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Normal Modes of Germanium by Neutron Spectrometry*

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The frequency wave-number relations of the lattice vibrations in germanium which propagate in the symmetric [100] and [111] directions (and some results in other directions) have been obtained by studying energy distributions of neutrons scattered by a germanium single crystal. The characters of the phonons were ascertained from the intensities and positions of the neutron groups in the reciprocal lattice. The methods are discussed. The results cannot be fitted by simple models using the Born-von Kármán theory, but explain satisfactorily the specific heat. The far-infrared spectrum of germanium can be interpreted as combination bands in terms of our results.

I. INTRODUCTION

IT is possible to measure the frequency wave-number relation of the normal modes of a crystal by studying the energy distributions of initially monoenergetic neutrons after scattering by the crystal.[1] The lattice frequency spectra of germanium are of particular interest from several points of view. Because of its interest as an important semiconductor many properties of germanium in which lattice vibrations play a part have been extenstively studied so that knowledge of the lattice vibrations is of special usefulness. The diamond-type lattice of germanium is perhaps the simplest lattice with more than one atom per unit cell, and hence offers the possibility of studying optical vibrations in an uncomplicated way. Finally, the elastic constants satisfy an identity due to Born according to which the forces in germanium might be peculiarly simple. We have determined the frequency wave-number relation for the lattice waves propagating in the symmetric directions,[2] and have also made some measurements in other directions. In the paper a brief statement of scattering theory for a crystal with more than one atom per unit cell is given, and the use of this theory in determining the lattice frequencies is discussed. The results verify that in the uncharged germanium lattice the optical branches are degenerate at $q=0$. The measurements cannot be fitted by simple models[3] in the Born-von Kármán theory,[3,4] general forces out to at least third neighbors being required. The results are compared with previously published measurements of the specific heat, and infrared absorption. The specific heat is satisfactorily accounted for in terms of our dispersion relations. By comparison with the infrared absorption edge measurements of MacFarlane *et al.*[5] and with other measurements it is verified that the minimum of the conduction band in germanium is at or near the 111 zone boundary. The far-infrared spectra of Collins and Fan[6] and of Simeral[7] can be interpreted in terms of our measurements. The absorption spectrum at 77°K can be interpreted as two-phonon summation bands. The spectra at 300°K and 362°K contain in addition three-phonon combinations.

II. THEORY

1. Crystal Dynamics and Neutron Scattering

According to the Born-von Kármán theory of lattice dynamics,[3,4,8] a crystal approximates a harmonically bound system and heat motions can be analyzed in terms of lattice waves which are the normal modes of the crystal. The frequencies of the normal modes (ν) are related to their wave vectors ($\mathbf{q}$) by the dispersion relation

$$\nu=\nu_j(\mathbf{q}), \tag{1}$$

where the index j signifies a particular branch of the multivalued function. For a crystal with n atoms per primitive unit cell there are $3n$ branches to the frequency spectrum. Three branches are acoustic branches for which $\nu\rightarrow 0$ as $\mathbf{q}\rightarrow 0$; the other $3n-3$ branches are optical branches for which ν tends to a finite value as $\mathbf{q}\rightarrow 0$. In certain special directions the normal vibrations are strictly transverse or longitudinal because of symmetry, but in general the polarization is neither longitudinal or transverse but is determined by the details of the interatomic forces. The lattice vibrations have amplitudes

$$C_j(\mathbf{q})\xi_{kj}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_l)/(NM_k)^{\frac{1}{2}},$$

where N is the number of cells in the crystal, M_k is the mass of the kth atom in the unit cell, and $\mathbf{R}_l$ is the position of the origin of the lth unit cell. The numbers

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† Guest scientist from Atomic Energy Establishment, Bombay, India, now returned.

[1] See B. N. Brockhouse and A. T. Stewart, Revs. Modern Phys. **30**, 236 (1958) for a general discussion and references.

[2] Some results for the [111] direction were previously given [B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **108**, 894 (1957)].

[3] H. M. J. Smith, Trans. Roy. Soc. (London) **241**, 105 (1948).

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).

[5] MacFarlane, McLean, Quarrington, and Roberts, Phys. Rev. **108**, 1377 (1957).

[6] R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954).

[7] W. G. Simeral, thesis, Michigan, 1953 (unpublished).

[8] A good review article is that of J. deLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

$C_j(\mathbf{q})$ are the complex normal coordinates. The wave vector $\mathbf{q}$ ranges over one zone of reciprocal space. The polarization vectors $\boldsymbol{\xi}_{kj}(\mathbf{q})$ in general are complex quantities of order $n^{-\frac{1}{2}}$ which satisfy certain orthonormality relations.[9]

When neutrons are scattered coherently by a crystal there are interference conditions on the scattering process, and energy must be conserved. If the crystal orientation, angle of scattering, and wavelength are such that Bragg scattering cannot occur, then a process in which one phonon is created or annihilated is usually the most important.[10] By virtue of Eq. (1) the scattered neutrons occur in groups in the energy distribution such that

$$\mathbf{k}_0-\mathbf{k}'=2\pi\boldsymbol{\tau}-\mathbf{q}, \tag{2a}$$

$$|E_0-E'|=h\nu, \tag{2b}$$

where $\mathbf{k}_0$ and $\mathbf{k}'$ are the initial and final propagation vectors of the neutron, E_0 and E' are its initial and final energies, and $\boldsymbol{\tau}$ is a vector of the reciprocal lattice. By means of Eqs. (2) each observed neutron group yields a pair of values of ν and $\mathbf{q}$ belonging to the dispersion relation (1), which can be thus constructed by repeated observation.[1]

The dispersion relations are probably chiefly of interest as an approach to the interatomic forces. On the Born-von Kármán theory the quantities ν^2 are eigenvalues of a $3n\times 3n$ determinant, the elements of which are complex functions of the force constants and of $\mathbf{q}$. In the general case determination of the force constants from the dispersion relation is difficult. Without knowledge of the polarization vectors (the eigenvectors) the force constants cannot be determined by inversion,[11] and a least-squares fitting to special models results in ambiguity unless approximate values of the force constants are known. For $\mathbf{q}$ in a symmetry direction one has some knowledge of the eigenvectors, and this permits simplification of the experiment on the one hand, and of the mathematical analysis on the other. For example, if $\mathbf{q}$ is in a mirror plane then there are n branches with their polarization vectors normal to the plane, and $2n$ branches with their polarization vectors in the plane. Correspondingly the $3n\times 3n$ determinant factors into $n\times n$ and $2n\times 2n$ determinants. Other symmetry operations can reduce the determinants further. However, one must be able to assign a value of ν obtained experimentally to the correct factor. This can be done by correlating the intensities of the neutron groups with their positions in the reciprocal lattice.

The theory of the inelastic scattering by a crystal with more than one atom per unit cell has been given by Waller and Froman.[12] The cross section for production of a neutron group with creation or annihilation of one phonon is, after some manipulation,

$$\sigma_j(\mathbf{k}_0\rightarrow\mathbf{k}')=\frac{\hbar}{4\pi}\frac{k'}{k}\begin{Bmatrix} N_j \\ N_j+1\end{Bmatrix}e^{-2W}\frac{g_j^2(\mathbf{q},\boldsymbol{\tau})}{|J_j|} \tag{3}$$

per 4π steradians per unit cell. For phonon annihilation (neutron gain of energy), $N_j=[\exp(h\nu/k_BT)-1]^{-1}$ is used; for phonon creation, N_j+1 is used. The factor

$$J_j=1+(\epsilon h/2E')[\mathbf{k}'\cdot\mathrm{grad}_q\nu_j], \tag{4}$$

where $\epsilon=+1$ for neutron energy loss and -1 for neutron energy gain, sums over the number of normal modes which contribute to one neutron group, and e^{-2W} is the Debye-Waller factor. The quantity

$$g_j^2(\mathbf{q},\boldsymbol{\tau})=\left|\sum_k \frac{b_k\mathbf{Q}\cdot\boldsymbol{\xi}_{jk}(\mathbf{q})}{[M_k\nu_j(\mathbf{q})]^{\frac{1}{2}}}\exp(i\mathbf{Q}\cdot\mathbf{R}_k)\right|^2 \tag{5}$$

is analogous to the structure factor in elastic scattering. Here $\mathbf{R}_k$ is the position of the kth atom in the unit cell, b_k is its bound scattering length, and $\mathbf{Q}\equiv\mathbf{k}_0-\mathbf{k}'=2\pi\boldsymbol{\tau}-\mathbf{q}$ by virtue of Eq. (2a). It is observed that the structure factor g^2 depends on $\boldsymbol{\tau}$ and therefore does not repeat over one zone, but rather over a larger unit in reciprocal space. Comparison of Eq. (3) with measured cross sections permits assignment of the character of the observed phonons.

2. Lattice Dynamics and Neutron Scattering for Germanium

Germanium has the diamond structure consisting of two identical interpenetrating face-centered cubic lattices based on atoms at (0,0,0) and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in the cubic unit cell ($a=5.6575$ A). The primitive rhombohedral unit cell contains two atoms and there are thus six branches in the vibration spectrum. There are six mirror planes {110} and four three-fold axes of rotation [111]. The lattice dynamics have been extensively treated by Smith[3] and by others.[13–15] The dispersion relation is given by the solutions of the characteristic equation

$$|D-4\pi^2M\nu^2I|=0, \tag{6}$$

where D is the (6×6) dynamical matrix and I is the unit matrix. In the mirror planes the determinant factors into 2×2 and 4×4 determinants. The solutions of the 2×2 determinant belong to branches whose polarization vectors are perpendicular to the plane, and therefore do not contribute to neutron scattering experiments if $\mathbf{k}_0$ and $\mathbf{k}'$ are in the mirror plane. There are thus four branches effective in the mirror plane. In [100] and [111] directions the 4×4 determinant factors

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[9] Reference 4, Eqs. (38.25), p. 298.

[10] R. Weinstock, Phys. Rev. **65**, 1 (1944).

[11] This was pointed out to us some time ago by Dr. N. K. Pope. See also A. J. E. Forman and W. M. Lomer, Proc. Phys. Soc. (London) **B70**, 1143 (1957).

[12] I. Waller and P. O. Froman, Arkiv Fysik **4**, 183 (1952).

[13] K. G. Ramanathan, Proc. Indian Acad. Sci. **26**, 481 (1947).

[14] D. St. James, J. Phys. Chem. Solids **5**, 337 (1958).

[15] W. Harrison, thesis, University of Illinois, 1956 (unpublished).

again into two 2×2 determinants because of symmetry. These equations can be solved explicitly and have solutions of the form

$$4\pi^2 M\nu_j^2 = Y + Z_j(\mathbf{q},11) \pm |Z_j(\mathbf{q},12)| \qquad (7)$$

where Y is a linear combination of the force constants, $Z(\mathbf{q},11)$ is a real function of $\mathbf{q}$ and of the force constants between atoms on the same sublattice, and $Z(\mathbf{q},12)$ is a complex function of $\mathbf{q}$ and of force constants between atoms on different sublattices. One of the 2×2 determinants gives the transverse modes and the other the longitudinal modes. The positive sign in (7) applies to the optical branch and the negative to the acoustical branch.

For $\mathbf{q}$ in [100] or [111] directions the polarization vectors of the two atoms in the unit cell ($k=1, 2$) are in the same direction and either parallel to $\mathbf{q}$ (longitudinal) or perpendicular (transverse). Hence we can write

$$\boldsymbol{\xi}_{kj}(\mathbf{q}) = \boldsymbol{\xi}_j \xi_{kj}(\mathbf{q}),$$

where $\boldsymbol{\xi}_j$ is a unit vector, and for both polarizations and both directions the ratio

$$\xi_{1j}(\mathbf{q})/\xi_{2j}(\mathbf{q}) = \pm Z_j(\mathbf{q},12)/|Z_j(\mathbf{q},12)|. \qquad (8)$$

The + sign refers to optical modes and the − sign to acoustical modes. The structure factor is then

$$g_j^2(\mathbf{q},\boldsymbol{\tau}) = \frac{(b\boldsymbol{\xi}_j\cdot\mathbf{Q})^2}{2M\nu_j}\left|\frac{\xi_{1j}(\mathbf{q})}{\xi_{2j}(\mathbf{q})} + \exp\left(ia\mathbf{Q}\cdot(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4})\right)\right|^2, \qquad (9)$$

where a is the lattice constant of the cubic unit cell.

The reciprocal lattice is body-centered cubic. Figure 1 shows the (1$\bar{1}$0) plane of the reciprocal lattice, each point being surrounded by the zone over which $\mathbf{q}$ ranges. The structure factor, Eq. (9), repeats over the larger unit shown by bold lines. For diamond-type lattices with general forces between neighbors there are two independent force constants, α and β, and, according to Smith,[3] three second-neighbor constants, λ, μ, and ν. Other workers have added[16] an additional second-neighbor constant τ, which, however, is not effective in the symmetric directions. Smith gives equations for the elastic constants in terms of the force constants which are listed in Table I.

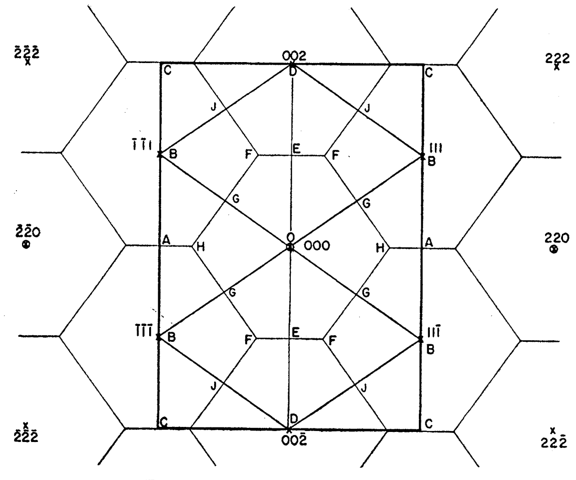

FIG. 1. The (1$\bar{1}$0) plane of the reciprocal lattice of germanium, each lattice point surrounded by its zone. The rectangular figure *CACDCACDC* is the unit over which the structure factor repeats.

TABLE I. Experimental and computed elastic constants. The errors on the experimental constants are believed less than 1%.

Constant	Experimental value[a] (dynes/cm²)	Expression on second-neighbor model	Best fit, second-neighbor model (dynes/cm²)
c_{11}	1.289×10^{12}	$ac_{11}=\alpha+8\mu$	1.280×10^{12}
c_{12}	0.483×10^{12}	$ac_{12}=-\alpha+2\beta$ $-4\mu-4\lambda+8\nu$	0.505×10^{12}
c_{44}	0.671×10^{12}	$ac_{44}=\alpha-(\beta^2/\alpha)$ $+4\lambda+4\mu$	(0.257×10^{12} calc)

[a] See reference 18.

The elastic constants of germanium[17,18] (Table I) satisfy to about 1% an identity due to Born[19]:

$$4c_{11}(c_{11}-c_{44}) = (c_{11}+c_{12})^2, \qquad (10)$$

which is a necessary, though not sufficient condition that only first neighbors be important. Dispersion relations for germanium have been computed by Hsieh[20] on the assumption that only first neighbor forces in fact occur. The specific heat computed by Hsieh did not fit the experimental measurements, though some resemblance was shown, and the dispersion relations do not agree with infrared absorption[5] and neutron scattering[2] measurements. The model is therefore clearly insufficient. Nevertheless it is likely that the first-neighbor model furnishes a useful first approximation.

With the values for α and β determined from the elastic constants on the first-neighbor model, the structure factors have been computed along the lines in reciprocal space shown in Fig. 1, and are presented in Fig. 2. By reason of symmetry the acoustical and optical longitudinal branches in the [100] directions actually form one continuous branch when plotted in reciprocal space and not in the reduced-zone scheme. This is the reason for the especially simple behavior of the structure factors for these branches. The exact shape of the other structure factors depends on the values of the force constants, but must pass through one of the points marked X at the zone boundary.

III. EXPERIMENTAL METHODS AND RESULTS

Energy distributions of initially monoenergetic neutrons scattered by a single crystal of germanium at room temperature were obtained. A crystal spectrom-

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[16] This was pointed out to us, individually, by Dr. M. Lax and Dr. F. Herman.

[17] Bond, Mason, McSkimin, Olson, and Teal, Phys. Rev. **78**, 176 (1950).

[18] H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

[19] M. Born, Ann. Physik **44**, 605 (1914), quoted in reference 3.

[20] Y-C. Hsieh, J. Chem. Phys. **22**, 306 (1954).

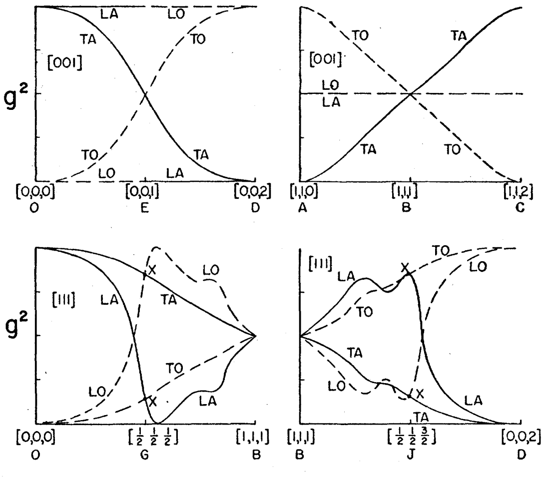

FIG. 2. Calculated structure factors on the first-neighbor model ($\alpha=7.27\times10^4$, $\beta=5.00\times10^4$ dyne/cm) in units of $(b\boldsymbol{\xi}\cdot\mathbf{Q})^2/2M\nu$.

eter at the *NRX* reactor supplied the initial monoenergetic neutrons, and another crystal spectrometer employing the (111) plane of an aluminum crystal analyzed the energy of the scattered neutrons. The angle of scattering (ϕ) and the crystal orientation were equally available as independent variables: for trivial experimental reasons the wavelength of the incoming neutrons could not readily be changed. Neutrons of 1.12 A were used in initial experiments, but most of the work was performed using 1.52 A neutrons. The monochromating and analyzing spectrometers each had an angular acceptance of about one degree full width at half-maximum, including crystal mosaic. The wavelength resolution of the incoming beam was about 0.04 A full width at half-maximum and the analyzing spectrometer also had this resolution. Detailed analysis of resolution effects is difficult because of correlations between the effects of the different resolution elements. Some details of experimental methods have been published elsewhere.[1,21]

Typical neutron groups observed with the germanium crystal in various orientations and for various angles of scattering are shown in Fig. 3. The neutron group produced by elastic scattering[22] from vanadium metal is also shown. The width of this group corresponds to the energy resolution of the apparatus. Two single-crystal specimens of germanium were used: a cylindrically symmetrical, irregular boule about 1 in. diameter and 3 in. long, and a rectangular parallelopiped[23] about 1 in.×2 in.×3 in. The crystals were aligned with their $[1\bar{1}0]$ axes vertical, so that the vectors k_0 and k' were always in the $(1\bar{1}0)$ plane. Because of the irregular shapes of the specimens good values for the intensities could not be obtained.

As was seen in Sec. II it is especially desirable to obtain the dispersion relations in the symmetric directions. It is not possible to do this directly so an experimental "method of successive approximations" was used, for which the multiple-axis crystal spectrometer is especially suitable because of its flexibility. The calculations of Hsieh[20] were used as a starting point and $\mathbf{k}_0$ and $\mathbf{k}'$ were calculated for a particular desired phonon by using Eqs. (2) and Hsieh's $\nu_j(\mathbf{q})$ relation. The magnitude of $\mathbf{k}_0$ was constant, being fixed by the wavelength of the incoming neutrons, and the direction of $\mathbf{k}_0$ was adjusted by changing the orientation of the crystal in the $(1\bar{1}0)$ plane. The direction of $\mathbf{k}'$ was adjusted by changing the angle of scattering ϕ. If the observed neutron group did not have $\mathbf{q}$ in the desired direction a new calculation, based on the phonon actually observed, was made and the process repeated. In all cases the position of the neutron group in the reciprocal lattice was selected to make the structure factors shown in Fig. 2 as large as possible, and the polarization factor $(\mathbf{Q}\cdot\boldsymbol{\xi})^2$ a maximum. Where possible, phonon creation (neutron energy loss) was used since the instrumental resolution improves as E' decreases. As far as possible, positions in reciprocal space which gave particularly sharp neutron groups were selected, and positions in which broad neutron group would occur were avoided.[24] As the real structure factors (g^2) are actually unknown, the philosophy was adopted that the structure factors of Fig. 2 could safely be used whenever they did not depend strongly on $\mathbf{q}$. For the longitudinal branches in the [111] directions g^2 depends strongly on $\mathbf{q}$, and here the zone boundaries were approached from safe regions,

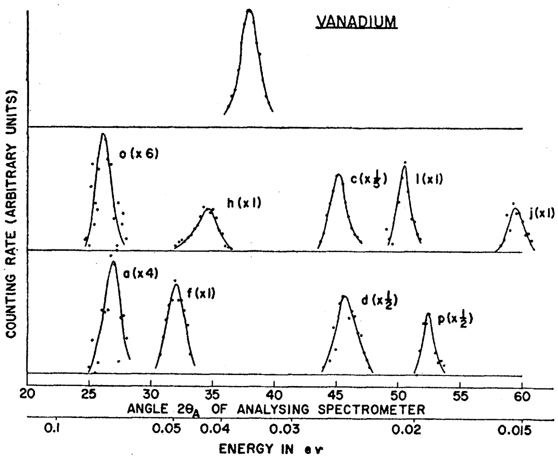

FIG. 3. Counting rates for typical neutron groups plotted as a function of the angle of the analyzing spectrometer.

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[21] B. N. Brockhouse, Phys. Rev. **106**, 859 (1957); Suppl. Nuovo cimento (to be published).

[22] B. N. Brockhouse, Can. J. Phys. **33**, 889 (1955).

[23] Kindly loaned by the Texas Instrument Company through the courtesy of Dr. W. R. Runyan.

[24] If the $\nu(\mathbf{q})$ relation is such that the quantity $|J|$ [Eq. (4)] is large ($\gg1$), then the groups will be sharp. If $|J|\ll1$, broad groups will be observed since then Eqs. (2) can be satisfied over a range of values of $\mathbf{k}'$. See references 1 and 12.

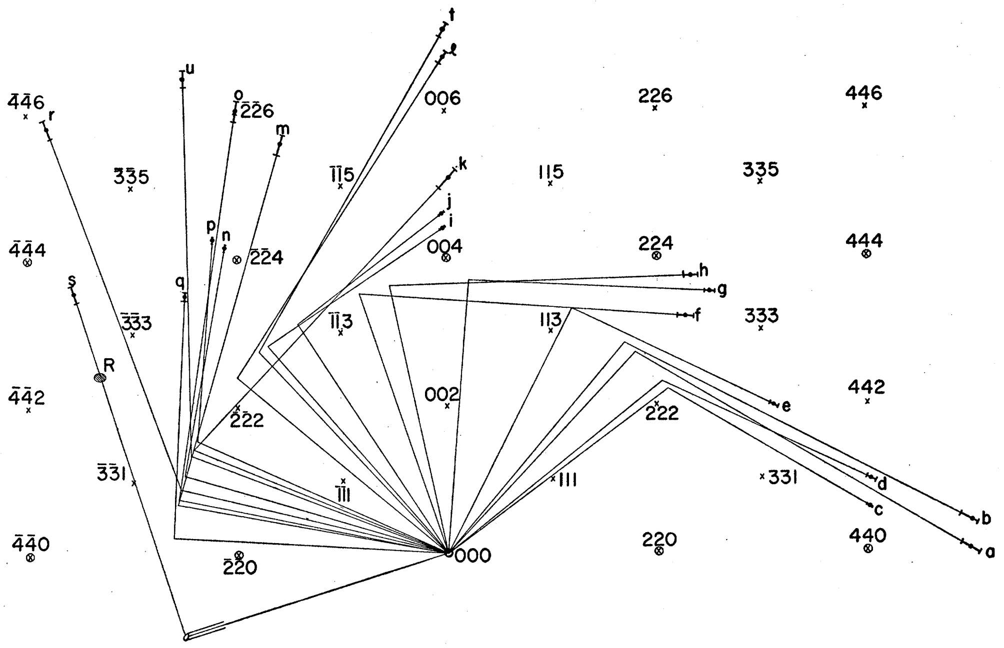

FIG. 4. The $(1\bar{1}0)$ plane of the reciprocal lattice, with neutron groups plotted according to Eqs. (2).

point by point with caution, to try to ensure that correct assignments of the branches were made.

Some typical results are shown in Fig. 4 plotted on the reciprocal lattice. The widths at half-maximum of the neutron groups are indicated by the heavy bars. A rough estimate of the resolution function (half-intensity contour) is shown as the shaded area "*R*". Neutron groups which gave $\mathbf{q}$'s within $\pm 5°$ of the desired directions were selected; their frequencies (ν) were calculated from Eq. (2b) and were plotted in Fig. 5 as ν (in units of 10^{12} cycles/sec) *vs* $\mathbf{q}$. Almost always the polarization and type (optical or acoustical) could be unambiguously determined from the fact that an intense phonon was observed at that particular position in reciprocal space. The small letters refer to the appropriate neutron distributions of Fig. 3 and to appropriate points on the reciprocal lattice of Fig. 4. The approximate errors were formally computed by taking them to be half of the variation produced on ν and $\mathbf{q}$ by the width at half-maximum of the neutron group. As probable errors they are likely conservative, particularly for the frequency. There are also errors connected with fixing the direction of $\mathbf{q}$ which are perhaps a little larger than the errors in the magnitude of $\mathbf{q}$. In the symmetry directions the first derivatives of ν in the direction perpendicular to $\mathbf{q}$ are zero. The second derivatives are probably negligible for the optical branches but not for the acoustical branches. For the *TA* branches the second derivatives are positive and therefore the frequencies of Fig. 5 for these branches are too high by a few percent. The errors given for ν in Fig. 5 may thus be reasonable probable errors except that the true values for the *TA* modes are more likely to lie on the low side than the high side of the points.

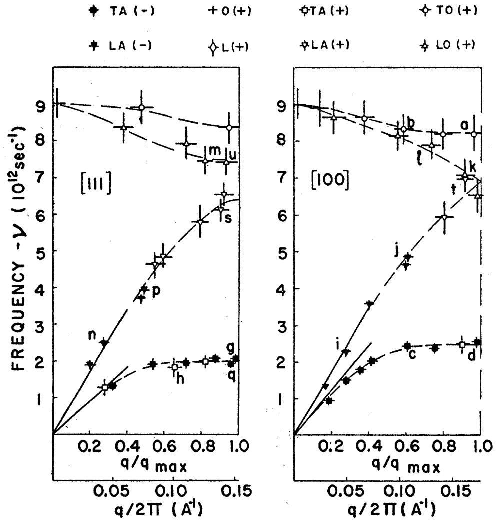

FIG. 5. Dispersion relations in [100] and [111] directions. The legend at the top indicates the polarization and character of the vibrations. The signs indicate neutron energy loss (—) or gain (+). The heavy lines indicate the slope of the appropriate velocity of sound as calculated from the elastic constants.

In the process of successive approximation it turned out that a little less than half the measured phonons were discarded.

Because it was thought that some forces might not appear in the symmetric directions, it was decided to obtain data in other directions. In Fig. 6, frequencies belonging to the branch which is transverse acoustic in the symmetric directions are presented for $\mathbf{q}$'s lying on the zone boundary. The capital letters refer to Fig. 1.

For small $\mathbf{q}$ the results of Fig. 5 probably agree within the errors with the elastic constants, the appro-

TABLE II. Frequencies of phonons at zone boundary and at $\mathbf{q}=0$ with probable errors.

Designation	This work (10^{12} cycles/sec)	Other work (10^{12} cycles/sec)	Reference	$4\pi^2 M\nu^2$ Second-neighbor model	Best fit second-neighbor (10^{12} cycles/sec)
TO [100]	8.25 ± 0.3			$4\alpha+4\beta+8\mu+8\lambda$	8.12
L [100]	6.9 ± 0.4	6.6	25	$4\alpha+16\mu$	7.12
TA [100]	2.45 ± 0.15			$4\alpha-4\beta+8\mu+8\lambda$	2.78
TO [111]	8.4 ± 0.3	8.6	26	$6\alpha+2\beta+8\mu+4\lambda-4\nu$	8.75
LO [111]	7.4 ± 0.3			$2\alpha+4\beta+8\mu+4\lambda+8\nu$	7.05
LA [111]	6.45 ± 0.3	6.65 6.65	5 26	$6\alpha-4\beta+8\mu+4\lambda+8\nu$	5.68
TA [111]	1.95 ± 0.10	1.88 2.06	5 26	$2\alpha-2\beta+8\mu+4\lambda-4\nu$	2.56
O [$q=0$]	9.0 ± 0.3	8.9	28	8α	9.04

priate velocities of sound being indicated by the slope of the heavy lines. A few measurements at special positions are also available for comparison. Within the errors our results agree with values for the transverse and longitudinal acoustic phonons at the zone boundary in the [111] direction obtained by MacFarlane *et al.*[5] from infrared measurements, with the longitudinal phonon at the zone boundary in the [100] direction deduced by Weinreich[25] from measurements on the acousto-electric effect, and with values for the transverse acoustic and optical phonons in the [111] direction obtained by Haynes[26] from emission spectroscopy measurements. All the results quoted here depend for their assignments on the assumption that the maximum in the valence band is at the origin and that the minimum in the conduction band is at the zone boundary in the [111] direction.[27] The agreement between our results and those quoted indicates once again the correctness of the placement of the electron bands. The optical frequency at $\mathbf{q}=0$ agrees with a value obtained from neutron measurements by Pelah *et al.*[28] The general level of the optical branches is in agreement with an observation of Pelah *et al.*[29] that a large number of phonons of unstated $\mathbf{q}$ have frequencies within 5% of 8.2×10^{12} sec^{-1}. Our results for some important points in reciprocal space, and the results of the authors quoted above, are listed in Table II. In assigning values and errors, account has been taken of the fact that the slopes of the $\nu(\mathbf{q})$ curves are zero at these points, except for the longitudinal [100] branch, and that the [111] and [100] transverse accoustic branches are local minima in the directions normal to $\mathbf{q}$. The errors are estimated probable errors "all things considered." No errors are available for the results of the other workers.

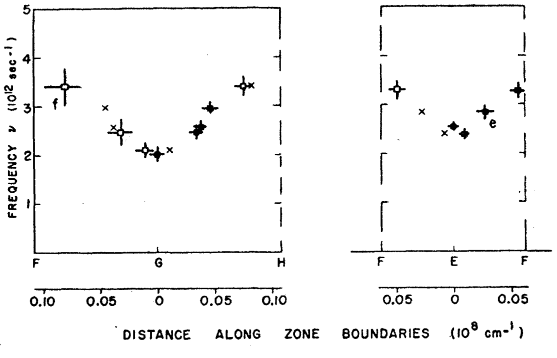

FIG. 6. Dispersion relation of "*TA*" branch along zone boundary. The crosses indicate phonons reflected through the symmetry directions.

IV. DISCUSSION

1. Force-Constant Models

As discussed in Sec. II, the elastic constants of germanium obey an identity which suggests that only the general first-neighbor force constants are important. The measured frequencies are, however, greatly different from the calculations of Hsieh[20] on this model. We have made computations using the general second-neighbor force model of Smith.[3] At the zone boundary the quantity $4\pi^2 M\nu^2$ is linear in the force constants for all branches in the two symmetric directions, as shown in Table II. The reststrahlen frequency at $\mathbf{q}=0$ and two of the elastic constants (c_{11} and c_{12}, Table I) are also linear in the force constants. We have made least-squares determinations of the five force constants on the second-neighbor model, using the ten experimental linear equations, weighted according to their inverse square errors. The calculated values for best fit are given in Tables I and II. The disagreement found persists for any reasonable assignment of weights and is not removed by omission of any single measurement from consideration.[29a]

2. Specific Heat

The specific heat of germanium has been measured by Hill and Parkinson,[30] and by Estermann and Weertman[31] at temperatures in the range 5°K to 200°K, and

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[25] Weinreich, Sanders, and White (private communication).

[26] J. R. Haynes (private communication via M. Lax).

[27] See F. Herman, Revs. Modern Phys. **30**, 102 (1958).

[28] Pelah, Eisenhauer, Hughes, and Palevsky, Bull. Am. Phys. Soc. Ser. II, **3**, 60 (1958).

[29] Pelah, Eisenhauer, Hughes, and Palevsky, Phys. Rev. **108**, 1091 (1957).

[29a] St. James (reference 14) suggests that still another condition may be derived from the elastic constants. This condition amounts to setting the force constant $\beta\simeq0$ and hence if St. James' ideas are valid the conclusion of lack of fit holds *a fortiori*.

[30] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

[31] I. Estermann and J. R. Weertman, J. Chem. Phys. **20**, 972 (1952).

by Keesom and Pearlman[32] at helium temperatures. The measurements are presented in Fig. 7 as a Θ_D *vs* T curve. The value of Θ_D at 0°K (Θ_0) is about in agreement with a value of 374° calculated[8] from the elastic constants. The calculated Θ_D *vs* T curve of Hsieh[20] is shown as a solid line. Hsieh computed the frequencies of all six branches at 29 points in reciprocal space, giving 174 frequencies. We have measured the frequencies at eight of his points in reciprocal space and find that the mean of the 48 frequencies is 82% of the mean of his corresponding values. Simply lowering his values of Θ_D by 18% as shown by the dashed line of Fig. 7 improves the fit considerably. Further consideration shows that this is probably an overcorrection as observed.

The value of Θ_D as $T \to \infty$ can be defined as

$$\Theta_\infty = 4h\bar{\nu}/3k_B.$$

If the average frequency $\bar{\nu}$ calculated from Hsieh's results is multiplied by 0.82 as before, Θ_∞ turns out to be 376°, in good agreement with Fig. 7. We conclude that our dispersion relations are consistent with the specific heat measurements.

3. Far Infrared Absorption

Lord,[33] Briggs,[34] Collins and Fan,[6] and Simeral[7] have measured the far-infrared absorption by germanium and find a complicated spectrum extending from 11 microns to beyond 100 microns wavelength. The measurements of Collins and Fan at 77°K and 300°K, and those of Simeral at room temperature are shown in Fig. 8. In the region of overlap the two sets of measurements agree perfectly for our purposes and only those of Collins and Fan are shown. First-order infrared absorption (absorption with creation of one phonon) is forbidden in germanium. Simeral considered the possibility that the absorption was a second-order[35] (two-phonon) process but could not get a fit with the then existing knowledge of the lattice vibrations, and introduced the idea that the presence of several isotopes in germanium causes a relaxation of the selection rules against first-order absorption. Collins and Fan considered their discovery of the temperature dependence to show that the normally forbidden absorption becomes permitted by virtue of the distortion of the lattice by the lattice vibrations, and suggested the possibility of the absorption being a second-order process, but interpreted the strong band at 10.4×10^{12} sec^{-1} as the reststrahlen frequency. Lax and Burstein[36] worked out the basic theory of the second-order process on the assumption that it arises from second-order terms in the phonon expansion of the electric moment; i.e., that a lattice vibration induces charges on the atoms which would otherwise not be present, and these fluctuating charges are coupled to the electromagnetic field by another lattice vibration. The two vibrations concerned must have wave vectors $(\mathbf{q}_1, \mathbf{q}_2)$ such that $\mathbf{q}_1 + \mathbf{q}_2 = \pm \mathbf{q}_\nu$, where $\mathbf{q}_\nu$ is the wave vector of the infrared radiation, in

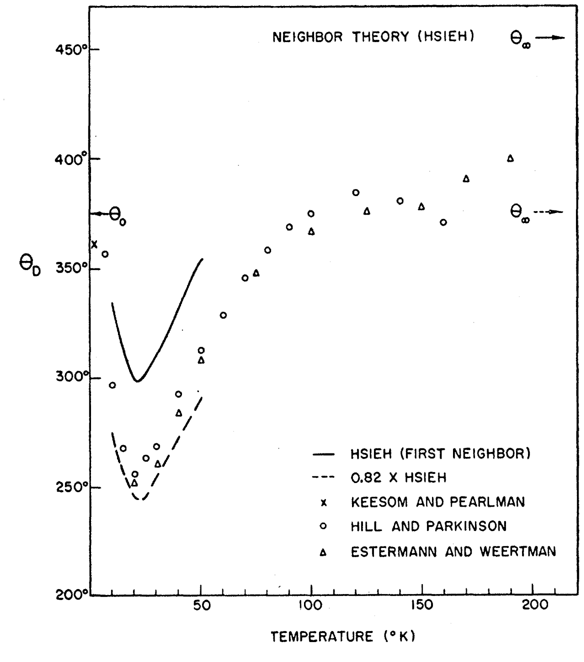

Fig. 7. Experimental and calculated Θ_D *vs* T curves for germanium.

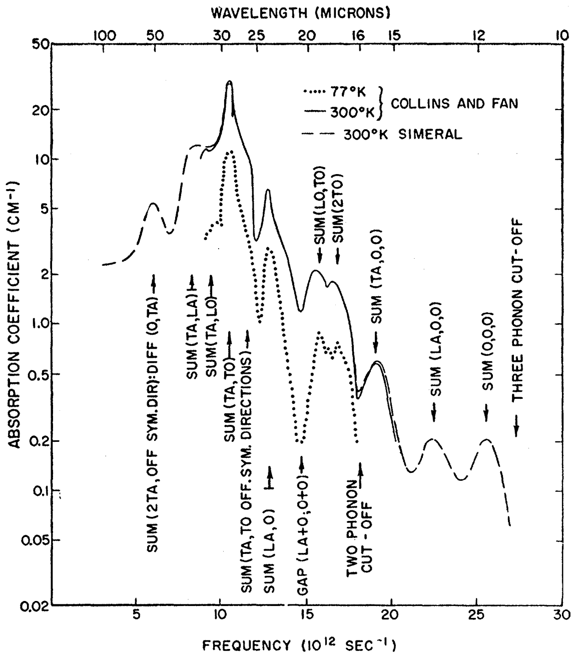

Fig. 8. Far-infrared absorption coefficient of germanium and assignments of combination bands.

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[32] P. H. Keesom and N. Pearlman, Phys. Rev. 91, 1347 (1953).
[33] R. C. Lord, Phys. Rev. 85, 140 (1952).
[34] H. B. Briggs, J. Opt. Soc. Am. 42, 686 (1952).
[35] M. Born, Revs. Modern Phys. 17, 245 (1945); N. K. Pope, thesis, Edinburgh, 1948 (unpublished); Burstein, Oberly, and Plyler, Proc. Ind. Acad. Sci. 28, 388 (1948).
[36] M. Lax and E. Burstein, Phys. Rev. 97, 39 (1955).

general very small. Lax and Burstein showed that absorption was forbidden if the two vibrations belonged to the same branch. Thus, since $\mathbf{q}_1 \simeq -\mathbf{q}_2$ and $\nu_j(\mathbf{q}) = \nu_j(-\mathbf{q})$, only phonons having the same wave vector but belonging to different branches (j,j') can combine. Other selection rules probably occur but these can be expected to cause vanishing of the matrix elements for particular **q**'s and not to forbid combinations of entire branches.[36a]

We find that, in fact, every major feature of the absorption of Fig. 8 can be readily explained as multiple-phonon processes in terms of our dispersion relations and the selection rule of Lax and Burstein. The positions of the various assigned combinations are indicated by the arrows in Fig. 8, as computed from the dispersion relations of Fig. 5. Because the two TA (and the TO) branches are degenerate in the symmetric directions, $(2TA)$ and $(2TO)$ combinations are forbidden by the selection rule of Lax and Burstein in these directions. Away from the symmetric directions these combinations are probably allowed, but the $(2TA)$ combination would have a considerably higher frequency than the 4 or 5×10^{12} sec^{-1} it would have in the symmetric directions as shown by Fig. 6. We note also that combinations (LA,LO) are forbidden for the [100] direction near the zone boundary and thus the gap between (LA,O) and (O,O) combinations is preserved. The intensities of the infrared absorption are roughly consistent with the multiple-phonon interpretation both as to dependence on frequency and on the temperature. The absolute absorption coefficient leads to a mean value[37] for the matrix element $|MH_{jj'}|$ in Lax and Burstein's theory of ~0.5 electronic charge/angstrom, a reasonable number in our estimation. Thus the far-infrared absorption of germanium at 77°K seems to be satisfactorily accounted for as two-phonon summation bands, with three-phonon summation bands and a two-phonon difference band also involved at room temperature. Individual errors in the assignments of Fig. 8 may well have occurred, but there can be little doubt of the over-all correctness in view of the excellent agreement.

4. General Discussion

The results of these neutron experiments thus seem to be in good agreement with other experimental data in the literature, but are not in agreement with any very simple model of the interatomic forces. This lack of a suitable model is disturbing. The Born-von Kármán calculation might be extended to more and more neighbors until agreement is reached, but then the satisfaction of Born's identity [Eq. (10)] must be dismissed as an accident. We, ourselves, wonder if the satisfaction of the Born identity is not actually significant, and if the deviations observed at short wavelengths are not the result of failure of the Born-von Kármán theory, perhaps in the adiabatic approximation. The magnitude of the infrared absorption indicates that appreciable readjustment of the electronic structure must take place because of the presence of a lattice vibration and if this readjustment cannot be completed in a short enough time the effective force constants may depend on the wave number and frequency of the vibration.

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[36a] *Note added in proof.*—See also M. J. Stephen, Proc. Phys. Soc. (London) **71**, 485 (1958).

[37] Using values for the dielectric constant $\epsilon=16$ and the refractive index $n=4$ [see H. Y. Fan, in *Solid State Physics*, edited by E. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 295]. The quantity E_e/E was assumed to be unity. The integrated absorption from Fig. 8 for particular (j,j') was estimated and mean values of the frequencies used. All wave vectors were assumed to contribute equally, and no polarization factor was included. The estimate is thus probably low.