our results for liquid  $NH_3$  and  $H_2S$  which are presented together with the results for gases in Figs. 1 and 2 show the effect of a hindrance of molecular rotation in the liquid  $NH_3$ , which again might be explained by the association of the substance, and a rather small effect of this hindrance for liquid  $H_2S$  which is in agreement with the look of any evidence of hydrogen bond in this substance.

## RESULTS FOR GASEOUS AND LIQUID CH3 SH

As presented in the appendix to the paper of JANIK et al. [1] the reported peaks in the cross-section versus neutron energy curve for  $CH_3SH$ 







molecules appeared to have been caused by Bragg-scattering which occurred in the walls of the vessels. Our new results, which do not show any peaks either for the gaseous or for the liquid substance, are shown in Fig. 5. It appears that the cross-section curves for the gaseous and the liquid CH<sub>3</sub>SH practically coincide. It seems natural to assume that due to a lack of association the hindered rotation frequency in the liquid CH<sub>3</sub>SH is not changed as compared with that in gas. It can also be seen from Fig. 5 that the experimental points lie above the Krieger and Nelkin curve which was obtained when applying a reasonable value of 1270 cal/mol. for the hindered rotation barrier height [9]. It is again natural to assume that the inelastic effects which in the calculations based on the Krieger and Nelkin theory are not taken into account, play a significant role. Due to the fact that at the temperature of the measurements, 360°K, the higher levels of hindered rotation are excited, thus giving a variety of possible inelastic transitions and to the fact of splitting of these levels, the total cross-section curve does not show any peaks.

It should be pointed out that a similar behaviour and a similar evidence of inelastic effects was also reported for the gaseous  $CH_3OH$  [10]. In this



Total neutron scattering cross-section per proton of CH<sub>3</sub>SH molecule.

case, however, the experimentally-obtained curve for the liquid substance lies above that for the gas, which might be explained by the known fact that the association in the liquid  $CH_3 OH$  significantly changes the hindered rotation frequency (from ca.  $300 \text{ cm}^{-1}$  to ca.  $600 \text{ cm}^{-1}$ ).

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## DISCUSSION\*

P. SCHOFIELD: I think the deviations you get from the Krieger-Nelkin theory must be due in part to the method of approximation of the Sachs-Teller mass tensor. This approximation is worst for highly asymmetric molecules and this is in conformity with the trend observed in your comparisons of experimental results with calculations.

<sup>\*</sup> See also discussion on the paper by D. Bally <u>et al</u> entitled "The Scattering of slow neutrons from hydrogen and ethylene".

NEUTRON SCATTERING CROSS-SECTIONS OF HYDROGEN

J. A. JANIK: If I understand correctly, you mean this difference between theory and experiment must arise from the approximative character of the Krieger-Nelkin theory, and it may be as you suggest. However, the Krieger-Nelkin theory assumes that there is no interaction between rotation and vibration and it may be that in the case of these molecules this should be taken into account.

P. SCHOFIELD: Yes, but this wouldn't be so important at the higher energies. I think the major error in small molecules, for example  $H_2S$ , may well be due to the form of averaging the mass tensor.

# INELASTIC SCATTERING OF NEUTRONS BY METHYL- ETHYL- AND n-AMYL ALCOHOLS

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### Abstract — Résumé — Аннотация — Resumen

INELASTIC SCATTERING OF NEUTRONS BY METHYL- ETHYL- AND n-AMYL ALCOHOLS. The energy transfer spectra of methyl-, ethyl- and n-amyl alcohols in the liquid state at room temperature have been measured by cold neutron scattering and beryllium detector methods. A description is given of the apparatus used for the latter measurements.

The principle feature observed in each case is a broad band of energy transfers from 0 to 50 mV. At higher energies there is some indication of the excitation of a level at 170 mV in the neutron energy loss spectra. This corresponds to the molecular vibrational mode in which the hydroxyl group bends with respect to the C-O bond observed by I-R spectroscopy at 170 mV. The C-O bond stretching mode at 128 mV was not observed.

The O - 50 mV band is discussed in relation to previous measurements of the variation of total crosssection for long wavelength neutrons and optical measurements of free and hindered internal rotation in alcohol molecules.

DIFFUSION INELASTIQUE DES NEUTRONS DANS LES ALCOOLS METHYLIQUE, ETHYLIQUE ET n-AMYLIQUE. Les spectres de transfert d'énergie des alcools méthylique, éthylique et n-amylique ont été mesurés à l'état liquide et à la température ambiante, au moyen de la diffusion de neutrons lents et par des méthodes de détection au béryllium. Les auteurs décrivent l'appareil employé pour ces dernières mesures.

La caractéristique principale observée dans chacun des cas est une large bande de transferts d'énergie allant de 0 à 50 mV. Pour des énergies supérieures, quelques indices donnent à penser que le niveau de 170 mV est excité dans les spectres de perte d'énergie des neutrons. Ceci correspond au mode de vibration moléculaire dans lequel le groupe hydroxyle se déplace vers la liaison C-O observée par spectroscopie infrarouge à 170 mV. Le mode d'extension des liaisons C-O à 128 mV n'a pas été observé.

Les auteurs étudient la bande de 0 à 50 mV en fonction de mesures précédentes de la variation de la section efficace totale des neutrons à grande longueur d'onde et des mesures optiques des rotations libres et des rotations internes amorties dans les molécules d'alcool.

НЕУПРУГОЕ РАССЕЯНИЕ НЕЙТРОНОВ В МЕТИЛОВОМ, ЭТИЛОВОМ И НОРМАЛЬНОМ АМИЛОВОМ СПИРТАХ. Измерены Спектры переноса энергии в метидовом, этидовом и нормальном амидовом спиртах в жидком состоянии при комнатной температуре методом рассеяния холодных нейтронов и с помощью бериллиевого детектора. Дается описание прибора, использованного для измерений.

Отличительной чертой в каждом случае является наличие широкой области переноса Энергии от 0 до 50 мв. При больших энергиях отмечается возбуждение уровня 170 мв в спектрах потери энергии нейтронов. Это соответствует уровню колебаний молекуд, при котором гидроксильная группа связана с группой С-0, наблюдавшейся с помощью инфракрасной спектроскопии при 170 мв. Вытянутая форма связи С-0 при 128 мв не наблюдалась.

Обсуждается область переноса энергии от 0 до 50 мв в связи с предмдущими измерениями различных величин полных поперечных сечений рассеяния нейтронов с большими длинами волн и оптическими измерениями свободных и несвободных внутренних вращений в молекулах спирта.

DISPERSIÓN INELÁSTICA DE NEUTRONES POR LOS ALCOHOLES METÍLICO, ETÍLICO Y n-AMÍLICO. Los autores han medido los espectros de transmisión de energía de los alcoholes metílico, etílico y n-amílico en estado líquido a la temperatura ambiente por el método de dispersión de neutrones fríos y del detector de berilio. Describen los aparatos utilizados para llevar a cabo esas mediciones.

La particularidad más notable que se observa en cada caso es una amplia banda de transmisiones de energía de 0 a 50 mV. Para energías más elevadas, hay indicios de la excitación de un nivel a 170 mV en el

espectro de pérdida de energía neutrónica. Ello corresponde al modo vibratorio molecular en que el radical hidroxilo se desplaza respecto al enlace C-O, observado por espectroscopia infrarroja a 170 meV. No se ha observado el modo tensor del enlace C-O a 128 mV.

Los autores estudian la banda 0 - 50 mV en relación con mediciones anteriormente efectuadas de la variación de la sección eficaz total para neutrones de onda larga, y con mediciones ópticas de movimientos rotatorios libres y restringidos en las moléculas de alcohol.

## INTRODUCTION

The dynamics of alcohol molecules have been extensively studied by the optical techniques of infra-red and Raman spectroscopy and results of this work are summarized by HERZBERG [1]. The frequencies of the various vibrational modes of the simplest aliphatic alcohol, methanol, have been measured and compared in both vapour and liquid phases. More recent interest in the behaviour of hydrogenous liquids as thermal reactor moderators has led to investigations of the neutron-scattering characteristics of organic molecules including the lower alcohols. Thermal and cold neutron scattering data are more sensitive to the lower energy transitions ( $\leq 0.1 \text{ eV}$ ) associated with translational and rotational motion of the molecules.

NASUHOGLU and RINGO [2] have measured the total scattering crosssections as a function of neutron wavelength between 5Å and 20Å of a series of the lower alcohols, and BRUGGER and EVANS [3] have reported inelastic scattering neutron spectra of ethyl and n-amyl alcohols by their spinning sample technique.

This paper describes measurements of the inelastic scattering of neutrons by liquid samples of methyl-, ethyl and n-amyl alcohols at room temperature using the complementary techniques of cold neutron scattering and the beryllium detector methods. The former measures the scattered neutron spectrum in the elastic and energy gain region, while the latter covers the energy loss spectrum from 40 mV to 230 mV.

### **EXPERIMENTAL DETAILS**

### (a) The beryllium detector apparatus

The beryllium detector apparatus, similar to that described by WOODS et al. [4], consists of an array of seven low pressure (40 cm Hg)  $B^{10}F_3$  proportional counters shielded by a polycrystalline beryllium filter and mounted on the arm of the Dido High Intensity Crystal Spectrometer. A schematic layout of the apparatus is shown in Fig. 1.

The scattering sample is mounted in the diffracted beam, energy Eo, produced by the single crystal monochromator. Neutrons scattered through  $90^{\circ} \pm 5^{\circ}$  in the horizontal plane enter the beryllium filter, but only those having a scattered energy, E', less than the beryllium Bragg cut-off, pass the filter and are detected.

With the present shielding arrangement the spectrometer arm can be moved in 1°, 20 min or 6 min increments through 30° to 60° with respect to the direction of the collimated reactor beam incident on the monochromator. For these experiments an aluminium single crystal was used. The crystal table is connected by a 1:2 tape and drum drive to the spectrometer arm,





Schematic of the Dido Crystal Spectrometer using the "beryllium detector" method.

and the monochromator mounted on this table can be oriented by remotelycontrolled electric motors to bring (111), (220), or (331) planes into the Bragg condition. By this means the incident neutron energy, Eo, can be varied from 15 mV to 350 mV.

A U<sup>235</sup> fission chamber monitors the intensity of the diffracted beams, and a remotely-controlled cadmium shutter between the monitor and the sample is used for background measurements. The highest measured monoenergetic neutron rate at the sample position is  $7 \times 10^6$  neutrons/s over an area of  $10 \text{ cm}^2$  at Eo = 30 mV.

The count rate in the beryllium detector per count from the monitor (which has a 1/Vefficiency dependence over most of the range) is proportional to  $\partial^2 \sigma / \partial \Omega \partial \epsilon$  ( $k_0/k'$ )  $4\pi/\sigma_b$  where  $k_0$  and k' are the incident and scattered neutron wave vectors,  $\partial^2 \sigma / \partial \Omega \partial \epsilon$  the differential cross-section and  $\sigma_b$  the bound atom scattering cross-section of the nucleus.

The mean energy transferred to the neutron by the scattering process is  $\epsilon = \overline{E}^{t}$ . Eo. where  $\overline{E}^{t}$  has been calculated to be 0.0034 eV taking into consideration the efficiency of the "end-on" BF<sub>3</sub> counters, the residual crosssection of the beryllium filter below the cut-off and the k<sub>0</sub><sup>-1</sup> dependence of the differential cross-section. The practical upper energy limit of the apparatus is determined by the count to background ratio which falls rapidly in the region of 0.10 to 0.25 eV, because of decreasing reactor spectrum intensity and poor monochromator reflectivity of planes with high Miller indices.

As the beryllium filter has a small but finite transmission above 0.005 eV the possibility of spurious peaks in the measured inelastic spectrum due to strong Bragg reflections cannot be discounted. This effect is only important for coherent scatterers but nevertheless each sample is checked by replacing the filter by a collimator and comparing the distributions obtained. The operation of the spectrometer is fully automatic, the output data being produced in the form of punched paper tape which allows data processing to be carried out directly by computer. The results are finally obtained in the form of a tabulation of normalized counts per monitor count against energy transfer,  $\epsilon$ . The data processing includes multiplication by the detailed balance factor,  $\exp(\epsilon/2k_{\rm B}T)$ , to give a cross-section proportional to the scattering law S(K, E) that is even in E.

Because the scattering from protons is largely incoherent there are no important interference effects in the observed cross-section which is governed only by the average dynamics of the individual atoms. No correction has been made for scattering from carbon and oxygen in the present experiments.

### (b) Cold neutron scattering apparatus

The cold neutron apparatus is described fully by HARRIS et al. in a paper in these proceedings entitled "A cold neutron monochromator and scattering apparatus". The particular features relevant to these experiments were a mean incident energy of 5 mV,  $8\mu$ s timing channels, and counters at 20°, 30°, 45°, 60°, 75° and 90°. An automatic sample changer brought the three alcohol samples and a vanadium standard into the scattering position in sequence for 10 min counting periods.

The results shown in this paper were all obtained with liquid hydrogen condensed into the cold neutron source described in a paper in these proceedings by WEBB and PEARCE entitled "The performance and automatic operation of the liquid hydrogen cold neutron source in Dido".

## (c) Samples

For the cold neutron scattering experiments, referred to as CN in this paper, the samples were used in transmission for scattering through angles of  $20^{\circ}$  to  $90^{\circ}$ . The sample cans consisted of a pair of plates of pure aluminium with a 0.020 in recess milled on the inner face of one to form the alcohol vessel. Each plate had a 2 in  $\times$  1.5 in window milled to 0.030 in thick and were assembled by bolting together with an indium wire gasket to form a liquid-tight seal.

For the beryllium detector experiments, referred to as ELB in this paper, the samples were used in reflection for scattering into the detector at 90°. In this case the sample can was formed by milling the recess into cadmium metal in order to reduce the scattering from material behind the alcohol film.

The thickness of the samples were designed to give about 15% scattering. For n-amyl alcohol the effective thickness had to be reduced by including a 0.012 in aluminium foil in the recess with the alcohol.

### RESULTS

Fig. 2 shows a series of spectra obtained by the CN method for MeOH. The recorded counts per timing channel have been corrected for background,



Fig.2

Scattered spectra for methyl alcohol using energy gain technique.

relative efficiency of the counters at the six different angles and for the timeof-flight dependent efficiency of each counter. Also included in Fig. 2 is the curve given by the vanadium standard at 90°. The vanadium scattering is assumed to be wholly elastic in the peak so that the curve shows the incident spectrum velocity analysed at the counter position.

Fig. 3 shows similar results at two angles,  $20^{\circ}$  and  $75^{\circ}$ , for each of the three alcohols.

Fig. 4 shows the results obtained for MeOH by the beryllium detector method using (220) and (331) monochromator planes. Here the curves are plotted in a form proportional to the energy symmetrical scattering law  $S(\underline{K}, \epsilon)$ . For direct comparison the 90° CN results, plotted in the same form, are shown by open points. The results obtained with the (331) monochromator planes are also plotted in the inset on an expanded vertical scale and in this case the detailed balance factor has not been removed from the data.

The following features appear in the spectra:

 (i) A quasi-elastic peak which decreases in amplitude and broadens with increasing scattering angle. This effect is less pronounced for the higher alcohols.



Scattered spectra for methyl, ethyl and n-amyl alcohols at scatter angles of 20° and 75°.

- (ii) A broad band of energy transfers up to 50 100 mV'. The shape of this distribution does not vary appreciably with angle but is flatter and less intense with respect to the quasi-elastic peak for the higher alcohols.
- (iii) A slight rise in the spectrum in the 170-220 mV region observed in the ELB measurements of MeOH and EtOH.

## DISCUSSION

(a) The quasi-elastic peak

The broadening of the incident spectrum in the near elastic region is characteristic of diffusive motions involving small energy transfers, i.e. characteristic of the long time behaviour (~10<sup>-12</sup> s). In the case of a simple diffusion molecule obeying Pick's Law the broadened width of a  $\delta$ -function incident spectrum measured at half-maximum would be  $\Delta E = 2\hbar D \left| \frac{K}{L} \right|^2$  where <u>K</u> is the scattering wave vector given by <u>K</u> = <u>k'</u> - <u>k\_0</u> (<u>k\_0</u> and <u>k'</u> are the incident



Results for methyl alcohol at room temperature using the "beryllium detector" method.

and scattered neutron wave vectors, and D is the self diffusion coefficient).

Recent studies of the diffusion broadening in the case of water and liquid metals have shown that the self diffusion coefficients derived by neutron methods are the same as the values obtained by macroscopic measurements if very small values of K are employed. At higher K the half-width is less than that given by the above formula.

 $\Delta E$  was obtained from each spectrum by measuring the widths in energy at half-maximum from corresponding alcohol and vanadium peaks, after subtracting the estimated "rotational" scattering in the quasi-elastic region, and assuming that the observed shape is a Lorentzian cross-section broadened by a Gaussian resolution function. Fig. 5 shows the results plotted against  $|\underline{K}_0|^2$  where  $\underline{K}_0$  is the scattering vector of elastically-scattered neutrons of the mean incident energy. The error bars include estimates of the error introduced by subtracting away the "rotational" inelastic distribution as well as an error due to statistical scatter of the cross-sections. Also shown on the graph are two lines given by  $2\hbar D K 0^2$  using macroscopic values of the self diffusion coefficients obtained for methyl- and ethyl alcohol by PARTING-TON, HUDSON and BAGNALL [5].

The experimental points for methyl alcohol are in reasonable agreement with their value of  $D = 2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , but those for ethyl alcohol exceed the predicted value by a factor of 2. In the case of amyl alcohol the observed value is about  $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . By comparison of viscosities, and also the variation of D with increasing molecular weight shown by Partington et al., the macroscopic self diffusion coefficient of n-amyl alcohol is expected to be less than the n-butyl alcohol value of  $0.50 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

The macroscopic measurements [5] were made with molecules labelled by substituting a deuteron for the proton in the hydroxyl group. A  $C^{14}$  tracer


Diffusion broadening of quasi-elastic peaks.

method was also used for MeOH and gave a similar value of D. If the same process was being observed by neutron scattering the experimental curve should approach the predicted line asymptotically as  $|K| \rightarrow 0$ . The accuracy of the present results is not sufficient to show whether this happens in the case of ethyl- and amyl alcohols. The results do suggest that for times of the order of  $10^{-12}$  s in the higher alcohols the hydrogen atoms (which govern the neutron scattering behaviour) are more mobile than the parent molecule.

(b) "Rotation" spectrum

NASUHOGLU and RINGO [2] deduced from the magnitude and variation of the total scattering cross-section per hydrogen atom for wavelengths  $5\text{\AA}$ to 20Å that in MeOH the hydrogen atoms behaved as if bound to a point mass < 6 a.m.u. From this they concluded that the methyl group was still comparatively free to rotate in the liquid state. Their identification of the methyl group depended on a comparison with the cross-section in the higher alcohols in which the majority of the hydrogens are in methylene groups, and also of the behaviour of the hydroxyl hydrogen atom in water. Optical spectroscopy [1] of the vibrational levels involving this group show pronounced frequency shifts between vapour and liquid phases and support the view that the hydroxyl group is involved in polymer bonding which would impede rotation of the whole molecule in the liquid.

The possibility that the spectra might be explained on a point mass model was tested by calculating the shape of a perfect gas spectrum of mass 1 and mass 3 and comparing these with the observed distributions (Fig. 2). The absolute scale for this comparison is arbitrary. Clearly the model is inadequate because perfect gas scattering is strongly dependent on scattering angle. Internal rotation of the methyl group with respect to the hydroxyl group has been observed in the infra-red spectrum of MeOH vapour [6] but at lower excitation energies this motion is hindered by a potential barrier which converts it into a torsional vibration. The height of this potential deduced from the infra-red spectrum is about 60 mV while the value obtained by thermal measurements is 160 mV [7]. Whichever value is taken few free rotation states will be populated at room temperature ( $k_B T = 25.3 \text{ mV}$ ) and the important motions would be torsional oscillations or hindered rotations. KOEHLER and DENNISON [8] suggested that the I-R absorption band at 270 an<sup>-1</sup>, corresponding to 33 mV, was the 1-0 transition of the torsional oscillator. No evidence of this transition appeared in the neutron scattering spectra.

The marked change in shape in the ethyl- and n-amyl alcohol"rotational" spectra suggest that the methyl group is not alone responsible, and that hydrogen atoms in the methylene group, CH<sub>2</sub>, which are expected to be more restrained from free rotation also contribute.

(c) Vibration spectrum

The experimental ELB results shown in Fig. 4 for methyl alcohol give no indication of excitation of levels at 128, 131 and 145 mV observed in Raman spectroscopy and assigned to C-O stretching, and two  $CH_3$  rocking modes respectively [1]. Above 160 mV a rise in the spectrum suggests that some or all of the O-H bending at 170 mV and two  $CH_3$  stretching vibrations at 181 mV may be excited.

A similar pattern is seen in ethyl alcohol, the only other case studied in sufficient detail. In neither case is the rise marked even allowing for the persistence of a background of scattering that appears to be associated with the "rotational" band.

#### CONCLUSIONS

The use of the complementary techniques of energy gain CN and energy loss ELB scattering has enabled the neutron spectra of the three alcohols to be studied in detail over a wide range of energy transfers. The principle features of these spectra are a quasi-elastic peak and a broad "rotational" bend. In comparison the well known internal vibrational modes of the alcohol molecules are shown to have a small effect, and in two possible cases no excitation was apparent.

The origin of the band between 0 and 100 mV which dominates all other processes in the lower alcohols at large scattering angles has been tentatively assigned to rotations involving principally the methyl group, but no correlation has yet been found with the hindered internal rotation observed by optical spectroscopy. The discrepancies noted in the cases of ethyl and n-amyl alcohol which give self-diffusion coefficients derived from the broadening of the quasielastic peaks that are higher than the corresponding macroscopic values, contrasts with the case of water [9] and liquid metals [10] in which observed coefficients are lower in the same region of momentum transfers.

#### ACKNOWLEDGEMENTS

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#### DISCUSSION\*

**P.A.** EGELSTAFF: I would like to ask a question for clarification. Were the diffusion constant measurements on ethylalcohol made by tracer techniques with respect to the oxygen and carbon?

J. WEBB (on behalf of D. H. Saunderson and V.S. Rainey): No. The measurements on methyl and ethyl were done using deuterium as the tracer, and with methyl alcohol carbon was used.

K.E. LARSSON: Fig. 2 shows spectra obtained at 90° and other fairly big angles. I suppose it would rather be difficult to analyse the quasi-elastic line in such cases so as to get the diffusion broadening? It would be very interesting to hear something about the method you used.

J. WEBB: The method was very simple. The large error bars on the graph of diffusion broadening included a generous allowance for the uncertainty - it was merely done graphically.

K.E. LARSSON: Could you reasonably separate this quasi-elastic peak from the inelastic background at 90° or so?

J. WEBB: Well, it certainly becomes very difficult at the end.

<sup>\*</sup> See also discussion on the paper by D. Bally <u>et al</u>. entitled "The Scattering of slow neutrons from hydrogen and ethylene".

# MOUVEMENTS MOLÉCULAIRES DANS LE MÉTHANE LIQUIDE

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#### Abstract — Résumé — Аннотация — Resumen

MOLECULAR MOTIONS IN LIQUID METHANE. The molecular motions of methane in the liquid state are studied using the beryllium detector method. The rotational motions are found to be completely free at 102°K. A symmetrical splitting of the level L=1 is observed. A comparison of the experimental results with transition probabilities calculated only from degrees of degeneracy gives good agreement for transitions  $\Delta L \ge 2$  and for those transitions  $\Delta L = 1$  which have  $L \ge 2$  as the initial state. These transitions, therefore, appear to be rather independent of L. Furthermore, the experiments indicate that with respect to their translational motions the molecules behave as in a gas.

MOUVEMENTS MOLÉCULAIRES DANS LE MÉTHANE LIQUIDE. Les auteurs ont étudié les mouvements moléculaires du méthane à l'état liquide, en employant la méthode du détecteur au béryllium. Ils ont trouvé que les rotations sont complètement libres à la température de 102°K. Ils ont observé, une séparation symétrique du niveau L=1. Les résultats expérimentaux ont été comparés aux probabilités des transition calculées en se fondant uniquement sur les degrés de dégénérescence; l'accord entre eux est bon pour les transitions  $\Delta L \ge 2$  et pour les transitions  $\Delta L=1$ , dans lesquelles  $L\ge 2$  a l'état initial. Il semble donc que ces transitions soient indépendantes de L. De plus, les expériences montrent qu'en ce qui concerne les mouvements de translation, les molécules se comportent comme les molécules d'un gaz.

МОЛЕКУЛЯРНЫЕ ДВИЖЕНИЯ В ЖИДКОМ МЕТАНЕ. При помощи бериллиевого детектора изучаются молекулярные движения в жидком метане. Было установлено, что при 102°К вращательные движения совершенно свободны. Наблюдается симметричное раздвоение уровня L = 1. Сравнение экспериментальных результатов с вероятностью перехода, подсчитанной только на основании степени вырождения, дает хородую согласованность для переходов  $\Delta$  L >2 и для тех переходов  $\Delta$  L = 1, которые в качестве исходного состояния имеют L >2. Поэтому эти переходы, по-видимому, не зависят от L. Более того, эксперименты указывают, что в отношении своих поступательных движений молекулы жидкости обладают такими же свойствами, как и молекулы газа.

MOVIMIENTOS MOLECULARES DEL MET ANO LÍQUIDO. Los autores estudian los movimientos moleculares del metano en estado líquido por el método del detector de berilio. Han comprobado que los movimientos de rotación son completamente libres a  $102^{\circ}$ K; asimismo han obtenido un desdoblamiento simétrico del nivel L=1. La comparación de los resultados experimentales con las probabilidades de transición calculadas únicamente en función de los grados de degeneración da resultados satisfactorios para las transiciones  $\Delta$  L $\geq$ 2 y para las transiciones  $\Delta$  L=1 cuyo estado inicial es L $\geq$ 2. Por tanto, estas transiciones parecen ser bastante independientes de L. Además, los experimentos muestran que las moléculas se comportan como en un gas, en lo que respecta a sus movimientos de translación.

#### 1. INTRODUCTION

Le but de cette recherche était d'abord d'observer des transitions entre les états de rotation pure de la molécule CH<sub>4</sub>. Bien que ces rotations aient pu être étudiées indirectement dans les spectres optiques de vibration [1], une observation directe est intéressante, surtout si elle peut être comparée à des observations faites à des températures inférieures, où l'on peut s'attendre à trouver un certain empêchement des rotations. Dès 1930, PAULING [2] avait déjà supposé l'existence d'un empêchement de ce genre pour expliquer une anomalie du type  $\lambda$  observée à 20,4°K dans la chaleur spécifique du méthane solide [3]. Plus tard, des mesures en résonance protonique [4, 5] ont cependant révélé que ce changement de phase se produit sans donner naissance aux rotations libres, et que ces dernières apparaissent progressivement à des températures plus élevées (~ 65°K). Les résultats d'une investigation neutronique du CH<sub>4</sub> solide au dessus et en dessous de 20°K sont présentés dans une autre communication à ce congrès.

Le second objectif était l'étude des translations dans l'état liquide. On peut en effet s'attendre à ce que le méthane liquide se comporte beaucoup moins comme un cristal que l'eau ou les métaux liquides puisque l'interaction entre les molécules est certainement faible (en vertu de la symétrie tetraédrique, le moment octupolaire est le premier moment multipolaire électrique non nul).

### 2. MÉTHODE EXPÉRIMENTALE

Nous avons mesuré la distribution en énergie des neutrons diffusés au moyen d'une méthode innovée par BROCKHOUSE [6] et par STILLER et DANNER [7]. On place l'échantillon dans un faisceau de neutrons d'énergie  $E_0$  tandis qu'un filtre est inséré entre l'échantillon et le détecteur, de sorte que seuls les neutrons d'énergie inférieure à l'énergie de coupure  $E_f$  du filtre peuvent atteindre le détecteur. Le nombre  $N(E_0)$  de neutrons comptés est proportionnel à

$$N(E_0) \propto \int_{-\infty}^{\infty} R(E_0 - \epsilon) d\epsilon \int_{0}^{E_f} S(\epsilon - E) dE$$
(1)

où  $R(E_0 - \epsilon)$  est la fonction de résolution de l'appareil et  $S(\epsilon - E)$  est la distribution en énergie des neutrons diffusés. Par cette méthode intégrale, un pic dans la distribution en énergie des neutrons diffusés est transformé en un seuil de la courbe  $N(E_0)$ ,

L'appareillage utilisé est représenté à la figure 1. On change l'énergie





des neutrons incidents par rotation discontinue du cristal monochromateur M. Les plans réflecteurs, d'espacement 9.963Å, sont les plans [001] du thermica\*.  $K_1$  et  $K_2$  sont des collimateurs d'égale divergence (4,4 · 10<sup>-3</sup> rad.).

L'échantillon de  $CH_4$  liquide (pureté: 99,9%), d'une épaisseur de 1 mm, est obtenu par condensation dans un réservoir P, maintenu à -171°C. Les neutrons diffusés sont observés en réflection sous un angle  $\Phi = 70^{\circ}$ .

Comme filtre F nous utilisons un bloc de Be de 7 cm de longueur. Sur la figure 2, la courbe B, qui représente la transmission du filtre, présente





Courbe A : taux de comptage dans le faisceau incident en fonction de l'angle d'incidence sur les plans réflecteurs, le filtre étant inséré entre le monochromateur et le détecteur. Courbe B : transmission du filtre

<sup>\*</sup> Pour plus de détails, consulter [7,8].

deux coupures importantes à des énergies respectives  $E_f = 6,32$  et 5,20 meV. De la transmission mesurée, on déduit\* que la largeur à mi-hauteur  $2\Delta\epsilon$  est égale à 0,15 ± 2 meV à  $E_0 = 5,2$  meV. Enfin, le détecteur Z est un compteur proportionnel à  $BF_3$ .

Deux difficultés apparaissent lorsqu'on utilise cette méthode pour des neutrons froids :

- a) Les réflections d'ordre supérieur du monochromateur ne permettent plus de contrôler le flux des neutrons incidents au moyen d'un moniteur.
- b) Pour chaque position du monochromateur, non seulement les neutrons ayant perdu une énergie  $E^{\bullet} \ge E_0 - E_f$  peuvent atteindre le détecteur, mais encore ceux ayant perdu des énergies  $E^{\bullet} \ge n^2 E_0 - E_f$ (n = 2, 3, ...),

La première difficulté a été surmontée en effectuant une normalisation des mesures prises à intervalles de temps égaux \*. Quant à la seconde difficulté, on montrera ci-dessous qu'elle ne joue pas dans notre cas particulier.

## 3. RÉSULTATS EXPÉRIMENTAUX

Les résultats expérimentaux sont donnés aux figures 3, 4 et 5 dans lesquelles les cercles représentent la différence entre les intensités dif-



#### Résultats expérimentaux.

Les cercles O représentent la différence entre l'intensité observée  $I_s$  et le bruit de fond  $I_a$  (mesuré avec le réservoir vide) pour différentes valeurs de l'énergie  $E_0$  des neutrons incidents. Les points . représentent les mêmes données normalisées.

\* Pour plus de détails, consulter [7,8].





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fusées  $I_s$  et le bruit de fond  $I_u$  (mesuré avec le réservoir vide), tandis que les points représentent les mêmes données normalisées  $N(E_0)$ . Les courbes montrent douze seuils caractérisés par un nombre romain, mis entre parenthèses lorsque la résolution des seuils est quelque peu incertaine.

On donne dans le tableau I les transferts d'énergie  $E_0$  -  $E_f$  correspondant aux différents seuils (pour  $E_0$  on choisit la valeur pour laquelle il y a

#### TABLEAU I

TABLEAU DES ENERGIES E <sub>0</sub> AUXQUELLES SE PRODUISENT
LES DIFFÉRENTS SEUILS ET DES TRANSFERTS D'ÉNERGIE,
E <sub>0</sub> -E <sub>f1</sub> OU E <sub>0</sub> -E <sub>f2</sub> , CORRESPONDANT AUX DEUX COUPURES
DU FILTRE

Marche	E <sub>o</sub>	$2\Delta\epsilon_1$	, <sup>E</sup> 0 <sup>-E</sup> f1	E <sub>0</sub> -E <sub>f2</sub>	9E 0-Ef	2∆ <b>€</b> 3
I	19,8	1,15	14	.2	170	160
п	17,3	0,98	11	.6	148	84
ш	14,2	0,70	8	,5	121	60
īv	11,5	0,55	5	.8	102	37
v	10,3	0,45	5,10	3,90	87	27
VI	9,1	0,37	3,90	2,75	76	18
νп	8,15	0,32	2,95 · 1,80		68	14
VШ	7,40	0,27	2,20	1,05	61	10,7
· 1X	6,05	0,21	0,85	0,20	49	6,5
x	5,30	0,16	0,10	1,15	42	4,4
xı	4,92	0,14	0,28	1,43	39	3,5
ХШ	4,25	0,13	0,95	2,10	32	2,5

changement de pente). Les nombres de la troisième colonne représentent les valeurs calculées de la largeur à mi-hauteur,  $2\Delta\epsilon$ , de la fonction de résolution pour les différentes valeurs de  $E_0$ . On voit que pour  $E_0 \ge 11$  meV la résolution de l'appareil ne permet pas de distinguer entre les deux coupures du filtre. On prend donc dans cette région une valeur de  $E_f$  moyenne entre  $E_{f1}$  et  $E_{f2}$ . Dans les sixième et septième colonnes, on donne les transferts d'énergie 9  $E_0 - E_f$  (le thermica ne donne pas de réflection du second ordre) et les valeurs correspondantes de la largeur à mi-hauteur  $2\Delta\epsilon_3$  de la résolution. On constate que ces transferts d'énergie peuvent seulement contribuer à  $N(E_0)$  sous la forme d'un socle, puisque tous les seuils sont plus étroits.

#### 4. DISCUSSION

#### a) Niveaux de rotation

On a comparé les transferts d'énergie observés avec les énergies des transitions entre les niveaux de rotation BL(L+1) calculées pour la molé-

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cule libre (B = 0,647 meV [9]). Les flèches dans les figures 3, 4 et 5 indiquent les énergies  $E_0$  pour lesquelles un seuil dans  $N(E_0)$  résulterait de l'excitation de telles transitions. Pour  $E_0 < 11$  meV, les grandes et les petites flèches correspondent respectivement aux coupures  $E_{f1}$  et  $E_{f2}$ . Les nombres indiqués donnent les valeurs du nombre quantique L associés aux deux niveaux impliqués dans la transition.

Les seuils I à VI peuvent s'interpréter sans aucun doute comme résultant de transitions entre des états de rotation libre de la molécule CH<sub>4</sub>.

Les positions des seuils VII, VIII et XII peuvent être expliquées par une décomposition symétrique du niveau L = 1 d'une quantité  $\pm$  0,36 meV puisque, d'une part, la transition 1  $\rightarrow$  2 se trouve exactement au centre des seuils VII et VIII, et puisque, d'autre part, le seuil XII se trouve déplacé de la transition. 1  $\rightarrow$  0 par une énergie égale à la moitié de la distance entre VII et VIII. Cette décomposition du niveau L = 1 ne peut pas être observée dans les transitions de ce niveau vers des états avec L > 2, comme on peut le voir en consultant la colonne 3 du tableau I.

Enfin les seuils IX, X et XI résultent probablement de la superposition de plusieurs effets, parmi lesquels éventuellement des transitions entre le niveau L = 0 et les deux composantes du niveau L = 1 et peut-être aussi une transition entre ces dernières, et certainement les pics élastiques relatifs aux deux coupures en  $E_{f1}$  et  $E_{f2}$ .

#### b) Etude des transitions entre les niveaux de rotation

Un examen des figures 3, 4 et 5 révèle l'absence de certaines transitions. Une étude rigoureuse de l'intensité relative des différentes transitions exigerait le calcul des éléments de matrice pour cestransitions.Comme ce serait extrêmement compliqué, nous calculerons ces intensités en tenant compte uniquement des autres facteurs, c'est-à-dire la polulation thermique des niveaux et leur dégénérescence. En comparant les nombres obtenus avec les intensités observées on doit pouvoir déduire quelque information concernant la dépendence en L des éléments de matrice.

A cette approximation, la probabilité d'une transition  $L_a \rightarrow L_b$  s'écrit

$$W(L_{a}, L_{b}) = W_{th}(L_{a}) \left\{ (1 - W_{a}) \sum_{s} W_{s}(L_{a}) W_{s}(L_{b}) + W_{a}[W_{0}(L_{a})W_{1}(L_{b}) + W_{2}(L_{a})W_{1}(L_{b}) + 3/4 W_{1}(L_{a})W_{0}(L_{b}) + 1/4 W_{1}(L_{a})W_{2}(L_{b})] \right\}$$
(2)

 $W_{th}$  est la poulation thermique du niveau initial. S est le spin nucléaire total de la molécule et peut prendre les trois valeurs 0, 1 ou 2.  $W_s$  (L) est la dégénérescence de l'état S, L.  $W_a$  est la probabilité pour que le spin d'un proton soit renversé lors de la diffusion du neutron; sa valeur est 0,655\*. La première sommation dans la parenthèse s'étend aux transitions  $\Delta S = 0$ ; la seconde (terme entre crochets)aux transitions  $\Delta S = \pm 1$ . Les  $W_s$  (L) ont été calculés par la théorie des groupes [10]. Si on tient compte des différents modes de vibration de la molécule, ils prennent les valeurs du tableau II [11].

<sup>\*</sup> Pour plus de détails, consulter [8].

#### TABLEAU II

L				0.			
	0	1	2	L /	0	1	2
0	2	3	5	6	182	741	455
1	6	45	15	7	210	1035	525
2	30	105	75	8	306	1275	765
3	42	231	105	9	342	1653	850
4	90	351	225	10	462	1953	1155
5	110	561	275	11	506	2415	1265

## DÉGÉNÉRESCENCE DE L'ÉTAT DE SPIN NUCLÉAIRE TOTAL S ET DE NOMBRE QUANTIQUE ROTATIONEL L

La troisième colonne du tableau III donne les probabilités de transition calculées au moyen de la formule (2).

#### TABLEAU III

PROBABILITÉS W( $\Delta$ L) DES TRANSITIONS L<sub>a</sub>  $\rightarrow$  L<sub>b</sub> ET DES INTENSITÉS CALCULÉES, I( $\Delta$ E), POUR L'EXCITATION DES TRANSITIONS  $\Delta$ E

∆E (meV)	L	<b>W(</b> ΔL)	I(ΔE)	E (meV)	ΔL	W(ΔL)	I(∆E)
1.29	0→1	30	12	9, 06	6→7	4195	275
2, 59	$1 \rightarrow 2$	397	136		2→4	3633	
		10.35	10,35	7→8	2424	78	
	2→3	2195	400		0-10	1000	
3.88	0→2	82	437	(	8-79	1269	
			417	11.65	°3→5	5513	208
5,18	3→4	3→4 3719			1→4	1320	
	4→5	5570		19.04	0-10	37.9	
6.47	1+3	786	416	12, 54	3-710		
				{	10→11	170	
	5→6	5195		14,23	4 ↔ 6	7812	169
7.76	0→3	162	259				

Avec notre technique expérimentale, l'intensité  $I(\Delta E_{\mu})$  d'une transition avec un changement d'énergie  $\Delta E_{\mu}$  est proportionnelle à

$$W(\Delta E_{\mu}) / \sum_{\nu=0}^{\mu} W(\Delta E_{\nu})$$

si W( $\Delta E$ ) est la somme des probabilités pour toutes ces transitions  $\Delta L$  qui conduisent au même changement d'énergie  $\Delta E$ . La probabilité W( $\Delta E_0$ ) pour la diffusion élastique a été estimée en comparant la hauteur I( $\Delta E_0$ ) du pic

élastique (figure 5) à la hauteur  $I_{\nu} = I(\Delta E_3)$  de la marche V (figure 4) :

$$I(\Delta E_0)/I(\Delta E_3) = [W(\Delta E_0) + \sum_{\nu=1}^3 W(\Delta E_{\nu})]/0.8 W(\Delta E_3).$$

Le facteur 0,8 au dénominateur représente la transmission relative du filtre à  $E_{f2}$ , puisque  $\Delta E_3$  à V se réfère à  $E_{f2}$ , tandis que  $\Delta E_0$  se réfère à  $E_{f1}$ . On trouve alors  $W(\Delta E_0) \simeq 2500$ . Les valeurs de I( $\Delta E$ ) données dans la quatrième colonne du tableau III ont été calculées avec cette valeur de  $W(\Delta E_0)$ .

Nous comparons dans la figure 6 les hauteurs relatives calculées  $I_{calc.}$  aux hauteurs relatives observées  $I_{obs.}$ des différentes marches. L'accord



Comparaison des hauteurs calculées et observées des différents seuils.

est généralement bon, excepté pour les marches VI et VII + VIII, qui sont causées par, ou qui contiennent une contribution de la transition  $1 \rightarrow 2$ . Le bon accord indique que pour les transitions  $\Delta L = 2$  et  $\Delta L = 3$ , ainsi que pour les transitions  $\Delta L = 1$  qui ont un moment angulaire initial  $L \ge 2$ , les éléments de matrice ne dépendent pas fortement de L et  $\Delta L$ . Le désaccord pour la transition  $1 \rightarrow 2$  ne pourrait être que très partiellement expliqué par une erreur sur l'estimation de la probabilité  $W(\Delta E_0)$  de la diffusion élastique. Comme par ailleurs des mesures sur le méthane solide ont révélé la présence à cet endroit d'un spectre de vibrations cristallines, on pourrait peutêtre expliquer ce désaccord en supposant que l'intensité observée contient une contribution due à des vibrations cristallines résiduelles. S'il n'en était pas ainsi, on devrait admettre que l'élément de matrice pour cette transition a une valeur nettement différente de celle des autres éléments de matrice.

#### c) Mouvements de translation

La superposition des différents effets au voisinage des coupures du filtre ne permet pas une détermination précise de la hauteur et de la forme du pic élastique. Si on suppose une forme donnée par la courbe en pointillés dans la figure 5, on trouve une largeur à mi-hauteur de 1,62 meV, ce qui correspond à une valeur de la largeur intrinsèque  $2\Delta E_{gl}$  du pic élastique de 1,60 meV<sup>\*</sup>, mais l'incertitude sur cette valeur ne permet pas d'obtenir des informations détaillées sur les mouvements de translation.

Pour des molécules qui se déplacent librement, la largeur à mi-hauteur du pic élastique est donnée par [12, 13].

$$2\Delta E_{el} = 2\hbar DK^2$$

où D est la constante de diffusion. Avec  $K \simeq 2k$ .  $\sin \Phi/2 = 1,80 \text{ Å}^{-1} \text{ a} E_0 = 5,20 \text{ meV}$ on trouve pour la constante de diffusion à  $-171^{\circ}$ C la valeur D =  $3,8 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ .

Malheureusement la diffusion dans le méthane liquide n'a pas été mesurée. On peut la déduire de [14].

$$D = kT/3\pi R\eta$$

si pour la viscosité  $\eta \ge -170^{\circ}$  on prend la valeur [15]  $1,42 \cdot 10^{-3}$  poise. R est le rayon effectif de la molécule. On trouve D =  $4,2 \cdot 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup> avec

R = 
$$\left(\frac{3}{4\pi N}\right)^{1/3}$$
 = 2,49 Å.

Cette valeur du coefficient de diffusion est en assez bon accord avec celle que nous pouvons déduire de la largeur du pic élastique.

#### REMERCIEMENTS

Les auteurs tiennent à remercier M. Nève de Mévergnies pour l'intérêt constant manifesté pendant ce travail. L'un de nous (H. Stiller) exprime sa gratitude pour l'hospitalité reçue au CEN.

<sup>\*</sup> L'appendice de [7] donne la méthode pour déterminer, à partir d'une marche dans  $N(E_0)$ , la largeur d'un pic dans la distribution en énergie des neutrons diffusés

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#### DISCUSSION\*

H. HAHN: Although Dr. Stiller forbade me to mention it, I want to say that the beryllium filter method used here and in many of the other experiments was actually applied independently by Dr. Stiller at the same time as Dr. Brockhouse was using it.

H. H. STILLER: I should just like to mention that, in calculating the transition probabilities, it is necessary to take into account the distribution of the spin states on the rotational levels and the probability of spin flip during scattering.

P.A. EGELSTAFF: You mean the evidence for the spin-flip process actually occuring is quite strong?

H.H. STILLER: Yes.

\* See also discussion on the paper by D. Bally <u>et al</u>. entitled "The Scattering of slow neutrons from hydrogen and ethylene".

## SCATTERING OF SLOW NEUTRONS BY GASEOUS METHANE\*

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#### Abstract — Résumé — Аннотация — Resumen

SCATTERING OF SLOW NEUTRONS BY GASEOUS METHANE. Slow neutron scattering by molecular gases is discussed. The most detailed comparison between theoretical and experimental results has been on gaseous methane which shows conclusively that the quantum nature of the rotational levels must be explicitly taken into account to obtain agreement with the experimental results. It is also shown theoretically that interference scattering, that is interference scattering between two distinct atoms of the molecule, has an effect which can be observed. This effect has been observed experimentally in methane and apparently also for propane. It is pointed out that the theory makes quite definite predictions at smaller momentum transfers than has been measured. Thus experiments at smaller momentum transfers are needed.

DIFFUSION DES NEUTRONS LENTS DANS LE MÉTHANE GAZEUX. L'auteur étudie la diffusion des neutrons lents dans les gaz moléculaires. Il compare de manière détaillée les résultats théoriques et expérimentaux relatifs au méthane gazeux; il en conclut qu'il faut tenir compte explicitement de la nature quantique des niveaux de rotation pour obtenir un bon accord avec les résultats expérimentaux. Il montre également d'une manière théorique que la diffusion d'interférence, c'est-à-dire la diffusion entre deux atomes distincts de la molécule, a un effet qui peut être observé. Cet effet a été effectivement observé expérimentalement dans le méthane et aussi, semble-t-il, dans le propane. L'auteur indique que la théorie permet de faire des prévisions certaines pour des transferts d'impulsion inférieurs à ceux qui ont été mesurés. Par conséquent, il faudra procéder à des expériences pour des transferts d'impulsion plus petits.

РАССЕЯНИЕ МЕДЛЕННЫХ НЕЙТРОНОВ ГАЗООБРАЗНЫМ МЕТАНОМ. Рассматривается рассеяние медленных нейтронов в модекулярных газах. Тщательное сравнение теоретических и опытных данных, полученных при работе с газообразным метаном, определенно показывает, что квантовая природа вращательных уровней должна быть, безусловно, принята в расчет, чтобы добиться соответствия теоретических данных с опытными. Теория также указывает на возможность регистрации действия интерференционного Рассеяния, т.е. рассеяния между двумя определенными атомами молекулы. Это действие отмечено в опыте с метаном и, очевидно, может наблядаться в опыте с пропаном. Указывается на то, что теория предсказывает наличие момента передачи еще меньших импульсов чем те, которые уже были замерены. Подчеркивается необходимость дальнейших опытов в этом направлении.

DISPERSIÓN DE NEUTRONES LENTOS EN EL MET ANO GASEOSO. El autor estudia la dispersión de neutrones lentos por gases moleculares. La comparación más detallada entre resultados teóricos y experimentales, que se ha realizado en el caso del metano gaseoso, demuestra de manera concluyente que la naturaleza cuántica de los niveles de rotación ha de tenerse explícitamente en cuenta para lograr concordancia con los resultados experimentales. El autor también demuestra teóricamente que la dispersión por interferencia, esto es, la dispersión por interferencia entre dos átomos distintos de la molécula, ejerce un efecto observable. Este efecto se ha comprobado experimentalmente en el metano y también, según parece, en el propano. El autor señala que la teoría permite formular previsiones muy concretas acerca de transmisiones de cantidad de movimiento interiores a las que se han medido, por lo que es preciso realizar experimentos relativos a la transmisión de cantidades de movimiento más reducidas.

\* Work performed under the auspices of the United States Atomic Energy Commission.

#### I. INTRODUCTION

Precise theoretical formulae for the partial differential cross-section for the scattering of slow neutrons by molecules were presented by ZEMACH and GLAUBER[1] several years ago. At the time there were no experimental results available so they had to be content with making comparisons [2] with experiments on the differential cross-section (angular distribution) of methane. Later KRIEGER and NELKIN [3] made use of the formulas of Zemach and Glauber to derive approximate formulas containing the masstensor introduced by SACHS and TELLER [4]. The formulas of Krieger and Nelkin have been much used in the analysis of the experimental results. For many of the experimental results their formulas are apparently sufficient.

When some experiments on the scattering of slow neutrons by gaseous methane, which were conducted at the Materials Testing Reactor, were analysed [5] it was found that there were serious disagreements between the experimental results and the results predicted by the use of the formulas of Krieger and Nelkin. This discrepancy indicated that a quantum description of the rotational levels was needed.

In deriving their formulas Zemach and Glauber introduced operator representations which permitted the sums over the final molecular states to be taken consistent with the conservation laws. However this procedure did not result in formulas which are convenient for numerical purposes. Consequently the author [6] formulated the problem so that operator representations were used for the translational and vibrational modes but not for the rotational mode. This procedure resulted in formulas which are quite convenient for numerical purposes.

In Section II the theory is presented and discussed. Analytical expressions for a spherical molecule (methane) are obtained for the case in which vibrational levels are not initially excited nor is the incident neutron energy sufficient to excite them. The methods used can be applied to obtain analytical expressions for any type molecule. It might be of interest to remark that to obtain a given numerical result for a spherical molecule using these formulas takes about an order of magnitude more computing time than the time to get the corresponding result using the formulas of Krieger and Nelkin.

In Section III the theoretical results are presented. Comparisons with the available experimental results shows there is satisfactory agreement. Of particular interest is that an influence of the gain of energy from the rotational levels is predicted and is observed in the experiments. It is also shown that with an appropriate incident neutron energy the influence due to an energy loss to the rotational levels can be observed. It is predicted that the influence of interference scattering from carbon-proton and proton-proton pairs can be observed. There are convincing indications that such an effect has been observed [7].

Section IV mainly recommends additional experiments which would be helpful for a further understanding of the scattering by gaseous methane. It also points out a need for scattering experiments on liquid and solid methane.

# II. ANALYTICAL EXPRESSION FOR THE PARTIAL DIFFERENTIAL CROSS-SECTION AND $S(\kappa^2, \epsilon)$

The partial differential cross-section for the process in which the neutron momentum changes from  $\underline{k}_0$  to  $\underline{k}$  with an energy transfer  $\epsilon$  in a collision with a molecule which simultaneously undergoes a transition from an initial state  $\psi_i$  to a final state  $\psi_f$  has been shown by Zemach and Glauber to be given by

$$\sigma_{\rm fi}({\rm E}_0,\epsilon,\theta) = (2\pi)^{-1} \sum_{\nu,\nu'} a_{\nu\nu'} \int \langle {\rm k}/{\rm k}_0 \rangle e^{-i\epsilon t} \langle {\rm fi}/\nu\nu' \rangle {\rm d}t,$$

with

 $a_{uv} = A_{u}A_{v} + \delta_{uv} C_{v}C_{v}$ ,

and

$$\langle \mathbf{f} \mathbf{i} | \boldsymbol{\nu} \boldsymbol{\nu}' \rangle = \mathrm{e}^{\mathrm{i}(\mathbf{E}_{\mathrm{i}} - \mathbf{E}_{\mathrm{f}})\mathbf{t}} \langle \boldsymbol{\psi}_{\mathrm{i}} | \exp(\mathrm{i}\underline{\kappa} \cdot \underline{\mathbf{r}}_{\nu}) | \boldsymbol{\psi}_{\mathrm{f}} \rangle$$

$$\times \langle \boldsymbol{\psi}_{\mathrm{f}} | \exp(-\mathrm{i}\underline{\kappa} \cdot \underline{\mathbf{r}}_{\nu}) | \boldsymbol{\psi}_{\mathrm{i}} \rangle.$$

In (1)  $A_{\nu}$  and  $C_{\nu}$  are the bound coherent and incoherent scattering lengths of the  $\nu$ th nucleus and  $\underline{r}_{\nu}$  its position vector. The scattering angle is given by  $\hat{\theta}$ , and  $\underline{\kappa}$  is the momentum change of the neutron during the collision. The initial and final total energy of the molecule are denoted by  $E_i$  and  $E_f$  and the initial energy of the neutron is given by  $E_0$ . The system of units are such that **h** has unit magnitude. The quantity to be compared with the experimental observations is the partial differential cross-section obtained by summing over all final states and taking a thermal average over all initial states in (1), that is

$$\sigma(\mathbf{E}_{0}, \epsilon, \theta) = \sum_{i, f} p_{i} \sigma_{fi} (\mathbf{E}_{0}, \epsilon, \theta), \qquad (2)$$

where p<sub>i</sub> is the probability that the struck molecule is in a given initial state. In our formulation we will assume that the total energy of the initial

state of the molecule is given by the sum

 $(E)_i = (E_r)_i + (E_r)_i + (E_v)_i$ 

where  $(E_t)_i$ ,  $(E_r)_i$  and  $(E_v)_i$  are the initial energy of the translational, roational, and vibrational modes of the molecule. A similar assumption is made for the total energy of the final state. Thus in both the initial and final total energy the interaction energy between the rotational and vibrational modes is neglected. As a consequence of this assumption the molecular wave function can be written as a product

$$\psi = \psi_{\rm f} \psi_{\rm f} \psi_{\rm v}$$

of the wave functions for the translational, potational and vibrational modes

for both the initial and final molecular states. The position vector  $\underline{r}_{\nu}$  of the  $\nu$ th nucleus is given by the sum

$$\underline{\mathbf{r}}_{\boldsymbol{y}} = \underline{\mathbf{R}} + \underline{\mathbf{b}}_{\boldsymbol{y}} + \underline{\mathbf{V}}_{\boldsymbol{y}}$$

with <u>R</u> being the molecular centre of mass,  $\underline{b}_{\nu}$  the displacement vector of the equilibrium position of the  $\nu$ th nucleus from the centre of mass, and  $\underline{V}_{\nu}$  the displacement vector of the  $\nu$ th nucleus from its equilibrium position. It will be assumed at the outset that rotational and vibrational effects are separable so  $\langle fi | \nu \nu' \rangle$  in (1) can be written as a product given by

$$\int \langle fi | \nu \nu \rangle = \langle fi | \nu \nu \rangle_{t} \langle fi | \nu \nu \rangle_{r} \langle fi | \nu \nu \rangle_{v} , \qquad (3)$$

where

$$\langle \mathrm{fi} | \nu \nu' \rangle_{\mathrm{t}} = \exp \{ \mathrm{it} [(\mathbf{E}_{t})_{\mathrm{i}} - (\mathbf{E}_{t})_{\mathrm{f}}] \} \langle (\psi_{t})_{\mathrm{i}} | \exp(\mathrm{i}\underline{\kappa} \cdot \underline{\mathbf{R}}) | (\psi_{t})_{\mathrm{f}} \rangle$$

$$\times \langle (\psi_{t})_{\mathrm{f}} | \exp(-\mathrm{i}\underline{\kappa} \cdot \underline{\mathbf{R}}) | (\psi_{t})_{\mathrm{i}} \rangle$$

and similar expression for those quantities referring to the rotational and vibrational modes. In order to avoid confusion it should be pointed out that i and f on the left hand side of (3) refer to the initial and final molecular states while i and f in the various brackets on the right hand side refers to the initial and final states of that particular mode. For example i and f in  $\langle fi | \nu \nu \rangle_t$  refer to the initial and final states of the translational mode. Analogous interpretations are given in the remaining expressions.

Introducing the Hamiltonian operators  $H_t$  and  $H_v$  associated with the translational and vibrational modes and assuming the final states of each mode form a complete set, the summation over the final states of these modes is performed. The summation over the rotational states is considered later. With the understanding that the only final state summation remaining is that over the rotational state, (3) reduces to

$$\langle fi | \nu \nu' \rangle = \langle fi | \nu \nu' \rangle_{r} \langle \langle \psi_{v} \rangle_{i} | e^{i \underline{\kappa} \cdot \underline{V}_{\nu}(t)} e^{-i \underline{\kappa} \cdot \underline{V}_{\nu}(0)} | \langle \psi_{v} \rangle_{i} \rangle$$

$$\times \langle \langle \psi_{\tau} \rangle_{i} | e^{i \underline{\kappa} \cdot \underline{R}(t)} e^{-i \underline{\kappa} \cdot \underline{R}(0)} | \langle \psi_{\tau} \rangle_{i} \rangle \qquad (4)$$

where  $\underline{R}(t)$  and  $\underline{V}(t)$  are the Heisenberg operators corresponding to the position coordinate of the centre of mass and the position displacement due to vibration.

Since the molecule with which the neutron collides can have any given orientation it is necessary to average (4) over the initial molecular orientations. The dependence upon molecular orientations is contained in the rotational and vibrational factors of the product in (4). The assumption is made that the average of the product with respect to molecular orientations is equal to the product of their averages. This assumption has been investigated for gaseous methane [8] in which the rotational states were treated classically, the molecule was in its ground vibrational state, and the energy of the neutron was insufficient to excite the vibrational levels. For that case, it was found that this assumption is a good approximation. The

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justification of this assumption for the case in which the rotational states are to be treated quantum-mechanically is based partly on this result but more conclusively upon comparison of the numerical results with the experiments.

Zemach and Glauber have evaluated the thermal average of the expectation value of the translational mode in which the translational energy of the molecule is distributed according to a Boltzmann distribution. Their result is

$$\langle \psi_{t} \rangle_{i} | e^{i\kappa \cdot R(t)} e^{-i\kappa \cdot R(0)} | \langle \psi_{t} \rangle_{i} \rangle_{T} = \exp\left[-\kappa^{2}(it + t^{2}T)/(2M)\right]$$
 (5)

in which the temperature T of the gas is expressed in units of Boltzmann's constant and M is the mass of the molecule.

Zemach and Glauber have also evaluated the thermal average of the expectation value of the vibrational mode. If it is assumed that the molecules are in their ground state and that the neutron does not have sufficient energy to excite a vibrational state their result is

$$\left\langle \left\langle \psi_{\nu} \right\rangle_{i} e^{i\underline{\kappa} \cdot \underline{\nabla}_{\nu}(t)} e^{-i\underline{\kappa} \cdot \underline{\nabla}_{\nu}(0) \left| \left\langle \psi_{\nu} \right\rangle_{i}} \right|_{T = 0} = \pi_{\lambda} \exp \left[ - \left( 4 \omega_{\lambda} \right)^{-1} \left[ \left( \underline{\kappa} \cdot \underline{C}_{\nu}^{(\lambda)} \right)^{2} + \left( \underline{\kappa} \cdot \underline{C}_{\nu}^{(\nu)} \right)^{2} \right] \right]$$

where  $\underline{C}_{\nu}^{(\lambda)}$  is the amplitude vector of the  $\nu$ th nucleus and  $\lambda$ th vibrational mode and  $\omega_{\lambda}$  the angular frequency of the  $\lambda$ th mode. Krieger and Nelkin have averaged over the molecular orientations in an approximate manner by averaging in the exponents of the exponentials. Their result is

$$\langle (\psi_{\nu})_{i} | e^{\frac{i\kappa}{\kappa} \cdot \underline{\nabla} \iota(t)} e^{-\frac{i\kappa}{\kappa} \cdot \underline{\nabla} \iota(0)} | (\psi_{\nu})_{i} \rangle_{T,\Omega} = \exp(-\kappa^{2} \gamma_{\nu\nu'})$$
(7)

where

$$\gamma_{\nu\nu^*} = \sum_{\lambda} \left\{ \left( 12\omega_{\lambda} \right)^{-1} \left[ \left( C_{\nu}^{(\lambda)} \right)^2 + \left( C_{\nu^*}^{(\lambda)} \right)^2 \right] \right\}.$$

If necessary this average can be taken in a more exact manner. However it is easily shown that averaging the exponent of the exponentials is correct up to second order in an expansion of the exponential in powers of  $[(\kappa \cdot \underline{C}_{\nu}^{(\lambda)})^2 / (4\omega_{\lambda})]$ . This is sufficient for our comparisons with experiment.

Consideration is now given to the rotational term  $\langle fi | \nu \nu' \rangle_r$  in (4). It is necessary to sum over the final states, perform a quantum mechanical average over molecular orientations, and take a thermal average over the initial states. It might appear expedient to introduce the Hamiltonian operator  $H_r$ which permits an immediate sum of the final rotational states. However subsequent considerations of the resulting expectation values has led to the partial differential cross section being expressed by a classical description with a series of quantum corrections in which each are given by an expansion of a suitable parameter. As a result the expression for the cross-section appears quite formidable for numerical purposes. This is true for the linear molecule considered by Zemach and Glauber and the subsequent generalization to symmetric and asymmetric molecules by VOLKIN [9].

The procedure adopted by the author is to evaluate

$$\langle \langle \psi_{\rm r} \rangle_{\rm i} \left| \exp \left( {\rm i}_{\underline{\kappa}} \cdot \underline{{\rm b}}_{\nu} \right) \right| \langle \psi_{\rm r} \rangle_{\rm f} \rangle \langle \langle \psi_{\rm r} \rangle_{\rm f} \left| \exp \left( - {\rm i}_{\underline{\kappa}} \cdot \underline{{\rm b}}_{\nu'} \right) \right| \langle \psi_{\rm r} \rangle_{\rm i} \rangle$$

occurring in  $\langle fi | \nu \nu' \rangle_{r}$  which then must be averaged over all possible initial

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orientations with respect to  $\underline{\kappa}$  and summed over all possible final orientations. RAHMAN [10] has done this for linear, spherical, and symmetrical molecules. Since we are primarily interested in gaseous methane, which is a spherical molecule, only the results for this case will be given. There are four distinct combinations for the scattering from the nuclei of methane. These are  $\nu$  and  $\nu'$  denote scattering from the same proton,  $\nu$  and  $\nu'$  scattering from different protons,  $\nu$  and  $\nu'$  scattering from a carbon nucleus and a proton, and  $\nu$  and  $\nu'$  scattering from the carbon nucleus. The results listed in the above order are:

$$\left\langle \left( \Psi_{r} \right)_{i} \left| \exp \left( i\kappa \cdot b_{\nu} \right) \right| \left( \Psi_{r} \right)_{f} \right\rangle \left\langle \left( \Psi_{r} \right)_{f} \right| \exp \left( -i\kappa \cdot b_{\nu} \right) \left| \left( \Psi_{r} \right)_{i} \right\rangle = \left[ \left( 2J+1 \right) / \left( 2j+1 \right) \right]$$

$$\times \sum_{n=|j-J|}^{j+J} j_n^2(\kappa \mathbf{b}_p); \qquad (8a)$$

 $\left< (\Psi_r)_i \left| \exp(i\kappa \cdot b_{\nu}) \right| (\Psi_r)_f \right> \left< (\Psi_r)_f \right| \exp(-i\kappa \cdot b_{\nu}) \left| (\Psi_r)_i \right> = \left[ 2(2J+1)/(2j+1) \right]$ 

$$\times \sum_{n=|j-j|}^{j+j} \{ j_0^2(\kappa b_p) - \frac{1}{3} j_1^2(\kappa b_p) - \frac{1}{3} j_2^2(\kappa b_p) \dots \} ;$$
 (8b)

$$\left\langle \left( \Psi_{\mathbf{r}} \right)_{\mathbf{i}} \middle| \exp\left( i\underline{\kappa} \cdot \underline{\mathbf{b}}_{\nu} \right) \middle| \left( \Psi_{\mathbf{r}} \right)_{\mathbf{f}} \right\rangle \left\langle \left( \Psi_{\mathbf{r}} \right)_{\mathbf{f}} \middle| \exp\left( - i\underline{\kappa} \cdot \mathbf{b}_{\nu'} \right) \middle| \left( \Psi_{\mathbf{r}} \right)_{\mathbf{i}} \right\rangle = 2 \mathbf{j}_{0} \left( \kappa \mathbf{b}_{p} \right) ; \qquad (8c)$$

$$\left\langle \left( \Psi_{r} \right)_{i} \right| \exp\left( i\underline{\kappa} \cdot \mathbf{b}_{\nu} \right) \right| \left( \Psi_{r} \right)_{f} \right\rangle \left\langle \left( \Psi_{r} \right)_{f} \right| \exp\left( - i\underline{\kappa} \cdot \mathbf{b}_{\nu'} \right) \right| \left\langle \Psi_{r} \right)_{i} \right\rangle = 1 ;$$
 (8d)

where j and J are the quantum numbers for the initial and final rotational states,  $j_n(x)$  is the spherical Bessel function of order n and argument x, and the choice of terms in the summation in (8b) is from |j-J| to (j+J). It is assumed that the initial rotational states are distributed according to a Boltzmann distribution for a spherical top given by [11]

$$B_{T}(j) = \{(2j+1)^{2} \exp[-j(j+1)/2IT\} / \{\sum_{j} (2j+1)^{2} \exp[-j(j+1)/(2IT)]\},$$
(9)

where I is the moment of inertia.

The partial differential cross-section is obtained by inserting (4) into (2) and performing the time integration. The result for methane is

$$\sigma(\mathbf{E}_{0},\epsilon,\theta) = 4\sigma_{pp} (\mathbf{E}_{0},\epsilon,\theta) + 12\sigma_{pp} (\mathbf{E}_{0},\epsilon,\theta) + 8\sigma_{Cp} (\mathbf{E}_{0},\epsilon,\theta) + \sigma_{CC} (\mathbf{E}_{0},\epsilon,\theta)$$
(10)

where p denotes a proton, p' a different proton, and C the carbon nucleus. In (10)

$$\sigma_{pp} = a_{pp}(2\pi)^{-1} (k/k_0) [(2\pi M)/(T\kappa^2)]^{\frac{1}{2}} exp(-\kappa^2 \gamma_{pp})$$

$$\times \sum_{j,J} exp[-(\epsilon + \alpha)^2 / (2T\kappa^2 / M)] [(2J+1)/(2j+1)]$$

$$\times B_T(j) \sum_{n=|j-J|}^{j+J} j_n^2 (\kappa b_p),$$

$$\sigma_{pp} = a_{pp} (2\pi)^{-1} (k/k_0) [(2\pi M)/(T\kappa^2)]^{\frac{1}{2}} \exp(-\kappa^2 \gamma_{pp})$$

$$\times \sum_{j,J} \exp[-(\epsilon + \alpha)^2 / (2T\kappa^2/M)] [2(2J+1)/(2j+1)]$$

$$\times B_T(j) \sum_{n=[j-J]}^{j+J} \{j_0^2(\kappa b_p) - \frac{1}{3} j_1^2(\kappa b_p) - \frac{1}{3} j_2^2(\kappa b_p) \dots \}$$

$$\sigma_{Cp} = 2a_{Cp} (2\pi)^{-1} (k/k_0) [2\pi M/(T\kappa^2)]^{\frac{1}{2}} \exp(-\kappa^2 \gamma_{Cp})$$

$$\times \exp\{-[(\epsilon + (\kappa^2/(2M))]/(2T\kappa^2/M)\} j_0(\kappa b_p),$$

and

$$\sigma_{\rm CC} = a_{\rm CC} (2\pi)^{-1} (k/k_0) [2\pi M/T\kappa^2]^{\frac{1}{2}} \exp\{-\kappa^2 \gamma_{\rm CC}\}$$
$$\times \{\exp - [(\epsilon + (\kappa^2/(2M))]/(2T\kappa^2/M)\}$$

where

$$\alpha = \left[\frac{\kappa^2}{2M} - \frac{j(j+1)}{2I} + \frac{J(J+1)}{2I}\right].$$

If the momentum transfer  $\kappa$  and the energy transfer  $\epsilon$  are considered to be independent variables then multiplying (10) by  $(k_0/k) \exp [\epsilon/(2T)]$  defines the function

$$S(\kappa^{2},\epsilon) = S_{pp}(\kappa^{2}, \epsilon) + S_{pp'}(\kappa^{2}, \epsilon) + S_{pC}(\kappa^{2}, \epsilon) + S_{CC}(\kappa^{2}, \epsilon)$$
(11)

where

$$S_{pp}(\kappa^2,\epsilon) = 4(k_0/k) \exp[\epsilon/(2T)] \sigma_{pp}(E_0,\epsilon,\theta)$$

and the other terms are similarly defined. It is easily verified that  $S(\kappa^2, \epsilon)$  is an even function of  $\epsilon$  for a fixed value of  $\kappa^2$ . Thus  $S(\kappa^2, \epsilon)$  satisfies the condition of detailed balance [12]. This function is useful to check on the consistency of the experimental results as well as the numerical calculations.

SCHOFIELD [13] has mentioned that besides the condition of detailed balance it is necessary that the moments of the energy transfer  $\epsilon$  for a fixed momentum transfer be satisfied. While this statement is true it should be mentioned that the expressions developed here cannot be expected to obey the moment theorems. For simplicity let us suppose

$$S_{1}(\kappa^{2},\epsilon) = e^{-\epsilon/2T}S_{pp}(\kappa^{2},\epsilon)$$
(12)

then it can be proved from general considerations and with suitable normalization that

$$\int_{\infty}^{\infty} S_1(\kappa^2, \epsilon) d\epsilon = 1.$$
 (13)

This is the zero moment of the energy transfer. On the other hand in the

analytical formulation the energy transfer  $\epsilon$  must be greater than or equal to the negative of the incident neutron energy  $E_0$ . Since the assumptions in the theory require that the incident neutron energy be smaller than the energy of the vibrational levels and in addition these levels are not populated it cannot be expected that even the zero moment be obeyed. However, if  $S_1(\kappa^2, \epsilon)$ , for a given momentum transfer, decreases rapidly so the integral from  $-\infty_0$  to  $-E_0$  is negligible compared to the integral from  $-E_0$  to  $\infty$  it would be obeyed in that sense. The situation regarding the higher moments is much more critical. Thus, in general, if physical information is to be obtained from the moment theorems it is necessary for experiments to be conducted over all initial energies and also the theoretical models to be valid for all initial energies.

#### III. RESULTS

The value of the parameters that were used in the computations are given in the Appendix.

#### (a) The partial differential cross-section

The computed partial differential cross-section for a selected example is compared with the experimental results in Fig. 1 together with results obtained by using the mass-tensor approximation method of Krieger and Nelkin. First, it should be noted upon comparing the two theoretical results the necessity of treating the rotational levels quantum-mechanically. Even for an incident neutron energy as large as 70.6 meV it was found there is still considerable deviation at an angle of 16.3°. However, as the scattering angle increases for a given incident neutron energy, the deviations between a quantum and a classical treatment decrease. The general situation is illustrated by comparing the graphs for 16.3° and 26.0°.

In comparing the theoretical results with the experiments it is necessary to recognize that the experimental results represent the integrated contributions from a counter bank which has a horizontal spread of  $\pm 3.5^{\circ}$  about the quoted scattering angle as well as a somewhat smaller spread in the vertical. This together with other effects such as the beam size will tend to broaden the width and depress the peak of the cross-section curve. In Fig. 2 the experimental results have been normalized so that the main peak is approximately the same magnitude as the theoretical results. As can be seen, the experimental width is broader due to the above-mentioned effects as would be expected. On the other hand, as can easily be seen in Fig. 1, if the rotations are treated classically the resulting theoretical curve is broader than the experimental curve. This discrepancy stimulated the work on treating the rotations quantum mechanically.

Of particular interest in Figs. 1 and 2 is the small peak indicated by an arrow on the left hand side of the main peak. This is due to a gain in energy by the neutron from the rotational levels. It might be expected that a similar influence due to a loss of energy to the rotational levels would be present. The appearance of an influence of the rotational levels on the cross-section due to energy gain and the non-appearance of such an influence due to energy





The experimental and computed partial differential cross-sections shown as a function of the scattered neutron wave-length. The solid line curve presents the results when the quantum nature of the rotational levels are considered. The dashed curve presents the results when the rotations are treated classically. The arrow indicates the maximum of that portion of the curve that is influenced by the rotations. The temperature of the gas is 21°C.

loss in these figures is qualitatively easy to understand. The importance of a possible rotational transition in the collision of a neutron with the molecule must depend on the relative population of the initial level. Suppose the Boltzmann distribution function has been normalized so

$$\sum_{j} B_{T}(j) = 1,$$

and  $R_j(\Delta E)$  is a function whose value is equal to the relative population of the initial level j with  $\Delta E$  being a specified energy difference between that level and some possible final level. Let us define the function  $P(\Delta E)$  as

$$P(\Delta E) = \sum_{i}^{\prime} R_{i} (\Delta E), \qquad (14)$$

where the normalization is so that P(0) = 1 and the prime on the summation



Fig.2

The experimental and computed partial differential cross-sections shown as a function of the scattered neutron wave-length. The experimental data has been normalized to the theoretical results so that the magnitude of the main peak is approximately equal. The arrow indicates the maximum of that portion of the curve that is influenced by rotations. The temperature of the gas is 21°C.

indicates that the sum is only over those states with the specified  $\Delta E$ . For example, suppose  $\Delta E = 12$  meV for which the possible transitions are  $9 \rightarrow 8$ ,  $5 \rightarrow 3$ , and  $4 \rightarrow 1$ ; then if the gas is at 21°C one finds  $P(\Delta E) = 0.323$ . Supposing that the gain of energy by a scattered neutron is entirely due to rotational transitions, this  $P(\Delta E)$  can be plotted as a vertical line on a graph of  $P(\Delta E)$ versus the scattered neutron wave-length at a wave-length of 1.48A. Such reasoning was used by the author to predict where an influence due to an energy gain might be expected to be observed. Such a case is shown in Fig.4, where both an influence due to a gain and loss of energy is present. Unfortunately, there are no experimental data to confirm this case.

Although the above simple argument is convenient to use, it is only a guide and in some cases might be misleading. To formulate the argument more correctly suppose interference scattering is neglected. Then it can be shown that the cross-section for the transition from j to J of the rotational mode is proportional to

$$\frac{k}{k_0} \frac{4}{[(2J+1)/(2j+1)]} B_{T}(j) \sum_{n=|j-j|}^{j+j} j_n^2(\kappa b_p).$$

Setting the function  $F_i$  ( $\Delta E$ ) equal to this expression and defining the importance function  $I(\Delta E)$  of a possible energy transfer  $\Delta E$  as

SCATTERING OF SLOW NEUTRONS BY GASEOUS METHANE

$$I(\Delta E) = \sum_{j} F_{j} (\Delta E)$$
(15)

gives the importance of a possible rotational transition in a collision of a neutron with the molecule. In (15) the importance function  $I(\Delta E)$  is normalized so that I(0) = 1 and the prime on the summation has the same significance as before. The importance function has been plotted on Fig. 3 to avoid con-



The computed partial differential cross-section shown as a function of the scattered neutron wave-length for three selected temperatures. The vertical lines terminated by a dot are a plot of the importance function which is discussed in the text. They are plotted for a temperature of 21°C.

fusing Figs. 1 and 2. It illustrates in a striking manner the reason for the appearance of an influence due to an energy gain and its absence for an energy loss in Figs. 1 and 2. An additional example of the importance function has been plotted on Fig. 4 which illustrates the reason for the appearance of a feature due to both an energy gain and an energy loss.

In the actual physical situation each of these lines are broadened by the translational motion of the molecule which gives the resulting structure of the cross-section curve. The broadening increases as the scattering angle increases. It should be noted that the appearance of a single importance line causes no apparent anomaly in the cross-section curve, but instead it is necessary for a number of the importance lines to be in close proximity for the influence of the rotational states to be observed.

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Fig.4

The computed partial differential cross-section shown as a function of the scattered neutron wave-length. This is an example showing both the influence of an energy loss and an energy gain. The vertical lines terminated by a dot are a plot of the importance function which is discussed in the text. The temperature of the gas is 21<sup>6</sup>C.

If the cross-section of the gas is compared at two temperatures it would be expected that the main peak would be lower and the width greater for the higher temperature. In addition the small peak due to an energy gain from the rotational levels would be expected to be higher and its width broader for the higher temperature. This is illustrated in Fig. 3 where the computed cross-sections are shown for temperatures of  $115^{\circ}$ C,  $21^{\circ}$ C, and  $-85^{\circ}$ C with a scattering angle of 16. 3°C and incident energies of 15 and 25. 2 meV.

(b) The function  $S(\kappa^2, \epsilon)$ 

If the function  $S(\kappa^2, \epsilon)$  as given by (11) is divided by  $(\sigma_b/4\pi)$ , where  $\sigma_b$ is the bound hydrogen cross-section, the resulting function is identical to the function considered by EGELSTAFF and collaborators [14]. Their discussions are in terms of dimensionless parameters  $\alpha = \lfloor \kappa^2/(2MT) \rfloor$  and  $\beta = \lfloor \epsilon/2T \rfloor$ . If the theory of Krieger and Nelkin was used to determine  $S(\kappa^2, \epsilon)$  these parameters would be very convenient since the resulting  $S(\alpha, \beta)$ would not depend explicitly on the sample temperature. However, the introduction of such parameters in (11) would not eliminate its explicit temperature dependence in the theory presented here which forms a fundamental difference in theoretical predictions. Instead of these variables it is much more convenient to discuss  $S(\kappa^2, \epsilon)$  as a function of the dimensionless parameter  $(\kappa b_n)^2$  for a specified  $\epsilon$  since this parameter appears as the argument of the spherical Bessel functions and is particularly convenient for the discussion of interference scattering which is observed.

In Fig. 5,  $S(\kappa^2, \epsilon)$  is shown as a function of  $(\kappa b_p)^2$  for a few selected values of the energy transfer  $\epsilon$ . To orient the reader, if Fig. 2 is consulted, the energy transfers correspond to scattered neutron wave-lengths of 2.36A, 2.13A, 1.97A, 1.76A and 1.45A for consecutive increasing values of the energy





 $S(\kappa^2, \epsilon)$  shown as a function of  $(\kappa b_p)^2$  for a few selected values of the energy transfer. The experimental points are for  $\epsilon = 0.0$ . The temperature of the gas is 21°C.

transfer. The curves that are shown are extended to approximately one order of magnitude smaller in momentum transfer than the experiments that have been performed. One feature of interest in this figure concerns the asymptotic value of  $S(\kappa^2, \epsilon)$  as  $(\kappa b_p)^2 \rightarrow 0$  with  $\epsilon \neq 0$ . This is the quantity needed to determine the generalized frequency distribution function introduced by EGELSTAFF [14, 15]. It would be thought that the curve labelled  $\epsilon = 3 \times 10^{-3} \, \text{eV}$  surely has reached its asymptotic slope value. However, performing calculations at smaller values of  $(\kappa b_p)^2$  shows that this is not the case for the curve bends and approaches more nearly the slope of  $\epsilon = 6 \times 10^{-3} \, \text{eV}$ . This suggests that caution must be exercised in the application of the methods of analysis introduced by Egelstaff.

A feature in Fig. 5 of particular interest concerns the influence of interference scattering as given by the second and third terms of (11) representing proton-proton and carbon-proton scattering. Confining our attention to zero energy transfer, the interference scattering is mainly responsible for the dip in the curve for values of  $(kb_p)^2$  lying between 5 and 15 and the subsequent hump between 15 and 30. Examining the contributions of the protonproton and carbon-proton terms it is found that there is a tendency for these terms to cancel for values of  $(\kappa b_p)^2 < 5$ , to give a negative contribution of about 10% of the total for  $5 < (\kappa b_p)^2 < 15$ , to give a positive contribution of about 10% of the total for  $15 < (\kappa b_p)^2 < 30$ , and for  $(\kappa b_p)^2 > 30$  the behaviour to be more complicated. This behaviour can be understood in terms of the spherical Bessel functions occurring in the theory.

The experimental data for  $\epsilon - 0.0$  bas been plotted on Fig. 5. Since there are considerable scatter in the experimental data it is not possible to conclude conclusively that the effect due to interference scattering has been observed. However, data for energy transfers of  $3 \times 10^{-3}$  eV and  $6 \times 10^{-3}$  eV supports such a conclusion. In addition, it would be expected that scattering results on gaseous propane should also show this effect. An examination indicates that this is the case. There was no difficulty experienced at small momentum transfers in comparing the theoretical results of this paper with the experimental results which was experienced in [5] where a comparison was made with the results of the mass-tensor formulation.

In Fig.6,  $S(\kappa^2, \epsilon)$  is shown as a function of  $\epsilon$  for various values of  $(\kappa b_p)^2$ . Neglecting deviations of the order of 5% due to interference scatter-



Fig.6

 $S(\kappa^2, \epsilon)$  shown as a function of  $\epsilon$  for a few selected values of  $(\kappa^2 b_p)^2$ . The temperature of the gas is 21°C.

ing, considering (13) and making an expansion of exp (- $\epsilon/2T$ ) then to second order in powers of ( $\epsilon/2T$ )

$$2\int_{0}^{\infty} S(\kappa^{2}, \epsilon) d\epsilon = 1.$$
 (15)

Thus if  $S(\kappa^2, \epsilon)$  decreases sufficiently rapidly as  $\epsilon$  increases for a fixed momentum transfer the area under the curves will be a constant. This is

found to be the case for the curves with  $(\kappa_{\rm bp})^2 < 1$  as expected. The small hump on the  $(\kappa_{\rm bp})^2 = 10$  curve near  $\epsilon = 0$  is due to the influence of interference scattering.

#### IV. CONCLUDING REMARKS

It has been shown that to explain the experimental results on the scattering of slow neutrons by gaseous methane it is necessary to take into account the quantum nature of the rotational levels. There are further experiments that would be desirable on gaseous methane. Below the vibrational threshold it would be of interest for experiments at smaller momentum transfers to be done so as to check further characteristics of the curve of  $S(k^2, \epsilon)$  with  $\epsilon \neq 0$ which are predicted in Fig. 5. Experiments at incident energies large enough to excite the vibrational levels would be of interest so that the importance of their influence on the scattering could be assessed.

Methane should be a very suitable substance for investigations of the liquid state. Investigations by Raman spectra techniques [16] indicates that the molecular rotations are relatively unhindered by intramolecular interactions. Thus it would appear the essential difference between the gaseous state and the liquid state would be in the restrictions on the molecular translational motion in the liquid state. Since the scattering by the gaseous state is well understood it would constitute a great aid in the analysis of experiments on liquid methane. Recently STILLER and HAUTECLER [17] have performed scattering experiments on liquid methane and observed a number of rotational transitions.

Finally scattering experiments on solid methane should be done. Such experiments would be helpful in understanding the liquid state. Experiments by Raman Spectra techniques [16] indicate that the rotations are still relatively free in the solid state. PAULING [18] proposed that the  $\lambda$ -point at 20°K in the specific heat curve was due to the cessation of the rotations. Subsequent experiments using nuclear magnetic resonance absorption techniques [19] indicated that this could not be the explanation. It would appear that neutron scattering experiments would be well suited to make a significant contribution.

#### ACKNOWLEDGEMENTS

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#### APPENDIX

The value of the parameters [3] [11] [20] used in the computations were  $C_C = 0$ ,  $A_C = 0.64 \times 10^{-12}$  cm,  $C_p = 2.52 \times 10^{-12}$  cm,  $A_p = 0.42 \times 10^{-12}$  cm,  $b_p = 1.093 \times 10^{-8}$  cm,  $\gamma_{pp} = 6.266 \times 10^{-19}$  cm<sup>2</sup>,  $\gamma_{CC} = 2.1375 \times 10^{-20}$  cm<sup>2</sup>,  $M = 26.757 \times 10^{-24}$  g, and  $I = 5.330 \times 10^{-40}$  g cm<sup>2</sup>.

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#### G.W. GRIFFING

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#### DISCUSSION\*

J. JANIK: To what extent is the symmetry of  $CH_4$  molecules necessary for your calculations? In other words do you consider it possible to extend the calculations to other, less symmetrical, molecules?

G. GRIFFING: Yes. The methane molecule is a spherical top and this fact is used. The methods can be used for any type of molecule.

D.T. GOLDMAN: Have you investigated the validity of the Krieger-Nelkin expression in the case where  $\kappa^2$  is very high? Krieger and Nelkin make the approximation that the average over orientation can be removed into the exponential. This corresponds to an expansion in powers of  $\kappa^2$ , keeping only the first term. This would seem to indicate that the theory cannot be applied where  $\kappa^2$  is high.

G. GRIFFING: If you go to sufficiently high momentum transfer, which is equivalent to saying, if the angle or the energy is large enough, I always found that the Krieger-Nelkin expression seemed to be very good.

<sup>\*</sup> See also discussion on the paper by D. Bally <u>et al</u>. entitled "The Scattering of slow neutrons from hydrogen and ethylene".

# THE SCATTERING OF SLOW NEUTRONS FROM HYDROGEN AND ETHYLENE

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#### Abstract — Résumé — Аннотация — Resumen

THE SCATTERING OF SLOW NEUTRONS FROM HYDROGEN AND ETHYLENE. The angular distribution of 1.61 Å wavelength neutrons scattered from hydrogen and ethylene has been measured.

For ethylene the pressure was varied from 15 to 60 atm and for hydrogen from 60 to 110 atm. The investigated angular range was between  $5^{\circ}$  and  $90^{\circ}$ . The experimental results obtained have been compared with the differential cross-section calculated using the Krieger-Nelkin formulae.

DIFFUSION DES NEUT RONS LENTS PAR L'HYDROGÈNE ET PAR L'ÉTHYLÈNE. Les auteurs ont mesuré la distribution angulaire des neutrons ayant une longueur d'onde de 1,61 Å diffusés par de l'hydrogène et par l'éthylène.

Ils ont fait varier la pression de l'éthylène de 15 à 60 atm et celle de l'hydrogène de 60 à 110 atm. Le domaine angulaire étudié était compris entre 5 et 90°. Les résultats des expériences ont été comparés aux sections efficaces différentielles calculées au moyen des formules de Krieger-Nelkin.

О РАССЕЯНИИ МЕДЛЕННЫХ НЕЙТРОНОВ ВОДОРОДОМ И ЭТИЛЕНОМ. Было измерено угловое распределение рассеянных в водороде и этилене нейтронов с длинов волны 1,61 Å.

Для этилена давление изменялось в пределах 15 - 60 ат, а для водорода - 60-110 ат. 06следованный угловой диапазон заключался между 5 и 90°. Полученные данные сравнены с расчетами по Формулам Кригера-Нелкина для дифференциальных поперечных сечений.

DISPERSIÓN DE NEUTRONES LENTOS POR HIDRÓGENO Y ETILENO. Los autores han medido la distribución angular de neutrones de longitud de onda igual a 1,61 Å, dispersados por hidrógeno y etileno.

En el caso del etileno, la presión varió de 15 a 60 atm y en el del hidrógeno, de 60 a 110 atm. Los autores han explorado ángulos comprendidos entre  $5^{\circ}$  y 90°. Comparan los resultados experimentales obtenidos con el valor de la sección eficaz diferencial calculado con ayuda de las fórmulas de Krieger-Nelkin.

#### I. INTRODUCTION

The angular distribution of 0.073 eV neutrons scattered from different gases was studied by ALCOCK and HURST [1, 2, 3]. The experimental results were analysed according to a semi-classical theory. The differential crosssections, corrected for "outer effect" and for molecular vibrations, agree with the measured ones for the gases  $O_2$ ,  $N_2$  and  $CF_{4.}$  The experimental points for carbon dioxide show a strong disagreement between experiment and theory at angles smaller than 20°. This disagreement was assigned to the fact that the gas is near the liquid phase. The measured angular distribution for methane was not compared with a theoretical curve. Later on POPE [4], ZEEMACH and GLAUBER [5], KRIEGER and NELKIN [6] developing the quantum theory of the neutron scattering from molecules used the ALCOCK and HURST results for methane [3] as a test for the theoretical curves. Recently RANDOLPH et al. [7] has measured the differential partial cross-section of 0.015 eV to 0.142 eV neutrons scattered from methane and compared the experimental results with the theoretical curves [5, 6].

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The Krieger-Nelkin formula for angular distribution of scattered neutrons was compared with the experiment only in the case of a spheric top molecule. It was interesting to compare the same formula with the experimental results obtained in the scattering of neutrons from a molecule having a symmetry different from the spheric top, e.g. the ethylene molecule [8]. Using the Krieger-Nelkin formula, JANIK <u>et al.</u>[9] calculated the neutron total cross-section of ethylene and obtained a good agreement with the MELKONIAN results [10]. The agreement between the calculated neutron total cross-section of hydrogen [6] and the measured one in the energy range from 0.05 eV to 0.5 eV [11] is not so satisfactory. This is due to the mass tensor approximation. In order to eliminate the error resulting from the use of a Maxwellian distribution for the rotation of hydrogen molecules, an effective temperature T' different from the sample temperature was introduced.

The purpose of the present work is to compare the measured neutron angular distribution for ethylene and hydrogen with that obtained from the Krieger-Nelkin formula.





The schematic drawing of the experimental device.

#### II. EXPERIMENTAL PROCEDURE

The scheme of the experimental device is illustrated in Fig.1. The energy of the monochromatic neutron beam incident on the sample was of  $(0.059 \pm 0.004)$  eV. The investigated angular range was between  $10^{\circ}$  and  $90^{\circ}$ . A monitor located in the monochromatic beam serves as time-basis for the counter placed on the spectrometer arm. The scheme of the sample vessel is shown in Fig.2. The thickness of the sample vessel walls was of  $(0.8 \pm 0.02)$ mm. The pressure range was between 15 atm and 60 atm for ethylene and between 65 atm and 110 atm for hydrogen. The sample pressure remained constant during the period of a cycle of measurements. In order to verify the pressure constancy the full sample vessel was weighed before and after every cycle of measurements.



The scheme of the sample vessel (A) and filling device (C).

The sample vessel weight was 150 g and the weighing was made on an analytical balance with a precision better than 0.005 g. The studied ethylene had a purity of 99.95%. The more important impurities were ethan (0.03%) and nitrogen (0.005%). Hydrogen had a purity of 99.9%, the more important impurities being oxygen and water vapour.

The measured background with the empty sample vessel was corrected for the absorption of neutrons in the sample. For this purpose the BOUTRON-MÉRIEL formula [12] was used. The tabulation shows that for the studied samples the correction factor is practically constant in the angular range between 0° and 90°. For this reason the incoherent background of the empty sample vessel was corrected by using a constant factor whose value is equal to the average transmission of the gas. The average transmission of the studied gases was between 0.57 and 0.88 for ethylene and 0.8 and 0.87 for hydrogen. The relatively small transmissions make the study of multiple scattering of neutrons desirable. The calculations of ALCOCK and HURST [2] for a sample geometry different from the present sample shows that the correction factor for double-scattering is practical isotrope. A similar result was obtained also in [7]. An angular dependence of the double scattering is obtained by applying VINEYARD'S calculations [13]. These calculations point to a relative simple expression for double-scattering on a plane sample. But if the formula for a plane sample is used to calculate the double-scattering of a cylindrical sample whose average thickness is

equal to that of a plane sample, a value larger than the real one is obtained. For this reason the correction for double-scattering was not considered in the present measurements.

#### III. EXPERIMENTAL RESULTS

The expression of the differential cross-section was calculated using the Krieger-Nelkin formula :

$$\sigma(\theta) = \Sigma \ \sigma_{\nu\nu'}(\theta)$$

$$\sigma_{\nu\nu\prime}(\theta) = a_{\nu\nu\prime} \left(\frac{\widetilde{M}}{2\pi T}\right)^{1/2} \int_{-E_0}^{\infty} \frac{d\epsilon}{\kappa} \frac{k}{k_0} j_0(b_{\nu\nu\prime}\kappa) \exp(-\kappa^2 \gamma_{\nu\nu\prime}) \exp\left[-\frac{\widetilde{M}_{\nu}}{2T\kappa^2} \left(\epsilon + \frac{\kappa^2}{2M_{\nu}}\right)^2\right] (1)$$
$$\underline{\kappa} = \underline{k} - \underline{k}_0 \qquad \epsilon = \frac{1}{2m} (k^2 - k_0^2) \qquad E_0 = \frac{1}{2m} k_0^2$$

where  $\theta$  is the scattering angle in the laboratory system,  $b_{\nu\nu'}$  is the distance between the nuclei  $\nu$  and  $\nu'$ ,  $\tilde{M}_{\nu}$  is an equivalent mass of the  $\nu$  nucleus and  $\gamma_{\nu\nu'}$  is a constant which depends on the molecular vibrations,  $a_{\nu\nu} = A_{\nu}^2 + C_{\nu}^2$  $a_{\nu\nu'} = A_{\nu} A_{\nu'}$ ,  $A_{\nu}$ , and  $C_{\nu}$  being the coherent and incoherent neutron scattering lengths of the  $\nu$  nucleus.

#### 1. Ethylene

For hydrogenous substances the differential cross-section is practically reduced to the incoherent contribution of hydrogen. Using the usual values of  $A_{\rm H}$ ,  $C_{\rm H}$ ,  $A_{\rm H}$  and  $C_{\rm c}$  the following values for  $a_{\nu\nu\nu}$ , were found:

$$a_{HH} = 6.577 \times 10^{-24} \text{ cm}^2;$$
  $a_{CC} = 0.41 \times 10^{-24} \text{ cm};$   
 $a_{HC} = -0.269 \times 10^{-24} \text{ cm}^2;$   $a_{HH} = 0.176 \times 10^{-24} \text{ cm}.$ 

The coefficients  $a_{\nu\nu'}(\nu \neq \nu')$  being small compared to  $a_{\rm HH}$  and having an opposite sign, the sum of the interference terms may be neglected in the formula [1]. The contribution of carbon at the incoherent differential cross-section was calculated in the approximation in which the vibrational factor  $\exp[-\kappa^2 \gamma_{\nu\nu'}]$  is equal to unity. Using the following values for the interatomic distance and for moments of inertia:  $b_{cc'} = 1.353$  A;  $I_{\kappa} = 5.752 \times 10^{40}$  g. cm<sup>2</sup>;  $I_{\gamma} \approx I_{z} = 30.96 \times 10^{40}$  g. cm<sup>2</sup> the value  $M_{c} = 19.45$  m was found. The  $\delta_{cc}(\theta)$  calculated in this approximation is practical isotrope and equal to 5% from  $\delta_{\rm HH}(\theta)$  only.

The differential neutron cross-section  $\delta_{\rm HH}(\theta)$  was calculated using the following values of molecular constants  $\bar{\omega} = (4 \gamma_{\rm HH} {\rm m})^{-1} = 0.1055 {\rm eV}$  and  $\widetilde{M}_{\rm H} = 5.8109 {\rm m}^*$ . The theoretical curves and the experimental points are represented in Fig.3. As can be seen, in a large pressure range (from15 atm to 60 atm) the experimental points are in agreement with the calculated curves. This shows that the Krieger-Nelkin formula is also applicable to

<sup>\*</sup> These values were kindly placed at our disposal by Dr. J. Janik.

a molecule whose symmetry is different from the spheric top. A similar result was recently obtained by STRONG et al.[14].



The angular distributions of neutrons scattered by ethylene at four different pressures. The theoretical curves does not include the carbon contribution.

#### 2. Hydrogen

Using the values  $\widetilde{M}_{H} = m/0.2944$  and  $\overline{\omega} = 0.1656$  eV [6] the differential cross-section for two temperatures (the effective temperature T' = 289°K and the sample temperature T = 300°K) was calculated.



Fig.4

The angular distribution of neutrons scattered from hydrogen at two pressures.
Although the differential neutron cross-sections differ from one another with about 2% in this temperature range, the angular dependence remains practical unchanged. In Fig. 4 are represented the theoretical curve calculated for  $T' = 289^{\circ}K$  and the experimental points for pressures of 65 atm and 110 atm. The good agreement between the calculated angular distribution and the measured one shows that the mass-tensor approximation may be used for such a purpose even in the case of molecules with a great rotational constant B.

As it was expected for hydrogen as well as for ethylene the rise of pressure does not lead to a diminution of the intensity at small angles because the "outer effect" is negligible. For ethylene at the room temperature the pressure of 60 atm is near the critical point. The agreement between the calculated  $\delta_{\text{HH}}(\theta)$  and the experimental angular distribution of neutrons shows that the influence of the deviation of the gas from ideal state on the formula [1] is not important for hydrogenous molecules.

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## DISCUSSION

P. EGELSTAFF: I would like to make a general remark regarding the last few papers. The Krieger-Nelkin model replaces the rotational part of the scattering by a perfect gas term using an effective mass. The vibrations are allowed for by modifying the Debye-Waller factor. If the experimental results are taken in a region where this model applies, it seems to me that this automatically means that they do not include the basic information that one wishes to obtain on the physical properties of the scatterer. Would any theoretician like to comment on this point, please?

D.T. GOLDMAN: Yes, The detailed physical properties of the nucleus cannot be determined unless the energy resolution gets very much better. On the other hand an understanding of the nature of the rotations themselves extends our knowledge of physical systems.

## THE INELASTIC SCATTERING OF COLD NEUTRONS BY METHANE, AMMONIA AND HYDROGEN

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#### Abstract — Résumé — Аннотация — Resumen

THE INELASTIC SCATTERING OF COLD NEUTRONS BY METHANE. AMMONIA AND HYDROGEN. The differential cross-sections for the scattering of 4 Å neutrons through angles of 20°, 30°, 45°, 75° and 90° have been measured on the Harwell cold neutron apparatus for three gases at room temperature - methane, ammónia and hydrogen. Methane and ammonia gave similar results; at the smaller angles the spectrum of scattered neutrons consisted of a quasi-elastic peak of roughly the same wavelength as the incident neutrons, but several times broader, and an inelastic peak at shorter wavelengths. At larger scattering angles the quasi-elastic peak moved to shorter wavelengths, and merged into the inelastic peak, which remained at the same wavelength. These peaks are consistent with scattering from a perfect gas of mass 16 or 17, together with inelastic scattering in which neutrons gain energy at the expense of molecular rotations. The short wavelength edge of the inelastic peak is the same for all scattering angles, as it is determined by the Boltzmann factor (corresponding to room temperature) governing the excitation of the molecular rotations. (At room temperature the excitation of molecular rotations). (At room temperature the excitation of scattering from a gas of mass 2, and the peaks due to scattering by molecular rotations and molecular translations overlap.

DIFFUSION INELASTIQUE DES NEUTRONS FROIDS PAR LE MÉTHANE, L'AMMONIAC ET L'HYDROGÈNE. L'auteur a mesuré les sections efficaces différentielles de diffusion de neutrons ayant une longueur d'ondes de 4 Å, aux angles de 20°, 30°, 45°, 75° et 90°, avec l'appareil à neutrons froids de Harwell, dans trois gaz différents (méthane, ammoniac et hydrogène), à la température ambiante. Le méthane et l'ammoniac ont fourni des résultats semblables; aux petits angles, le spectre des neutrons diffusés consiste en un pic quasiélastique se produisant pour à peu près les mêmes longueurs d'ondes que les neutrons incidents, mais plusieurs fois plus larges et en un pic inélastique pour les longueurs d'ondes plus courtes. Pour les angles de diffusion plus grands, le pic quasi élastique se déplace vers les longueurs d'ondes plus courtes et disparaît dans le pic inélastique qui, lui, reste situé à la même longueur d'ondes. Ces pics concordent avec les résultats relatifs à la diffusion dans un gaz parfait de masse 16 ou 17 ainsi qu'avec une diffusion inélastique dans laquelle les neutrons gagnent de l'énergie aux dépens des rotations moléculaires. Le versant du pic inélastique situé dans les longueurs d'ondes courtes est le même pour tous les angles de diffusion étant donné qu'il est déterminé par le facteur de Boltzman (correspondant à la température du laboratoire) régissant l'excitation des rotations moléculaires. (A la température du laboratoire, l'excitation des vibrations moléculaires est négligeable.) Pour l'hydrogène, même aux petits angles de diffusion, le spectre incident est élargi considérablement comme on peut s'y attendre pour la diffusion dans un gaz de masse 2, et les pics dus à la diffusion par des rotations moléculaires et translation moléculaire se recouvrent.

НЕУПРУГОЕ РАССЕЯНИЕ ХОЛОДНЫХ НЕЙТРОНОВ В МЕТАНЕ, АММОНИИ И ВОДОРОДЕ. Дифференциальные поперечные сечения рассеяния нейтронов с длиной волны 4 Å при углах 20,30,45,75 и 90° измерены на установке по производству холодных нейтронов в Харуэлле для трех газов: метана, аммония и водорода (при комнатной температуре). Для метана и аммония получены одинаковые результаты; при меньших углах спектр рассеянных нейтронов состоял из максимума квазиупругого рассеяния нейтронов приблизительно одних и тех же длин волн, как и бомбардирующие нейтроны, но этот спектр в несколько раз шире и имеет максимум неупругого рассеяния в области более коротких волн. При больших углах рассеяния максимум квазиупругого рассеяния сдвигался в область более коротких волн и сливался с максимумом неупругого рассеяния, который оставался в одной и той же области. Эти максимуми согласуются с рассеянием в идеальном газе с массой 16 или 17 вместе с неупругим рассеянием, в результать те которого нейтроны получают энергию за счет вращений молекул. Граница области коротких волн максимума неупругого рассеяния одна и та же для всех углов рассеяния, как и определено козффициентом Больцмана, регулирующим возбуждение вращений молекул. (При комнатной температуре можно пренебречь возбуждением колебаний молекул.) Для водорода даже при небольших углах рассеяния спектр бомбардирующих частиц значительно расширен, как можно было бы ожидать при рассеянии в газе с массой 2, а максимумы перекрываются благодаря вращению молекул и их перемещению.

DISPERSIÓN INELÁSTICA DE NEUTRONES FRÍOS POR METANO, AMONIACO E HIDRÓGENO. En el aparato para neutrones fríos de Harwell se han medido, a temperatura ambiente, las secciones eficaces diferenciales de dispersión de neutrones de 4 Å en ángulos de 20°, 30°, 45°, 75° y 90°, correspondientes a tres gases: metano, amoniaco e hidrógeno. El metano y el amoniaco han dado resultados análogos; en los ángulos pequeños, el espectro de los neutrones dispersados consiste en un pico cuasi elástico de longitud de onda aproximadamente igual a la de los neutrones incidentes, pero varias veces más ensanchado, y en un pico inelástico para menores longitudes de onda. En los ángulos de dispersión mayores, el pico cuasi elástico se desplaza hacia las longitudes de onda más cortas y se confunde con el pico inelástico, que permanece en la misma posición. Estos picos son compatibles con la dispersión por un gas perfecto de masa 16 ó 17, acompañada de dispersión inelástica en que los neutrones ganan energía a expensas de las rotaciones moleculares. El borde del pico inelástico correspondiente a las ondas cortas es igual para todos los ángulos de dispersión, puesto que queda determinado por el factor de Boltzmann que rige la excitación de las rotaciones moleculares (a temperatura ambiente, la excitación de las vibraciones moleculares es despreciable). En el caso del hidrógeno, el espectro de los neutrones incidentes resulta considerablemente ensanchado, incluso para pequeños ángulos de dispersión, como suele ocurrir en la dispersión por un gas de masa 2, y los picos debidos a la dispersión por rotación molecular y traslación molecular se superponen.

#### INTRODUCTION

Many experiments have been performed to investigate the effect of molecular rotation on neutron scattering, but in none of the experiments have rotational effects been clearly separated from effects due to translations and vibrational motions of the molecule. Recent detailed measurements on methane [1] and propane [2] suggest that rotational effects are present, and GRIFFING [3] has explained the results theoretically assuming discrete rotational levels, but their presence is a matter of inference rather than observation.

This paper describes preliminary measurements of the differential scattering cross-sections of three gases - methane, ammonia and hydrogen at room temperature for 5 meV neutrons, in which molecular rotation effects have been observed. As the spacing of the lowest rotational levels in ammonia, for example, is only 2.5 meV, and at room temperature the most populated levels would give transitions around 25 meV, it is only by using such low energy neutrons that rotational effects can clearly be observed.

Methane was chosen for these experiments as it has a spherically symmetrical molecule - the rotational levels cannot be investigated directly by infra-red spectroscopy. Ammonia has a simple molecule, a symmetrical top, and it has been the subject of detailed infra-red examination. In addition it is suitable for future investigations on the hindrance of molecular rotations in the liquid state as it can be liquefied at room temperature by the application of only 8 atm pressure. In experiments on hydrogen it washoped to observe directly the transition from ortho-hydrogen to para-hydrogen.

#### APPARATUS

The neutron scattering apparatus described by HARRIS et al. [4] was used to measure the differential scattering cross-sections of methane, ammonia and hydrogen at room temperature for neutrons of about 0.005 eV energy at scattering angles of 20°, 30°, 45°, 75° and 90°. In the first experiment ammonia was contained at a pressure of 4 atm. (absolute) in a cylinder of aluminium-magnesium alloy, 5 cm diam., the walls of which were turned down to 0.75 mm thickness over the central 5 cm of their length. (A preliminary run was made with the cylinder evacuated, and the small contribution due to scattering from the walls subtracted from the subsequent results). The ammonia sample scattered about 10% of the incident beam. Only about 5% of the scattered neutrons were multiplely-scattered, and this effect has been neglected. For calibration of the efficiencies of the five counter arrays, so that absolute cross-sections could be determined. the ammonia sample was replaced by a sheet of vanadium as a standard comparison sample. These first measurements were made using a low resolution rotor running at 280 c/sec.

The first experiment suffered from the disadvantage that the width of the incident neutron spectrum was comparable with the broadening expected in scattering from a perfect gas of mass 17. Further measurements were therefore made on ammonia, and also on methane and hydrogen, using a high speed rotor (625 c/sec) with higher resolution. Aluminium cylinders, similar in dimensions to that used in the first experiment, were filled with methane to a pressure of 3 atm (absolute), with ammonia to 4 atm (absolute) and with hydrogen to 6 atm (absolute). The methane and ammonia samples scattered about 10% of the incident beam, but the hydrogen sample scattered only 7%, so the hydrogen results obtained has smaller statistical accuracy. A four-position rotary sample changer carried the samples, and rotated each sample into the beam in turn for a ten minute counting period. In each run two gas samples were counted, together with the evacuated cylinder and the calibration sample.

The use of vanadium in the first experiment as a comparison sample is not ideal, as the vanadium was in the shape of a sheet, while the ammonia sample had the shape of a cylinder. Thus different counter arrays may have had different views of the vanadium sheet and the ammonia sample. This leads to uncertainties in the relative magnitude of the results at different angles. In the second experiment a specimen of terviene (Melinex) film was used as the calibration sample to determine the relative efficiencies of the five counter arrays. The film, 0.001 in thick, was wound in a spiral on two grooved plates, rather like a photographic film in a developing tank. The terylene film was distributed fairly evenly over the volume of a cylinder the same size as the gas specimens, so each counter array would see the same amount of this comparison sample as it did of the gas samples. The scattering from terylene is not perfectly elastic, but ignoring inelastic scattering introduces an error of less than 1% in the relative efficiencies of the counters. This error could safely be ignored, as greater errors arose due to variations in counter efficiencies between the different runs.

The total cross-section of the terylene comparison sample was not measured, so it is not possible to deduce the absolute differential cross-

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sections of the gases. However the preliminary experiment on ammonia showed that the measured differential cross-sections were of the correct order of magnitude. The relative cross-sections at different angles deduced from the higher resolution measurements by comparison with the terylene sample should be of greater accuracy.

## PRELIMINARY MEASUREMENTS ON AMMONIA

The incident neutron spectrum transmitted by the rotor was measured by scattering from vanadium, and is shown in Fig. 1. Vanadium scatters almost entirely elastically and isotropically, so the results from all five counter arrays lie on the same curve. (A correction has been applied for absorption in the vanadium sheet). With the rotor running at 280 c/sec the number of neutrons transmitted was a maximum, though the shape of the incident spectrum was complicated by the presence of a sharp dip at 1100  $\mu$  s/m due to a Bragg reflection from the bismuth crystal in the beam.

Fig. 1 also shows the results of scattering from the ammonia sample. Scattering at 20° shows a "quasi-elastic" peak centred at  $1000 \,\mu\,s/m$ , about twice as broad as the peak in the incident spectrum. At  $500 \,\mu\,s/m$  there is a separate peak, corresponding to a neutron energy gain of about 0.02 eV. At 30° the quasi-elastic peak has moved to  $900 \,\mu\,s/m$ ; the energy gain peak has grown in magnitude, but its position is unchanged. At 45° the quasielastic peak has almost disappeared, and at 75° and 90° it has completely merged into the energy gain peak. All the curves have the same high energy limit at about  $200\mu\,s/m$ , and all have a long tail on the low energy side (only part of which is shown in Fig. 1).

These results have been compared with the computed cross-sections for a perfect gas of mass 17. To take account of the width of the incident neutron spectrum, the spectrum scattered elastically by vanadium has been approximated as shown by the dotted curve, by four components centred at 1000, 1100, 1200 and  $1300 \,\mu$ s/m. The scattering due to these for components has been added together. This method of approximating the incident spectrum and introducing experimental broadening into the computed perfect gas curves is equivalent to neglecting the time-broadening if the incident neutron burst, and assuming the whole width of the vanadium curve is due to the spread of neutron velocities. The only parameter normalizing these curves is ratio of the cross-section of ammonia [5] to the bound-atom-section of hydrogen.

#### MEASUREMENTS ON METHANE, AMMONIA AND HYDROGEN

The results of the higher resolution measurements on methane, ammonia, and hydrogen are shown in Figs. 2, 3 and 4 respectively. In this experiment the incident spectrum was measured by a monitor counter in the neutron beam, at the same distance from the sample as the counters detecting scattered neutrons. This would be the spectrum observed at any of the counter arrays of the specimen scattered perfectly elastically. The width of the incident spectrum is only one sixth of the minimum broadening introduced by scattering from any of the gases. The results for ammonia show the same

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Inelastic neutron scattering from ammonia (low resolution).

qualitative features as observed in the preliminary experiment. The results for methane are identical with those for ammonia within the experimental error. The scattering from hydrogen is quite different in its general ap-



Fig.2

Differential scattering cross-section of methane.

pearance; at all angles there is a single broad spectrum of scattered neutron energies, and no appearance of an elastic peak.

The scattering from perfect gases of mass 16, 17 and 2 respectively, has been computed and compared with the results. The width of the incident spectrum, though less important in these high resolution experiments, has been included in these computations as before by taking three bands of incident velocities, centred at 1010, 1040 and 1070  $\mu$ s/m, and calculating the weighted mean of the perfect gas scattering. The absolute differential crosssection of the terylene comparison sample is not known, so an arbitrary normalization factor has been applied to the results on each gas to compare them with the perfect gas cross-sections. Even in the range of energies where vibrational and rotational effects are not obvious in the scattered neu-



Differential scattering cross-section of ammonia.

tron spectrum, their effect on the translational scattering must be considered. A Debye-Waller factor has therefore been included, multiplying the perfect gas cross-sections. The magnitude of the Debye-Waller factor was estimated from the mean energies of rotational and vibrational transitions in the three gases.

## DISCUSSION

The preliminary results on ammonia show clearly that part of cold neutron scattering resembles scattering from a perfect gas, and part is quite different. The quasi-elastic peak at 20° is very similar to scattering from a gas of mass 17, and at higher angles the quasi-elastic peak moves to



Differential scattering cross-section of hydrogen.

higher energies as would be expected in gas scattering. There is some discrepancy in the magnitudes of the quasi-elastic peaks; the peak at 30° is higher than that at 20°. This is assumed to be caused by inaccuracy in the normalization, due to the different geometry of the ammonia and vanadium samples. Apart from the quasi-elastic peaks, there is a separate energy gain peak, which for all scattering angles has its maximum at about  $500\mu s/m$ . The peak corresponds to energy gains in the range 10 to 100 meV, which is just the range occupied by rotational transitions in a molecular gas at room temperature. The energy gain peaks are therefore presumably due to molecular rotations giving up energy to the neutrons. At 20° and 30° the rotational effects and translational effects are well separated. The high energy limit is set by the Boltzmann factor corresponding to room tem-

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perature. Vibrational transitions are in the neighbourhood of 100 meV, and so would not be excited at room temperature (kT = 25 meV).

In the higher resolution measurements the normalization of the perfect gas curves is arbitrary, and the choice of Debye-Waller factors is approximate, but clearly the quasi-elastic peaks observed at low angles in methane and ammonia are due to the translational motions of the gas molecules. At higher angles, where the translational peaks merge into the energy-gain peaks, and in scattering from hydrogen, where there is no separation of the translational effects at any angle, there is a considerable area of the curve unexplained by perfect gas behaviour. This is in the region where the energy gain is of the correct magnitude to be attributed to molecular rotations.

A simple way of analysing the rotational part of the scattering curve is to make use of the function  $p(\beta)$  suggested by EGELSTAFF [6]. This function is defined by

$$p(\beta) = \beta^2 \lim_{\alpha \to 0} \frac{1}{\alpha} S_s(\alpha, \beta)$$
(1)

where  $S_s$  is the "self" part of the scattering law. For scattering from hydrogen atoms the interference part of the scattering law can be neglected. Since the hydrogen cross-section is much larger than nitrogen and carbon crosssections,  $S_s$  may be assumed to represent the scattering of the whole molecule as observed in these experiments. The value of  $p(\beta)$  may be deduced directly from the experimental results at the five different scattering angles using Eq. (1).

This step has been performed for ammonia; the results are shown in Fig. 5. For small values of  $\beta$ , that is in the neighbourhood of the quasi-





Experimental and theoretical values of  $p(\beta)$ .

elastic peak, it becomes increasingly difficult to extrapolate  $S/\alpha$  to  $\alpha = 0$ . There is almost a delta function in  $p(\beta)$  at  $\beta = 0$ , representing the perfect gas behaviour; and therefore the data at  $\beta$  values less than a resolution width (i.e.  $\beta < 0.1$ ) are of no value to this analysis. However at slightly larger values of  $\beta$  the curve passes through a minimum and increases sharply as the origin is approached. At the higher values of  $\beta$  the data are not sensitive to the resolution function.

The function  $p(\beta)$  is related to the velocity auto-correlation function, and so it may be calculated readily by assuming a suitable theoretical model. EGELSTAFF has derived it for a hard sphere model [7]. Ammonia was approximated by a spherical molecule, with its moment of inertia the mean of the principal moments of ammonia, and  $p(\beta)$  evaluated from the expression (which is accurate for  $\beta > 2$ )

 $p(\beta) = \sqrt{\frac{2}{\pi}} \frac{\beta^2}{Z^3} e^{-\beta^2/2Z^2}$ (2)

where  $Z^2 = \hbar^2 / IkT$ .

The result is shown in Fig. 5: the normalization is arbitrary. p ( $\beta$ ) shows a peak in the region of  $\beta = 0.4$ , as does the experimental curve, but at higher  $\beta$ 's it falls off rapidly.

SCHOFIELD [8] has suggested an improved model, in which the velocity correlation of a hydrogen atom moving on the surface of a rotating sphere is considered. This leads to a  $p(\beta)$  of the form (for  $\beta \ge 2$ )

$$p(\beta) \sim \beta^4 e^{-\beta^2/2Z^2}$$

This expression has a maximum in the right region, but it still falls off too rapidly as  $\beta$  increases, though less rapidly than Egelstaff's formula.

GRIFFING [3] has obtained the differential scattering cross-section of methane by assuming discrete rotational transitions. His treatment seems to approximate to a classical model in the range of  $\beta$  observed in these experiments. Any divergence would be expected at small values of  $\beta$  comparable to the spacing of the discrete rotational transitions, that is 2.5 meV which corresponds to  $\beta = 0.1$ . Thus the p ( $\beta$ ) derived from his calculations would be similar to those of EGELSTAFF [7] and SCHOFIELD[8].

To test how sensitive the differential cross-section is to the exact shape of  $p(\beta)$ , the differential cross-section for scattering through 20° was computed from the expression (2) for  $p(\beta)$  to which was added a perfect gas term (M = 17). The calculated cross-section had a peak at  $600\mu s/m$ , but its width was much smaller than the rotational peak observed in the experiment. In particular it fell to half its peak value at  $470\mu s/m$ , and to zero at about  $300\mu s/m$ . The experimental curve only falls to zero below  $200\mu s/m$ . This is reflected by the difference in the  $p(\beta)$  curves.

Further computations are necessary to check that the curve of  $p(\beta)$  deduced by extrapolating the experimental results to  $\alpha = 0$  is sufficient to explain scattering results at all energies and all angles. If it is justified it may imply that the moment of inertia to be used in these models is much larger than expected, or that the vibrational levels are very broad and extend into the rotational region.

#### CONCLUSIONS

These experiments show the type of results which can be expected from the scattering of cold neutrons by simple molecules. In particular, the effects of translational and rotational motions of the molecules are clearly separated. In comparison, measurements at higher neutron energies (15 meV to 142 meV) on methane [1] and propane [2] do not show this clear separation, though the results cannot be explained on a perfect gas model, and molecular rotations and vibrations have to be included to give tolerable agreement with theory. Thus measurements with cold neutrons will be most useful for detailed examination of the effect of molecular rotations on neutron scattering.

Analysis of the results for ammonia shows that the neutron scattering cannot be explained on two simple models of the rotating molecule; in particular the observations for large energy transfers are inconsistent with the theoretical models. Further experiments of higher statistical and absolute accuracy, and further computations are necessary to show whether the effect of molecular rotations on cold neutron scattering can be adequately described by a classical model, or whether discrete rotational levels must be considered.

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## DISCUSSION

P. SCHOFIELD: With regard to the shape of your  $p(\beta)$ , might it not be that this type of molecule is of the same nature as the pathological case which Egelstaff demonstrated in presenting his first paper\*?

\* "Practical analysis of neutron scattering data into self and interference terms", See these Proceedings.

P. EGELSTAFF: You mean this case of the sharp peak at the origin?

P. SCHOFIELD: Yes.

J. WEBB: For what reasons?

P. SCHOFIELD: Well, in presenting his first paper Dr. Egelstaff showed this peculiar frequency distribution with a very sharp peak and then something else of much higher energy, and he showed that in this case the extrapolation procedure broke down completely and you got smeared-out distribution.

J. WEBB: The extrapolations are quite easy at the high values of  $\beta$ .

P. SCHOFIELD: They might be easy but wrong.

J. WEBB: Yes, that might be true.

G. GRIFFING: I have two comments. (1) You normalize p and until you put your experimental results on an absolute basis it is incorrect to conclude that you are experimentally getting higher values than are yielded by my computations in the region of energy gain. (2) We have run an identical experiment at the Materials Testing Reactor, at the same incident energy as you had, and we found no evidence of the experimental results being higher than the theoretical results. Indeed we should expect the contrary to be the case, bearing in mind resolution effects.

J. WEBB: Yes, I might mention one point about our normalization. In our first experiments, we put a sheet of vanadium in the beam and measured the scattering at the various angles, but this is not really satisfactory as the vanadium was a sheet and our gas samples were cylinders so one could never be sure that each of the counters viewed exactly the same sample. In our later work, therefore, we replaced this vanadium by a scroll of terylene film, which gave very nearly elastic scattering - a result which seems rather surprising in view of the polythene results that were presented yesterday - and we used this as an isotopic elastic scatterer to calibrate the relative efficiencies of our counters. Unfortunately, we didn't measure the absolute scattering from the sample but in the more accurate measurements, which we hope to do in a few weeks' time, this will, of course, be done.

H. STILLER: I wonder whether the occupations due to spin states have been taken into account in these calculations; it is a surprising fact that if the spin states are taken into account, then specifically the high-energy rotational states are occupied much more (by a factor of 1.5 or so) than one would expect from thermal occupation and ordinary degeneracy. I think this might explain the discrepancy between the experimental results and the theoretical ones.

J. WEBB: Certainly, we have made no allowance for this at all.

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