ENERGY DISTRIBUTIONS OF NEUTRONS SCATTERED FROM GRAPHITE, LIGHT AND HEAVY WATER, ICE, ZIRCONIUM HYDRIDE, LITHIUM HYDRIDE, SODIUM HYDRIDE AND CHLORIDE BY THE BERYLLIUM DETECTOR METHOD

CRNP 948

by

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ABSTRACT

Energy distributions of neutrons scattered from various moderators
at room temperature, and from several hydrogenous substances, have been
measured mainly over the range of energy transfers 0.02 ev to 0.24 ev. Neut-
rons of variable energy \(E_0\) from a crystal spectrometer were scattered by
the specimen, and detected by a \(\text{Be}^{10}\text{F}_3\) counter shielded with four inches of
beryllium. The counter was thus sensitive only to scattered neutrons with
energy \(E' < 0.005\) ev. The energy transfer is given by \(\hbar \omega = E_0 - \langle E'\rangle \approx E_0 - 0.003\) ev. Experiments have been performed with graphite, light and heavy
water, ice, zirconium hydride, lithium hydride, sodium hydride and ammonium
chloride.

Results are as follows: Graphite: Structure was observed at
\(\hbar \omega = 0.18\) ev, 0.118 ev, 0.102 ev, 0.078 ev and 0.058 ev. Water: An energy
distribution from \(\hbar \omega = 0.03\) to 0.24 ev showed continuous intensity attributed

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to the hindered rotational band, with a maximum at 0.07 ev. Heavy Water: This distribution also showed continuous intensity but with a maximum at ~ 0.05 ev as expected because of the greater mass of the deuterium atoms. Ice: The distribution at 90°K showed three broad peaks at $\hbar \omega = 0.105$ ev, 0.078 ev and 0.19 ev. Zirconium Hydride: A peak at 0.140 ev did not change very much between 296°K and 95°K. The observed width of 0.025 ev is thus probably due to the distribution of optical normal modes. Lithium Hydride: A distribution extending from 0.06 ev to 0.19 ev had a strong maximum at 0.098 ev and a weaker maximum at 0.130 ev. The range covered by the optical modes is in good agreement with anomalous reflection measurements (infra-red). Sodium Hydride: This distribution was similar to that for lithium hydride with maxima at 0.078 ev and 0.110 ev. Ammonium Chloride: Peaks were observed at 90°K for $\hbar \omega = 0.178$ ev, 0.138 ev, 0.116 ev, 0.094 ev, 0.079 ev, 0.0485 ev and 0.023 ev. At 208°K the peaks were still in evidence but broadened. At 296°K, above the transition at 242°K only considerably broadened peaks at 0.177 ev, 0.045 ev and 0.021 ev remained, although the total diffuse intensity at other energies was about the same as the integrated intensity at 90°K.

1. INTRODUCTION

The feature of a continuously variable incident wavelength in the triple axis crystal spectrometer (1) has opened new possibilities for studying the high frequency optical vibrations in moderators and hydrogenous materials under rather favourable conditions using a new technique. Energy distributions of neutrons scattered from graphite, light and heavy water, ice, zirconium hydride, lithium hydride, sodium hydride and ammonium chloride have been measured, mainly for energy transfers in the range 0.02 ev to 0.24 ev. In some substances, particularly ammonium chloride, distributions were measured at several different temperatures.
A beam of monoenergetic neutrons of variable energy, $E_o$, was scattered by the specimen into a $\text{B}^{10}\text{F}_2$ counter which was shielded with four inches of beryllium. Only those neutrons which were scattered so that their final energies, $E'$, were less than 0.005 ev were thus able to enter the counter. The energy transfer is given by $\hbar \omega = E_o - \langle E' \rangle \approx E_o - 0.003$ ev.

This energy transfer is accompanied by a momentum transfer $\vec{Q} = \vec{k}_o - \vec{k}'$ where $\vec{k}_o$ and $\vec{k}'$ are the wave vectors of the incident and scattered neutrons respectively. Some of the advantages of this method are:

1. The efficiency of the analysing system remains constant and therefore the observed intensity does not require a correction for the poorly known sensitivity function of the analyser and the counter.

2. On the other hand the energy variation of the sensitivity of the thin fission counter monitor in the incident beam is well known.

3. Because an energy loss process is used, the high frequency transitions are not attenuated by the Boltzmann factor as in energy gain methods. Thus measurements at low temperature are possible.

4. The use of the beryllium shielded detector eliminates higher order effects in the analysing system. This also implies that the second and higher order contaminant neutrons in the incident beam are not as apt to be important as in a crystal analysing system.

5. Since the counter is required to be sensitive to very low energy neutrons only, a low pressure of $\text{B}^{10}\text{F}_2$ may be used. The fast neutron background is thus reduced while high efficiency for counting slow neutrons is preserved.

6. The experimental conditions can be made such that the counter presents a large solid angle to the specimen and as a result the intensity is high.

7. Insofar as the monitor counter has a $1/\nu$ sensitivity function it eliminates the factor $k'/k_o$ from the expression for the inelastic differential cross section, thus removing all explicit dependence on the initial and final
neutron energies and leaving only the Van Hove scattering function, \( S(q, \omega) \), which depends only on momentum and energy transfers [see reference (1)].

Disadvantages of the method are:

1. The wave vector of the scattered neutrons, \( k' \), is small so that the range of momentum transfers, \( Q \), is restricted for a given energy transfer (Fig. 1). The shaded portion in the figure shows the range of \( Q \) operative at the scattering angle of 60° used in most of these experiments. The experiment thus encompasses a rather narrow band through \( \omega - Q \) space.

2. High energy transfers are inevitably accompanied by high momentum transfers resulting in Doppler broadening of the high energy peaks, or in another language, multiple phonon transfer.

The measured energy distributions are believed to be closely related to the frequency distribution \( g(\omega) \) (3). The term \( q^2/\hbar \omega \) which occurs in both the coherent and incoherent scattering cross sections for the single phonon process (4) has a value which is close to unity in these experiments because of the small value of \( k' \) and hence does not provide any complication. Also the inelastic structure factor (5) in the expression for the incoherent scattering by the hydrides is believed to be changing only slowly in the region of interest in which the optical vibrations occur.

2. THE EXPERIMENT

A schematic diagram of the experimental arrangement is shown in Fig. 2. Monoenergetic neutrons of energy \( E_0 \) and wave vector \( k_0 \) are selected from the reactor spectrum by Bragg reflection from a chosen plane of the aluminum monochromator. The incident monochromatic beam then passes through the thin monitor counter and is scattered by the specimen. Before they can enter the counter, the scattered neutrons must pass through the beryllium filter which consists of eight \( \frac{3}{8}'' \times 1'' \) bars each four inches long. The bars are
interleaved with cadmium. Only those neutrons whose energies are below
the beryllium cutoff (0.005 ev) are transmitted by the filter. Neutrons are
counted in the signal counter for a fixed number of counts in the monitor
counter. The angle $2\theta_m$ is then changed by a predetermined increment (the
monochromator half angling at the same time) and the neutrons are recorded
for the same number of monitor counts at the new incident energy, $E_0$. The
procedure makes the experiment independent of the shape of the reactor
spectrum once some well known corrections have been applied.

3. TREATMENT OF RESULTS

The most useful form for the data is an energy distribution
rather than the recorded angular distribution. The transformation from the
angular to the energy distribution is made simply by changing the angular
scale to an energy scale. The intensity remains unchanged since the detector
has a window with a constant energy width and the changes in intensity of
the incident beam are automatically accounted for by the monitor.

A number of corrections had to be applied to the observed dis­
tributions because of contamination in the incident beam. This contamination
consists partly of fast neutrons and partly of neutrons which have a large
energy spread centred about the peak in the Maxwellian distribution (white
radiation).

For each point in the distribution the counting rate was measured
with a sheet of cadmium in the incident beam which stopped the slow neutrons.
Thus the room background and the effect of the fast neutrons on the specimen
were measured and could be subtracted point by point from the original distribution.

The effect of the contaminant slow neutrons in the beam was
measured by turning the monochromator so that it was no longer on a Bragg
peak and measuring the scattering of the residual neutrons by the specimen.
This intensity was then subtracted from the measured distribution. The effect
of this contamination was negligible at low energies but was important for
energies of the order of 0.2 ev.

The above procedure did not measure the scattering by the specimen of the second and higher order neutrons in the beam. However at low energies \( E_o < 0.05 \text{ ev} \) a six inch quartz crystal filter placed in the beam highly attenuated the higher order neutrons \((1,6)\). At much higher energies the second order component again becomes important. However, when \( E_o > 0.12 \text{ ev} \) the energy of the second order neutrons, \( 4E_o \), is greater than the energy of the cadmium cutoff \((\sim 0.4 \text{ ev})\). Thus, at these energies, when the cadmium shutter is in the beam to measure fast neutron effects, the scattering produced by the second order neutrons is also included. For these reasons it was felt that measurements of the second order content in the beam were not necessary.

After the contaminant components had been subtracted from the observed distributions it was necessary to correct the monitor counting rates (and hence the signal intensity) for the contaminant neutrons in the beam and also for any deviation of the monitor counter from a \( \frac{1}{v} \) characteristic. This was done by multiplying all counting rates by the ratio of the total incident beam intensity (as seen by the monitor) to the intensity of the monochromatic component (also as seen by the monitor). The corrected intensity, \( I \), is then given by the formula

\[
I = \left( I_R - I_{Cd} - C \right) \frac{(M + C_M)}{M} \text{ ev.}
\]

where \( I_R \) is the recorded intensity

\( I_{Cd} \) is the recorded intensity obtained with cadmium in the incident beam

\( C \) is the contribution of the slow neutron contamination in the beam

and was measured by recording the intensity (less background)

with the monochromator turned out of the Bragg position

\( M \) is the monitor counting rate for the monochromatic beam

\( C_M \) is the monitor counting rate for the contamination in the incident beam
M + C_M is the total monitor counting rate

e is the ratio of: the efficiency of the monitor counter assuming a

1/v characteristic, to the actual efficiency of the counter

The distributions displayed in the various figures have been corrected as described above, except as noted.

The measured distributions contain contributions from multiple scattering processes. In this preliminary work no attempt has been made to correct for multiple scattering. The effects of multiple scattering depend on two factors: the transmission of the specimen, and the extent to which single scatterings are elastic. If the Debye-Waller factor exp(-Q^2 u^2) is very nearly unity then multiple scattering has little effect on the spectrum except to increase the range of Q-space which is sampled in the experiment, beyond the band shown in Fig. 1. For some purposes this is actually a desirable effect, as in the case of graphite in these experiments. If the Debye-Waller factor is small then the multiple scattering is multiply inelastic and smears the spectrum. If the spectrum is a line spectrum it will introduce sum and difference lines. Accordingly for such materials the specimens must be thin, i.e. with transmission not far from unity.

Since u^2 (the mean square displacement of an atom from its 'equilibrium' position) is a constant, the exponent Q^2 u^2 increases rapidly with Q. Thus high energy transfers (in this experiment inevitably accompanied by high momentum transfers hQ) are more seriously affected by multiple scattering than are low energy transfers. Multiple scattering thus behaves much like multiple phonon scattering, except that it is dependent on the specimen thickness.

4. RESULTS

(a) Graphite

The corrected energy distribution for neutrons scattered from graphite at 296°K in the range 0.02 ev to 0.24 ev is shown in Fig. 3. At
high energies the data are poor because of the large corrections required for background and beam contamination. Because of the relatively low temperature of this specimen multiple inelastic scattering is probably negligible. It may be that the averaging over Q space in this experiment allows some comparison between this spectrum and the energy distribution of normal modes, g(ω). It is more probable, however, that the range of Q space covered was too restricted, and thus coherent effects too predominant, for the averaging process to be complete. Thus comparisons with calculations for g(ω), such as those of BALDOCK (7) are probably not meaningful. This spectrum does, however, represent the scattering function, S(Q,ω), over the narrow band through ω - Q space shown in Fig. 1.

(b) Water

The energy distribution (uncorrected for slow neutron contamination) for light water is shown in Fig. 4. The distribution shows a very broad maximum at 0.07 ev which has a steep slope on the low energy side but a gradual slope on the high energy side. The experiment revealed no structure at high energies. This may be partly due to the high Q necessarily used in these experiments, resulting in Doppler broadening of a possible vibration peak at ~0.2 ev. The maximum at 0.07 ev is probably associated with the hindered rotational band observed in the Raman spectrum (8) and in previous neutron energy gain experiments (9, 10). In energy gain experiments the assigned energies (~0.06 ev (9), 0.061 ev (10)) were strongly influenced by presentation as a wavelength distribution instead of as an energy distribution, and by the influence of the Boltzmann factor (9). The distribution multiplied by the Boltzmann factor exp (-ω/k_B T) is shown in Fig. 4 by a dashed line. This is the curve that would be obtained in an energy gain experiment. The hindered rotational band is thus extremely broad and ill-defined. The transmission of this specimen was nearly 90% so that multiple scattering effects were probably very small although multiple phonon effects were undoubtedly large especially at high energies.
(c) Heavy Water

The spectrum observed for heavy water and shown in Fig. 4 (also uncorrected for slow neutron contamination) is very similar to that observed for light water except that the maximum of the broad peak has shifted to about 0.05 ev. This may be expected because of the greater mass of the deuterium atoms (the ratio of the frequencies is proportional to the ratio of the square root of the masses of the atoms). Again the results do not yield reliable information about any structure in the high energy region. Multiple scattering is probably not important since the transmission of this specimen was nearly 90%.

(d) Ice

The corrected spectrum for ice at 90°K is shown in Fig. 5. There is a broad double peak with maxima at 0.078 and 0.105 ev both of which probably correspond to the very broad hindered rotational band in water. The figure also shows a disagreement between results taken with the (200) and (311) monochromating planes which is not understood at the present time. The maximum at 0.19 ev is possibly a bending vibration of the hydrogen atoms as identified from optical spectroscopy (8, 11), although it probably also contains contributions from multiple phonon and multiple scattering processes. The latter are probably important since the transmission of the specimen was only about 35%. The structure observed near 0.03 ev may correspond to peaks observed in the Raman spectrum (8, 11, 12).

(e) Zirconium Hydride

The distribution for zirconium hydride at 296°K is shown in Fig. 6 and extends from 0.01 ev to 0.34 ev. The peak centred at 0.140 ev has been observed before using the energy gain cold neutron technique (13, 14, 15). The quoted energy for this peak is $0.130 \pm 0.005$ ev (14, 15). The 7% discrepancy between the observed energies for this vibration is
partly accounted for by the fact that in the energy gain method the Boltzmann factor changes considerably over the width of the peak. The distribution which would be observed if an energy gain technique were used is shown by the dashed curve in Fig. 6. The centre of the distribution has now shifted to about 0.136 ev. The remainder of the zirconium hydride spectrum does not show any outstanding features. Below 0.02 ev there is some indication of the acoustic modes and at about 0.28 ev a double phonon and multiple scattering peak is in evidence. The manufacturers formula for the zirconium hydride was ZrH$_{1.8}$. The specimen had a transmission of about 70% so that the multiple scattering processes were probably important but not overwhelming.

The distribution from zirconium hydride was also measured at 95°K and is shown in the inset in Fig. 6. Very little difference in either the width or the shape of the distribution was observed. This suggests that the width observed at 295°K was not due to Doppler broadening but was probably just the energy distribution of the optical normal modes.

(f) Lithium Hydride

The distribution for lithium hydride is shown in Fig. 8. The spectrum shows maxima at 0.098 ev and 0.130 ev, possibly corresponding to peaks in the frequency distribution for the transverse and longitudinal optical normal modes respectively. Also indicated are the infra-red measurements of FILLER and BURSTEIN (16). The extent of their reflection peak agrees with this distribution. The arrows T0 and L0 indicate the positions of the transverse and longitudinal optical modes for infinite wavelength, deduced by them from the shape of their reflection curve. The increase in intensity at higher energies is most likely a multiple phonon and multiple scattering effect. This specimen had a transmission of about 60%, and since it was a solid well below its melting point the multiple scattering should be largely elastic, and the multiple scattering effects on the spectrum not too important.
(g) Sodium Hydride

Figure 8 also shows the distribution from sodium hydride at 90°K. The specimen was commercial sodium hydride of unknown purity. It had a transmission of about 60%. The characteristic double hump of ionic crystals is again observed for this material. In this case the sides of the distribution are steeper than for lithium hydride. There is little doubt that the intensity beyond 0.13 ev arises from multiple phonon and multiple scattering processes. The intensity below 0.025 ev probably arises from scattering from the acoustical modes.

(h) Ammonium Chloride

The distribution from ammonium chloride was studied at three different temperatures: 90°K, 208°K and 296°K; the results are shown in Fig. 9. The peak at 0.023 ev has been observed in optical spectroscopy (17) and is believed to be the optical vibration of the ammonium radical against the chlorine atom. The peak at 0.0485 ev has never been directly observed before but was postulated by WAGNER and HORNIG (17) to account for their infra-red absorption results. They considered it to be a torsional oscillation of the ammonium radical. The peak at 0.178 ev appears in the absorption spectrum and is attributed to the bending mode in the ammonium radical. The other four peaks at 0.070 ev, 0.094 ev, 0.116 ev and 0.138 ev are quite likely combination bands of the two peaks at 0.023 and 0.049 ev caused by multiple phonon and multiple scattering processes. The multiple scattering would be expected to be considerable since the transmission of the specimen was only about 55%.

At 208°K all of the peaks observed at 90°K are still in evidence but are now broader. The peak at 0.0485 ev has possibly decreased in energy by about 0.001 ev, the peak height has decreased by nearly 50% and the width has increased from 0.005 ev (which is just the resolution width of the apparatus) to about 0.007 ev.
At 296°K, above the ordering transition at 242°K (17), the three fundamental peaks are still present but they are now considerably broader than at 90°K. The combination bands are presumably no longer able to be resolved because of their increased width at this temperature. The integrated intensity in the region of these four combination bands (0.05 ev to 0.15 ev) is of the same order as at the other two temperatures.

5. CONCLUSION

The experiments described in this paper demonstrate the effectiveness and usefulness of the beryllium detector method for observing high frequency vibrations in certain substances, particularly hydrogenous materials. It should be emphasized that the experiments so far have been exploratory only and that the full potentiality of the method has yet to be realized. In particular, much higher intensities are possible by cooling the beryllium filter and by using a counter (or system of counters) which presents a much larger solid angle to the scattering specimen. With these improvements detailed studies of transitions of energy up to 0.5 ev would be quite feasible. Despite the preliminary character of these results, they are probably the most accurate measurements of high energy transfers yet made.

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REFERENCES

Fig. 1 - The wave vector transfer as a function of the energy transfer showing the range of $\omega$-$Q$ space which can be traversed for various scattering angles ($\phi$) when $E^t = 0.003$ ev. The shaded portion is the operative area in these experiments when $\phi = 60^\circ$, and shows $0 < E^t < 0.005$ ev.
Fig. 2 - A schematic diagram of the experimental arrangement.
Fig. 3 - The distribution of inelastic neutron scattering from graphite at 296°K. The estimated resolution function is indicated at two energies.
Fig. 4 - Energy distributions for water and heavy water (uncorrected for white radiation). The dashed curve indicates the form of the distribution for light water as it would be seen in an energy gain experiment.
Fig. 5 - The corrected energy distribution of neutrons scattered by ice at 90°K showing the planes of the monochromating crystal used in the measurement. The (331) plane results are uncorrected for white radiation effects.
Fig. 6 - Energy distributions for zirconium hydride at 296°K. The dashed curve indicates the form of the distribution as it would be seen in an energy gain experiment. The inset shows the 95°K distribution.
Fig. 7 - The energy distributions of neutrons scattered by lithium hydride (296°K) and sodium hydride (90°K). Infra-red measurements are also indicated for LiH.
Fig. 8 - The energy distributions of neutrons scattered by ammonium chloride at three temperatures.