Lattice Vibrations in Germanium by Scattering of Cold Neutrons*

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The dispersion relations for the optical and acoustical vibrations in the [100] and [110] directions in germanium have been determined by means of cold-neutron scattering measurements. An improved experimental method has provided data with smaller experimental error. The theoretical interpretation of the results indicates a long-range force between germanium atoms.

I. INTRODUCTION

SLOW neutrons are potentially of great value for studying the motions of atoms because of the similarity in mass of the neutron and the scattering nuclei. When neutrons of thermal energy suffer inelastic scattering and exchange energy with lattice vibrations, both the momentum and energy of the neutrons change by significant amounts. As a result, measurement of scattered neutrons gives information on the energy and momentum, or alternatively, the frequency and wave number of the lattice vibration phonons.

Although the inherent advantages of the method are great, the applications have thus far been limited because of insufficient neutron flux. As higher flux reactors are made available, the method has been developed and applied to more materials. The conversion of the measured changes in momentum and energy to properties of the lattice phonons is, in principle, very direct. The scattering theory and the relationship between the neutron effects and the phonons is discussed in detail by Placzek and Van Hove.[1] Experiments of the type following the theory of Placzek and Van Hove have been carried out for aluminum, by Carter, Palevsky, and Hughes[2] and Brockhouse and Stewart,[3] and for vandium by Eisenhauer *et al.*[4] Aluminum and vanadium are relatively simple applications of the inelastic scattering technique for both have one atom per unit cell. A more complicated and interesting case is that of germanium, which has two atoms per unit cell and hence will exhibit optical as well as acoustic vibrations. In work already reported by Brockhouse[5] the acoustic vibrations have been studied, and the optical vibration was found by Pelah *et al.*[6] The optical vibration in the limit of zero phonon momentum, that is, infinite wavelength, is the Raman line. On the basis of sound velocity measurement, Hsieh[7] theoretically estimated that the Raman frequency in Ge was approximately 360 cm^{-1}. The work of Pelah *et al.* with slow neutrons gave a smaller value, 300 ± 10 cm^{-1}. The direct way in which the optical vibration frequency could be measured with neutrons showed the inherent advantage of this direct method of measuring lattice vibrations.

The acoustical and optical dispersion relations for germanium were calculated by Herman,[8] using the Born-von Kármán theory and taking into account forces including fifth neighbors. The Brookhaven[6] and Chalk River[5] measurements at first seemed inconsistent with the calculations of Herman. It was decided to remeasure some of the frequencies important to the theory by an improved method to investigate the relationship of the theoretical calculation and the measured values with as much accuracy as possible.

II. EXPERIMENTAL METHOD

In the scattering experiments as developed at Brookhaven, the incident neutrons are of very low energy, or cold neutrons. When these cold neutrons are scattered by the sample under study the predominant process is gain of energy by the neutrons, usually one phonon being gained in a scattering process. The experimental equipment and the method,[2,4] in connection with measurements on vanadium and aluminum and the description will not be repeated here. For a material that scatters primarily coherently, such as germanium, it is essential to use a single crystal to investigate the complete relationship between the frequency and momentum of the phonons. The equations that must be satisfied to conserve momentum and energy are the following:

$$\frac{\hbar^2}{2m_n}(k_f^2-k_0^2)=\hbar\omega,$$

$$\mathbf{k}_f-\mathbf{k}_0=2\pi\tau+\mathbf{q},$$

where k_0 and k_f are the wave vectors of the incident and scattered neutrons, respectively, $\hbar\omega$ the energy and

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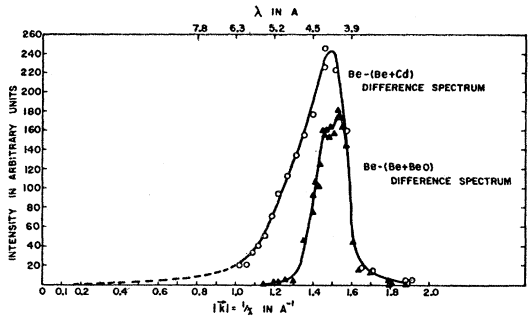

FIG. 1. Cold-neutron spectra. The open circles represent the spectrum used in the first experiments. The triangles represent the incident spectrum obtained by the Be-BeO filter difference method. Note that although the area under the latter spectrum is about ½ the area under the former, in the region between 4.0 and 4.7 A the Be-BeO filter difference spectrum contains approximately 75% of the Be filtered intensity.

$\hbar\mathbf{q}$ the momentum of the phonon excitation, and $2\pi\tau$ a reciprocal-lattice vector of the germanium lattice.

The first measurements that were made with germanium utilized essentially the same method as used for vanadium and aluminum. In this technique the incident neutrons are those formed by the cooled beryllium filter. The filter produces a band of neutrons that is not monoenergetic but has a sharp edge at a wavelength $\lambda = 3.95$ A and then decreases rapidly in intensity toward long wavelengths. However, the finite width of the distribution is sufficient to cause uncertainty in interpretation of the peaks in energy for scattered neutrons. In order to obtain a smaller spread in the momentum of incident neutrons and yet to maintain a high intensity of incident neutrons, a BeO difference technique was used. The results reported here were practically all obtained with the BeO difference technique.

When using the entire beryllium-filtered spectrum, a reading was made by observing the counting rate as a function of flight time. Then the background counting rate was obtained by inserting a piece of cadmium in the incident neutron beam. The cadmium removes all slow neutrons and the remaining counting rate is caused by fast neutrons in the beam, or by room-background slow neutrons. The new method consisted of inserting a piece of polycrystalline BeO in the beam rather than the thin sheet of cadmium. The BeO was 1 in. thick and this acount is sufficient to remove most of the neutrons of wavelength beyond the cutoff of BeO, namely 4.7 A, but not thick enough to affect the background of fast neutrons. Thus a BeO difference gives the effect of the neutrons between 4 and 4.7 A in just the way that a cadmium difference gives the effect of neutrons of all wavelengths greater than 4.0 A. Because of the shape of the pile distribution passing through beryllium, the intensity of neutrons in the beam is reduced by about a factor of 2, when only those neutrons between 4.0 and 4.7 A are used, compared with the spectrum of all wavelengths longer than 4.0 A. The BeO difference method gives a much narrower range in incident momentum but does not appreciably reduce the number of neutrons in the energy spectrum desired from 4.0 to 4.7 A. No backgrounds utilizing cadmium are measured, the only measurements being the two, beryllium filter and beryllium filter+BeO. Figure 1 shows the spectrum obtained by this method and the Be-filtered spectrum for comparison, as measured by scattering the filtered neutrons from vanadium. The purpose of these measurements is to observe the shape of the spectrum obtained in the BeO difference method. In using the method it is important that the BeO does not remove neutrons in energy regions other than the 4.0–4.7 A region, for these other neutrons would then be affecting the final results. The figure, however, shows that the BeO difference gives a response only in the desired energy region, and that no neutrons of other energies contribute to the measurements. Several scattering peaks were rechecked, using the BeO difference method that had already been run by the old method. The sharper incident momentum of the new method resulted in some cases in better resolved peaks in the distribution of scattered neutrons. (See Fig. 2.) The uncertainty that was associated with the previous method, concerning what part of the incident spectrum was primarily responsible for producing the peaks in the scattered spectrum, was reduced greatly. As a result it was possible to determine the frequency and wave number of the phonons with greater accuracy.

III. RESULTS

The method of scattering of cold neutrons could be used to give the complete relationship between the

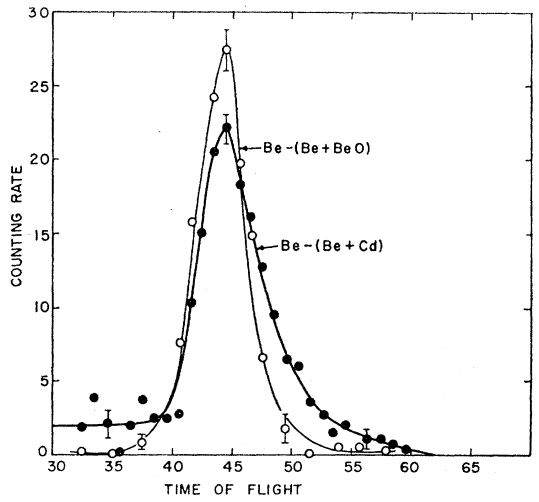

FIG. 2. Counting rate in arbitrary units as a function of the time of flight of neutrons inelastically scattered by Ge. The scale on the abscissae corresponds to the channel number of the 100-channel time analyzer. The filter difference counting rate has been multiplied by a factor of 2 for comparison purposes. The sharper incident spectrum is seen to result in a slightly narrower and more symmetrical peak in the scattered spectrum.

frequency and momentum of the optical and acoustic phonons. However, an extremely large number of phonons would have to be measured because the phonon momentum must be measured completely throughout the 3-dimensional space. Because of the impracticality of measuring so many phonons, it was decided to concentrate only on a few phonons whose momentum had values particularly relevant to checking the theoretical calculations. The reduced spread in incident neutron momentum resulting from the BeO difference method reduced the uncertainty in the final results by a factor of 2–3 smaller than could be obtained using the entire beryllium-filter distribution.

The experimental results in which the frequency of the measured phonons is given in terms of their momentum, are given in Table I. These data are plotted in Fig. 3. All phonons within an angle of ±5° of the direction given on the abscissa are indicated with solid error bars. The two points with dashed errors were about 8° from the labeled directions. The error in the optical frequencies is seen to be about ±5% and increases to approximately ±10% for the lower frequencies of the acoustical branches. The errors include contributions from the finite spread of the incident momentum spectrum as well as the resolution function of the slow chopper and the angular divergence of the incident and scattered neutrons. The solid lines through the points are intended for identification of the points with the various modes (branches) of vibration of the germanium lattice. The expression for the scattering of cold neutrons by the annihilation of one phonon, from a crystal with more than one atom per unit cell,

TABLE I. Experimental results. The phonon momentum is given in units of q_{max}, the momentum at the zone boundary. The phonon frequency is also given as an equivalent photon wave number.

Branch	q/q_{max}	Frequency ν in 10^{11} cps	Equivalent photon wave number $1/\lambda$
		[100] direction	
TA	0.06±0.03	24.3±2	81±7
TA	0.85±0.04	29.1±2	97±7
LA	0.87±0.04	47.7±4	159±12
LO	0.92±0.06	55.5±4	185±12
	0.94±0.06	56.4±5	188±16
TO	0.23±0.05	89.7±3	299±8
	0.84±0.05	86.1±5	287±16
	0.90±0.05	81.0±4	270±14
	0.96±0.04	81.9±5	273±16
		[110] direction	
TA_1	0.31±0.02	11.7±1	39±4
	0.46±0.03	16.8±1	56±3
	0.74±0.03	29.1±2	97±5
	0.80±0.03	27.9±2	93±5
TA_2	0.45±0.04	30.3±2	101±5
LA	0.95±0.06	49.2±4	164±12
	0.48±0.03	53.4±3	178±9
TO	0.30±0.10	85.8±5	286±18
	0.63±0.08	83.4±5	278±18
	0.73±0.08	81.9±5	273±16
	0.92±0.08	81.2±5	274±16
	0.99±0.04	81.0±4	270±14

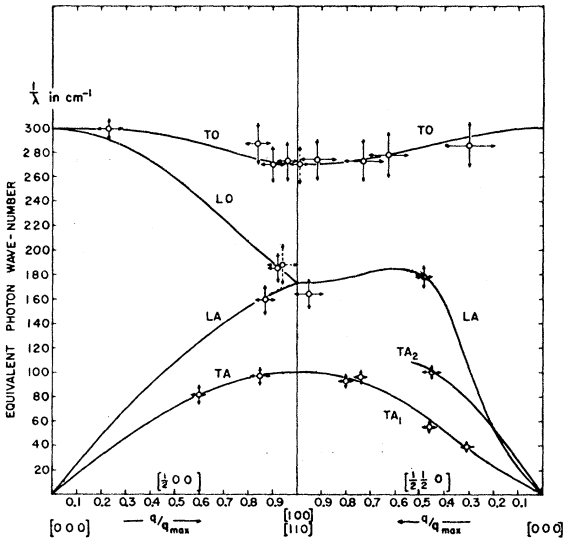

FIG. 3. Dispersion relations for germanium in the [100] and [110] directions. The solid lines drawn through the points are intended for identification of the points with the various modes of vibration of the germanium lattice. *TO* and *LO* are the transverse and longitudinal optical modes, respectively. *TA* and *LA* are the corresponding acoustical modes. In the [110] direction the degeneracy of the transverse acoustical branch is removed (TA_1 and TA_2).

has been given by Waller and Froman.[9] Assignments of the experimental points to the different branches were made by measuring the variation in intensity of the observed neutron groups as a function of the scattering angle and comparing with the approximate variation which can be computed for the various branches from the equations of Waller and Froman, using the lattice parameters of germanium. The work of identifying the branches associated with the various neutron groups was done by using only the beryllium-filtered spectrum.

Brockhouse[10] has reported results made by essentially the same method but using somewhat higher incident neutron energies and measuring the scattered-neutron energies with a crystal spectrometer. His measurement of the optical line agrees well with ours, but the acoustic vibrations, for example, in the [100] direction, differ from ours by somewhat more than the probable errors.

IV. CONCLUSIONS

The fact that the relationship between the frequency and momentum of phonons can be measured so directly with neutrons means that a direct test is then possible of theoretical calculations of the lattice vibrations. Here a most interesting matter is, for example, whether a simple Born-von Kármán calculation using nearest and next-nearest neighbors can account for the dispersion relations of Fig. 2. When the present results

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first become available, Herman[8] showed that such a calculation, even with the adjustment of the various force constants, could not account for the observations. It has now been shown by Herman[11] that by including the interaction between rather distant neighbors, say fifth or sixth, the theory can be adjusted to give the observed dispersion relations. As a result, sufficiently many parameters are available so that it is possible to fit a variety of measured results in a way that would not be possible if only nearest and next-nearest neighbors were important in lattice vibrations.

The necessity for including a force between distant neighbors seems to indicate that there is some mechanism in germanium giving rise to a long-range force. One such mechanism, a quadrupole distortion of the valence electron gas, has been postulated by Lax[12] but as yet calculations attempting to fit theory to experiment have not been made. It is hoped that by the inclusion in the calculation of some model for the long-range force, the theory will be able to explain the experimental results with only a few parameters.

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Low-Temperature Luminescence and Photoconductivity of AgCl*

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The magnitudes and the decay processes of the luminescence and the photoconductivity of AgCl have been simultaneously investigated between 4°K and 210°K. The decrease of the luminescence intensity with increasing temperature can be attributed to a competing recombination process, not accompanied by visible radiation, and having a thermal activation energy of $E=0.05$ ev. The decay times are not monotonic functions of temperature, but show maxima. These maxima can be explained in terms of a model in which energy is transported from the site of absorption to the luminescence center by mobile holes and electrons. Delay in this transport is caused by hole and electron trapping, and temperature dependence of the delay determines the temperature dependence of the decay times. Decay curves calculated on the basis of this model are in qualitative agreement with the observed data. The relative magnitudes of the luminescence and photocurrent decay times and the dependence of the decay and rise times on annealing indicate that if the major portion of the photoconductivity is due to electron motion, then luminescence occurs when holes are captured. It is suggested that this recombination occurs at silver ion vacancies.

I. INTRODUCTION

THE production of excited states of solids, such as conduction band electrons, by the absorption of light quanta may be thought of as the first step in a cyclic process whereby energy is absorbed, stored for a time, and then emitted either as photons or phonons. This paper is concerned with the electronic processes associated with the latter two steps in this cycle, i.e., storage and emission. The investigation was limited to low temperatures so that changes in the crystal due to the photographic process can be considered negligible.

It is possible to distinguish between two types of cycles. In one case energy transport is possible so that the sites of the absorption process and of the return to the ground state are not necessarily the same. In the second case transport is not possible so that the whole cycle of absorption, storage, and emission takes place in localized centers such as the luminescence center considered by Seitz.[1] In many materials it seems reasonable that both cycles may occur simultaneously. However, it is also apparent that under particular experimental conditions one or the other of the two types of cycles may be predominant as, for example, in the case of impurity activated luminescence.

In AgCl both the luminescence and the photoconductivity are excited by wavelengths in the tail of the fundamental absorption band, thus suggesting that luminescence and photoconductivity are part of the same cycle, a charge transport cycle. While the results of other experiments also suggest this relationship between the luminescence and photoconductivity,

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