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Phonon Dispersion Curves in Bismuth*

Abstract: Dispersion curves for phonons propagating in the trigonal direction in bismuth at room temperature and at 75°K have been obtained in a neutron inelastic scattering experiment. Observed frequencies (units 10^{13} rad/sec) at 75°K are as follows: at the zone center, $\omega_{TO} = 1.40 \pm 0.02$, $\omega_{LO} = 1.89 \pm 0.02$; at the zone boundary in the trigonal direction, $\omega_{TA} = 0.73 \pm 0.01$, $\omega_{LA} = 1.12 \pm 0.02$, $\omega_{TO} = 1.91 \pm 0.02$, $\omega_{LO} = 2.03 \pm 0.02$. At room temperature, the observed frequencies were about 1.5 percent lower. Data were also obtained for longitudinal phonons propagating in the binary direction at 75°K. It is interesting to note that the splitting between the zone boundary frequencies for the optical and acoustic branches for each polarization is quite large. This splitting is difficult to understand if bismuth is thought of as a slightly distorted simple cubic lattice. The experimental results may be qualitatively understood if bismuth is considered to be made up of a series of double layers normal to the trigonal axis. The atoms in each double layer form a crinkled hexagonal net with strong, probably covalent, bonds between atoms. The forces between atoms on adjacent double layers are relatively weak. This model is consistent with the easy cleavage of bismuth normal to the trigonal axis. Analysis of the trigonal dispersion curves in terms of a linear chain model indicates that there are significant forces connecting a given atom with atoms situated on the four planes on either side of it.

Introduction

Bismuth crystallizes in the trigonal system, class $R\bar{3}2/m$, with two atoms per unit cell. It has one trigonal axis, usually termed the Z axis, with a center of inversion located on it. Through the center of inversion, perpendicular to the Z axis, are three binary axes, each with a mirror plane normal to it. One of the binary axes is designated the X axis, and a Y axis is chosen to complete a right-handed orthogonal coordinate system. The Y-Z plane is one of the three mirror planes.

For phonons which propagate in the trigonal direction, the polarization directions are completely determined by symmetry, there being one longitudinal and two degenerate transverse modes. Since there are two atoms per unit cell, there will be one acoustic branch and one optical branch for each mode. The equations of motion for each mode are formally equivalent to those for a linear chain with two identical particles per unit cell, in which the force constants represent the forces between planes of atoms in the three-dimensional crystal. For phonons that propagate in the X and Y directions, only one of the three polarization directions is fixed by symmetry, and no corresponding simplification of the equations of motion occurs.

In this paper, we report measurements of the dispersion curves for phonons propagating in the trigonal direction in bismuth, at room temperature and at 75°K. These data are analyzed in terms of the vibrations of a linear chain to obtain interplanar force constants. An experimental dispersion curve for longitudinal phonons propagating in the binary direction at 75°K is also presented. Some early measurements of the dispersion curves for acoustic modes at room temperature were given in a previous report.[1]

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The experiment

The experimental dispersion curves were obtained by observing the coherent inelastic scattering of monoenergetic neutrons due to a process in which a single phonon is created in the sample crystal. If $\hbar\omega$ and $\hbar\mathbf{Q}$ are the energy and momentum transferred from the neutron to the crystal, then this "one-phonon" scattering can take place only when ω and $\mathbf{Q}$ are equal to the frequency and extended-zone wave vector of one of the phonons in the vibration spectrum of the crystal. The first-zone wave vector of the phonon is given by $\mathbf{q} = \mathbf{Q} - \mathbf{G}$, where $\mathbf{G}$ is 2π times a reciprocal lattice vector.

The conditions of the experiment were arranged to keep $\mathbf{Q}$ fixed at a desired value in the reciprocal lattice of the sample crystal, while scanning a preselected range of values of ω. A phonon of wave vector $\mathbf{Q}$ was indicated by the detection of a neutron group centered at the phonon frequency, and having a width determined by the instrumental resolution and the natural width of the phonon. The measurements were carried out on the Los Alamos three-axis neutron diffraction spectrometer, a diagram of which is shown in Fig. 1.

In this experiment, the phonon polarization directions were known from symmetry, and all that was needed was a means of assigning one of the known polarizations to each observed phonon. This was accomplished by means of a factor in the cross section for the one-phonon process, which makes the scattered neutron intensity due to a phonon with polarization vector ξ proportional to $(\mathbf{Q}\cdot\xi)^2$. For a given first-zone wave vector $\mathbf{q}$, it was possible to find an equivalent extended-zone wave vector $\mathbf{Q}$ such that the factor $(\mathbf{Q}\cdot\xi)^2$ was near zero for two polarization directions. Any phonon observed under these conditions could then be assigned the remaining polarization direction. This method of assigning polarizations was satisfactory except for the longitudinal acoustic branch in the trigonal direction, and for both longitudinal branches in the binary direction. In these cases, in addition to the expected longitudinal phonons, neutron groups were observed which apparently correspond to transverse phonons of the same $\mathbf{q}$. Such anomalous neutron groups have been observed in lead by Brockhouse et al.,[2] who ascribe them to a double scattering process, in which a one-phonon scattering is preceded or followed by Bragg scattering. In the cases in which anomalous neutron groups were observed, those corresponding to the desired polarization were identified by the use of secondary information, such as initial slopes of the acoustic branches calculated from elastic constants, independent measurements of the dispersion curves for the transverse branches, and a general knowledge of the trend of the dispersion curve in question. However, the identification of the polarization must remain less certain for these cases than for the others, in which only the expected neutron groups were observed.

An additional difficulty caused by the anomalous neutron groups in the case of the trigonal longitudinal acoustic branch was that for some values of $\mathbf{q}$ the two neutron groups were not well resolved, particularly in the room temperature data. This made the location of the centers of the desired groups more difficult, and consequently the

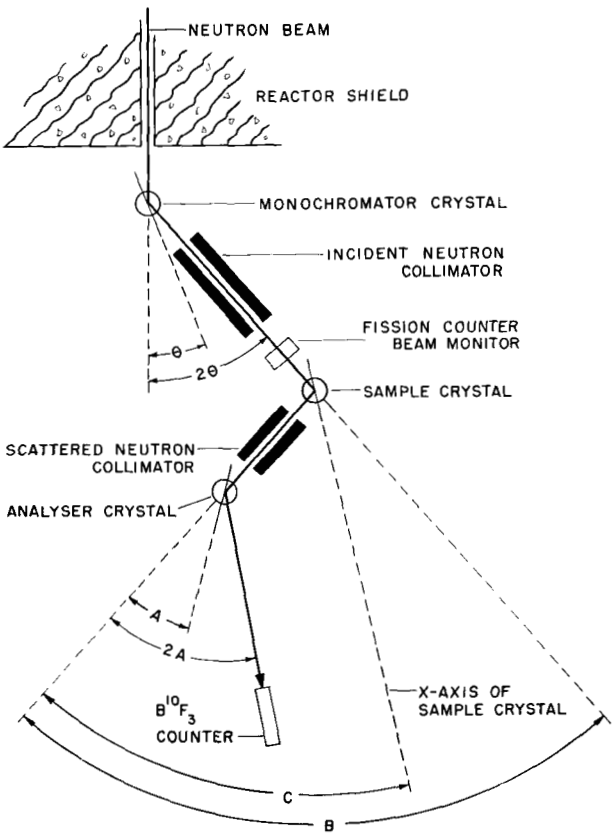


Figure 1 **Schematic diagram of the three-axis spectrometer used to determine dispersion curves in bismuth.**
Thermal neutrons from the Los Alamos Omega West Reactor fall on the monochromator crystal, which selects those having the desired incident energy by Bragg reflection, and directs them through the incident neutron collimator and monitor counter onto the sample crystal. Similarly, the scattered neutron collimator and analyzer crystal direct neutrons having the desired final energy into the $B^{10}F_3$ counter. The neutron momentum change is determined by the initial and final energies, and the scattering angle B. Orientation of the sample crystal with respect to the neutron momentum-change vector is accomplished by adjustment of angle C. The sample crystal is initially aligned so that a selected crystallographic plane is parallel to the plane of the spectrometer, and the orientation of some axis in that plane is known in terms of the spectrometer settings. In any given measurement, the incident neutron energy is held constant, while angles A, B, and C are varied automatically according to a precomputed program to produce the desired scan.

data for this branch are more subject to a systematic error than are those for the other branches.

A final experimental difficulty was caused by a large background, apparently due to multiphonon processes and to the tails of the intense Bragg peaks which occur whenever Q approaches one of the G's. In most cases, the background varied slowly over the width of a one-phonon group, and the center of the group could be located without difficulty. However, for low frequencies at small values of $|q|$ (corresponding to acoustic modes near the zone center) the rapidly varying background, combined with the poor resolution in $|q|$ which occurs when $|q|$ is small and $|Q|$ is large, made accurate determination of the phonon frequencies impossible. In this region, we feel that more accurate dispersion curves are obtained by setting the initial slope equal to that calculated from the elastic constants. In all cases, the background was larger at room temperature than at 75°K, and in many cases the room temperature one-phonon peaks seemed to be slightly broader than those observed at the lower temperature. However, the apparent broadening was small compared to the instrumental resolution, and depended strongly on the details of the form assumed for the background, so that it was not possible to make any reliable estimate of the natural width of the phonons at room temperature.

The bismuth lattice parameters reported by Cucka and Barrett[3] were used in this work. For directions of propagation which pass through reciprocal lattice points G, the dispersion curves are symmetric about a point halfway between the origin and the first reciprocal lattice point in the direction of propagation. We denote this midpoint by q_{max} and define a reduced wave vector z by the equation $q = zq_{max}$. The reduced wave vector z is dimensionless and varies between 0 and 1. The boundary of the first Brillouin zone occurs at some value of $z \leq 1$, depending on the structure of the reciprocal lattice.

The experimental dispersion curves are given in Table 1, and in Figs. 2 and 3. The random errors in the observed frequencies for the trigonal direction are of the order of 1 percent, as estimated from the deviations of the individual points from the best fitted curves. Possible systematic errors are more difficult to estimate; however, it seems unlikely that they are greater than 2 or 3 percent. The 75°K measurements are considered to be more accurate than those made at room temperature, and the data for the trigonal direction are more reliable than those for the binary direction, both in accuracy of the frequency determinations and in the certainty of the polarization identifications.

Linear chain model

Since bismuth contains two atoms per unit cell, we may think of it as being composed of two interpenetrating sublattices. The atoms are arranged on planes perpendicular to the trigonal axis. Alternate planes are made up of atoms from one sublattice, while the intermediate planes contain only atoms from the other. The distances between the planes also alternate, the larger spacing being approximately 1.5 times the smaller. Phonons which propagate in the trigonal direction represent lattice vibrations in which each plane of atoms moves as a rigid body. The equations of motion are formally equivalent to those for a linear chain of identical particles, with two particles per unit cell. Each particle represents an entire plane of atoms in the three-dimensional crystal, and the force constants represent the force on a given atom due to the displacement of an entire plane of neighboring atoms. Interactions may be assumed between any desired number of neighbors. The transverse and longitudinal modes are independent, and are both described by the same equation, with different numerical values for the force constants. A linear chain of the type under discussion is shown in Fig. 4.

The parameters K_2, K_4, P, R, S, and T in the expression for $M\omega^2$ as a function of z were determined by the method of least squares, using the experimental dispersion curves, with the initial slopes of the acoustic branches set equal to the values calculated from the elastic constants of Eckstein, Lawson, and Reneker.[4] The mass of a bismuth atom was taken to be 3.470×10^{-22} g. Fig. 5 shows the best fit obtained if K_2, K_4, S, and T are set equal to zero. This corresponds to interaction with the nearest plane on each side. It will be noted that this model fails to give even qualitative agreement for the optical branches. Fig. 6 shows the result of considering interactions with two planes on each side. In this case, K_4, S, and T are set equal to zero. With this range of interaction, the general trend of the optical branches is given correctly, although quantitative agreement is still lacking. No great improvement is obtained by considering three planes on each side, and it is only by letting all parameters vary, corresponding to interactions with four planes on each side, that a good fit is obtained. The results are shown in Fig. 7. Here, the standard deviation in the experimental frequencies, estimated from the goodness of fit assuming that the fitted function was of the correct form and that the percent error in ω was constant, was 0.6%. This value is in good agreement with our estimate of the point-to-point fluctuations of the data. (It does not, of course, include any possible systematic errors, which might be somewhat larger.) Fitting the room temperature trigonal dispersion curves gave results very similar to those obtained at 75°K. The standard deviation in ω, estimated as above from the fit using four planes on each side, was 1.0%.

The least-squares analysis yields directly the symmetric force constants K_2 and K_4, and the parameters P, R, S, and T, which are nonlinear combinations of the asym-

Table 1 **Observed frequencies (units 10^{13} radians/second) vs reduced wave vector z (dimensionless) for phonons in bismuth.** *Column headings give the branch, direction of propagation (in orthogonal axes XYZ where Z is the trigonal axis, X is one of the binary axes, and YZ is one of the mirror planes), and sample temperature.*

z	TA(001) 75°K	TA(001) 300°K	TO(001) 75°K	TO(001) 300°K	LA(001) 75°K	LA(001) 300°K	LO(001) 75°K	LO(001) 300°K	LA(100) 75°K	LO(100) 75°K
0.0			1.40	1.36			1.90	1.88		1.40
0.1			1.42	1.41			1.89	1.89		
0.2			1.51	1.51			1.92	1.87		1.61
0.3			1.61	1.61			1.97	1.93		1.74
0.4	0.354	0.36	1.71	1.71	0.622	0.62	2.01	1.97	0.95	1.83
0.5	0.435	0.44	1.79	1.78	0.765	0.77	2.04	2.00	0.98	1.85
0.6	0.523	0.52	1.88	1.84	0.883	0.88	2.05	2.05	0.92	1.86
0.7	0.603	0.60	1.88	1.86	0.984	0.97	2.06	2.02	0.75	1.84
0.8	0.665	0.66	1.91	1.87	1.04	1.04	2.05	2.01	0.61	1.80
0.9	0.706	0.69	1.92	1.91	1.11	1.10	2.03	1.99	0.54	1.73
1.0	0.730	0.70	1.91	1.89	1.13	1.13	2.04	2.02	0.50	1.68

Figure 2 **Dispersion curves for phonons propagating in the trigonal direction in bismuth at 75°K.**
The solid lines through the origin indicate the initial slopes calculated from the elastic constants. The dashed lines suggest the trend of the curves but have no theoretical significance. The room temperature data appear almost identical to those shown here, with the frequencies lowered by about 1.4 percent.

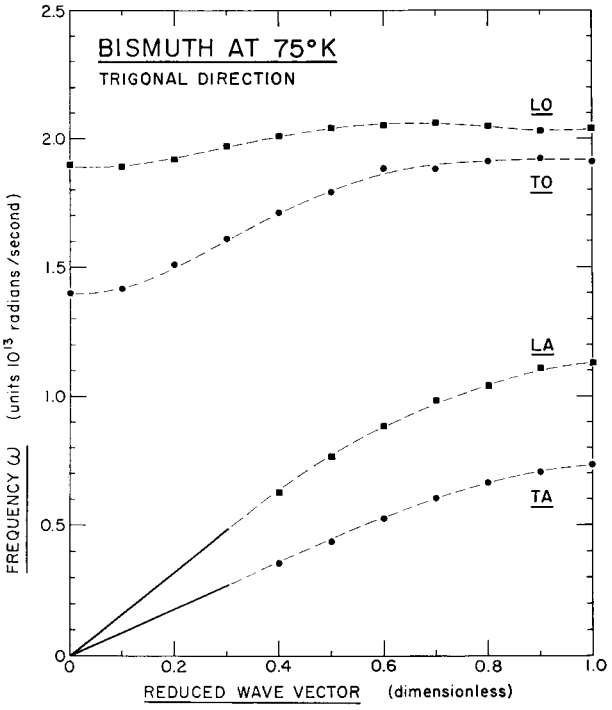
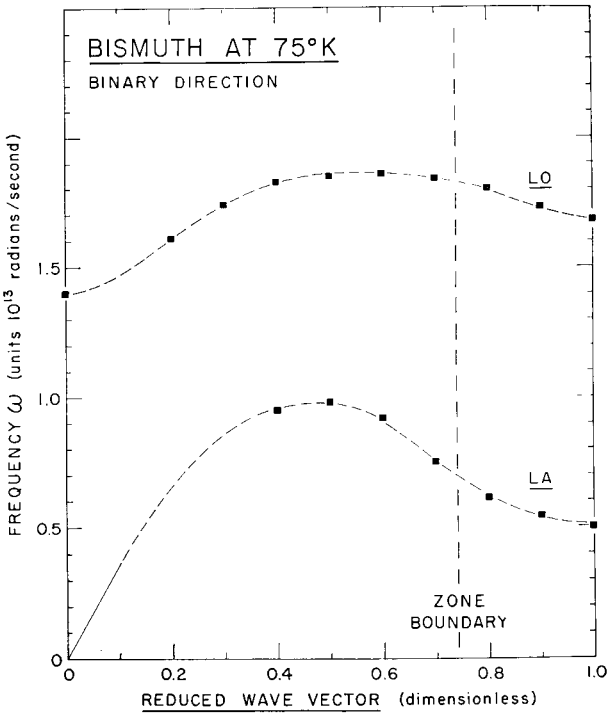
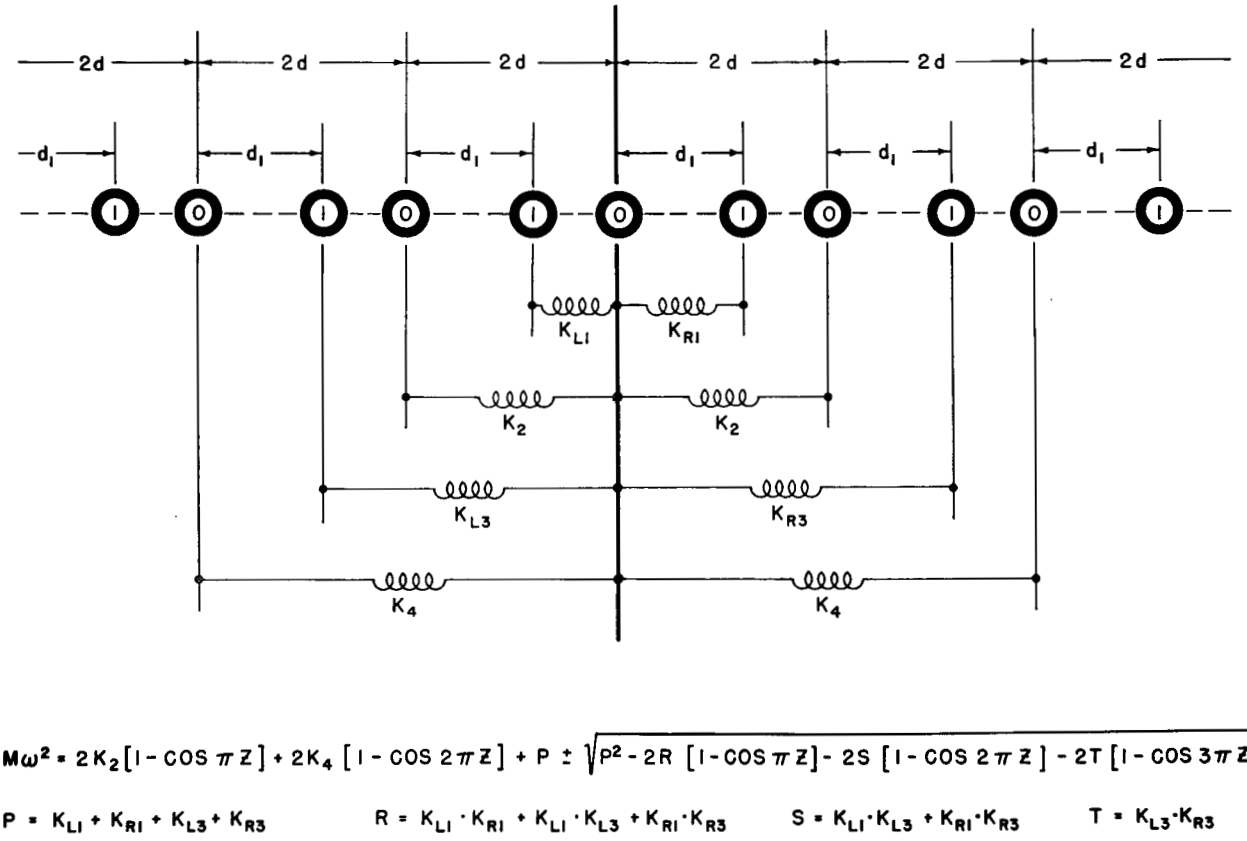


Figure 3 **Dispersion curves for longitudinal phonons propagating in the binary direction in bismuth at 75°K.**
The solid line through the origin indicates the initial slope calculated from the elastic constants. The dashed lines suggest the trend of the curves but have no theoretical significance.



metric force constants. The inverse relations are algebraic equations of fourth degree, and there will in general be four sets of asymmetric force constants equivalent to each set of values for P, R, S, and T. We have carried out the least-squares analysis for the longitudinal and transverse modes, each at two temperatures. The results in the four cases have much in common. In each case, there were four sets of asymmetric force constants which give identi-



$$M\omega^2 = 2K_2[1-\cos\pi Z] + 2K_4[1-\cos 2\pi Z] + P \pm \sqrt{P^2 - 2R[1-\cos\pi Z] - 2S[1-\cos 2\pi Z] - 2T[1-\cos 3\pi Z]}$$

$$P = K_{L1} + K_{R1} + K_{L3} + K_{R3} \qquad R = K_{L1}\cdot K_{R1} + K_{L1}\cdot K_{L3} + K_{R1}\cdot K_{R3} \qquad S = K_{L1}\cdot K_{L3} + K_{R1}\cdot K_{R3} \qquad T = K_{L3}\cdot K_{R3}$$

Figure 4 **Linear chain model for phonons propagating in the trigonal direction in bismuth.**
The two sublattices are labeled 0 and 1. The forces assumed to act on a particle of sublattice 0 are indicated by the springs. Note that the forces between particles on the same sublattice are symmetrical to the left and right, while those between particles on different sublattices are not. The forces acting on a particle of sublattice 1 are the same as those shown for sublattice 0, with the left and right asymmetric force constants interchanged. The relative spacing of the particles is the same as that of the planes perpendicular to the trigonal axis of bismuth. The equations give the dispersion curve in terms of the force constants. The frequency is given by ω, and the wave vector by $q = \pi z/2d$. M is the mass of an atom.

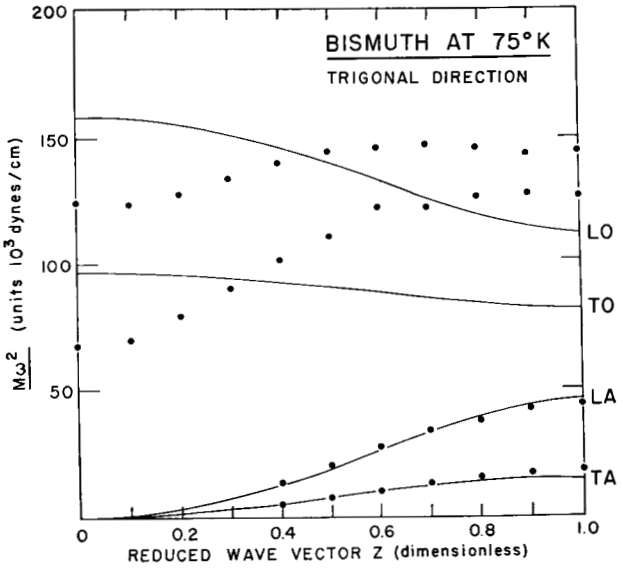


Figure 5 **Best fit of the trigonal dispersion curves in bismuth if forces from one plane on each side are considered.**

cal fits to the experimental dispersion curves. In each case one set may be eliminated immediately, since it assigns the largest force constant to the most distant plane and a very small one to the closest. The numerical results, including the three acceptable sets of asymmetric force constants for each case, are given in Table 2.

Table 2 **Interplanar force constants for vibrations propagating in the trigonal direction in bismuth.** *Owing to the structure of the equations, there are in each case three acceptable sets of asymmetric force constants which give identical fits to the experimental data. Values of each set are listed on the same horizontal row, and must be used together.* SD(K) *is the standard deviation of the force constants, calculated from the point-to-point fluctuations in the data. The actual uncertainties also depend on possible systematic errors in the data, and are perhaps two or three times the quoted errors. Force constants are in units of* 10^3 *dynes/cm.*

Mode	*Temp.*	K_{L1}	K_{R1}	K_2	K_{L3}	K_{R3}	K_4	SD(K)
T(001)	75°K	+41.28	−23.09	+9.68	+12.95	+2.89	+1.48	0.14
		+46.84	+3.87		−14.01	−2.67		
		+47.97	−0.28		−9.86	−3.80		
T(001)	300°K	+40.56	−22.60	+9.35	+12.60	+2.52	+1.72	0.22
		+45.10	+5.79		−15.78	−2.01		
		+47.34	−2.51		−7.49	−4.25		
L(001)	75°K	+55.51	+17.11	+7.99	−11.20	+0.33	+1.09	0.24
		+56.08	−10.04		+15.95	−0.23		
		+58.88	+4.69		+1.22	−3.04		
L(001)	300°K	+53.08	+17.61	+7.80	−11.65	+1.10	+0.97	0.40
		+55.17	−7.07		+13.03	−0.99		
		+56.86	+1.16		+4.81	−2.68		

Figure 6 **Best fit of the trigonal dispersion curves in bismuth if forces from two planes on each side are considered.**

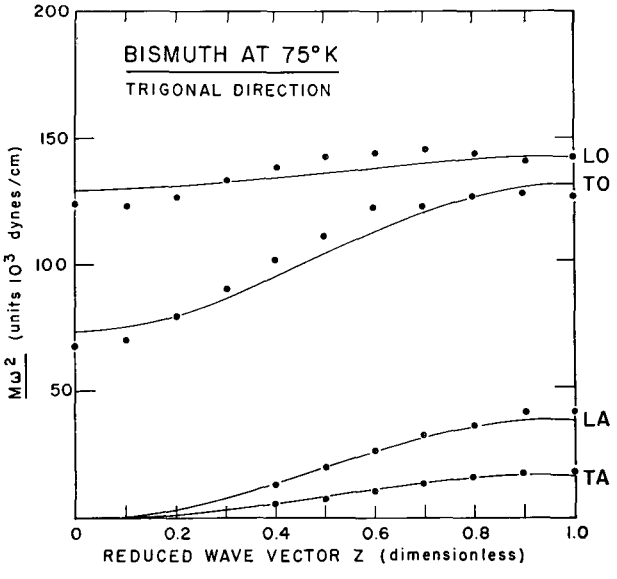
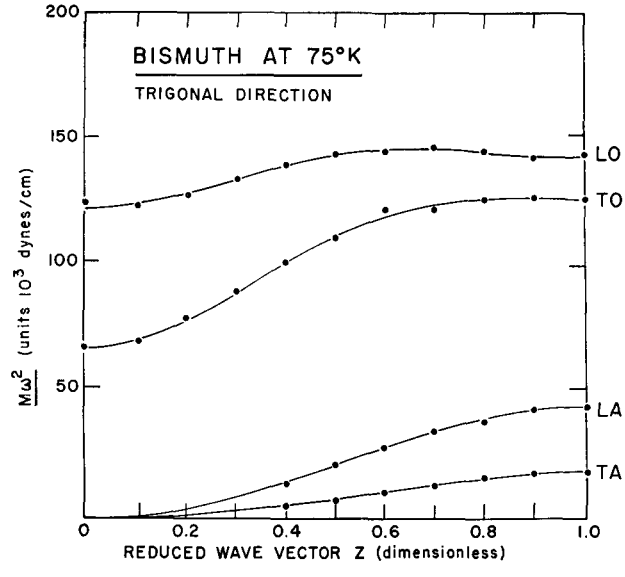


Figure 7 **Best fit of the trigonal dispersion curves in bismuth if forces from four planes on each side are considered.**
This corresponds to the situation shown in Fig. 4, and represents the data within the experimental error. Very similar results were obtained in fitting the room temperature data.



Discussion

We may first note that the zone boundary difference in $M\omega^2$ for the optical and acoustic branches, which we denote by Δ, is

$$\Delta = 2(K_{L1} - K_{R1}) - 2(K_{L3} - K_{R3}).$$

At 75°K, $\Delta_T = 127 - 18 = 109$ and $\Delta_L = 144 - 44 = 100$, in units of 10^3 dynes/cm. Since the expression for Δ involves only the differences between the force constants for corresponding asymmetric planes to the left and right, it is clear that these forces must be very different. The geometric arrangement of the atoms in the two planes connected by K_{L1}, the largest of the asymmetric force constants, is that of a crinkled hexagonal net. This arrangement is the one that would result if covalent bonds were assumed to connect each atom with three neighbors, assuming a bond angle consistent with that found in substances containing an atom with an electron configuration equivalent to that of bismuth.[5] It therefore seems reasonable to think of the bonding between atoms in nearest neighbor planes as being predominantly covalent. This picture is quite different dynamically from that of a slightly distorted primitive cubic lattice, which bismuth resembles geometrically. The cubic model would predict that the differences in the asymmetric force constants, and consequently the zone boundary splitting, should be small.

From the number of terms required to fit the trigonal dispersion curves, it appears that we need to consider forces between atoms in a given plane and those in two planes on each side to get even a qualitative picture of the lattice vibrations. For a quantitative description, it is necessary to include forces from atoms located as far as the fourth plane on each side.

The question of which set of asymmetric force constants is the correct one probably cannot be resolved until we have a more detailed model, one that is based on interatomic rather than interplanar forces.

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Discussion

Unidentified questioner: How important to the fit was the assumption that K_{L1} is different from K_{R1} and K_{L3} is different from K_{R3}?

J. L. Yarnell: Exceedingly important. If you assume that they are equal, then the optical and acoustic branches are not split at the zone boundary.

R. A. Smith: The fit using force constants between 3 neighboring planes is almost the same as that using 2, but on using 4 quite a significant change is obtained. The question arises as to whether the fitting procedure is converging, i.e., whether taking 5 or 6 planes would have a material effect. One test is whether taking in more planes significantly changes the values of the constants found using a smaller number of planes. Does taking in 4 planes change much the constants over those found using 2 or 3?

Yarnell: It doesn't change the largest nearest-planes force constants nor the symmetric force constants (those not under the square root), which come out uniquely. The smaller ones are changed somewhat.

M. H. Cohen: The displacement pattern of the optical modes at $\mathbf{k} = 0$ is exactly that of the static internal displacement carrying the simple cubic to the arsenic structure. We note that on Dr. Yarnell et al.'s data these optical mode frequencies are anomalously low. From the dielectric constants one can infer that the situation is even more extreme in the IV-VI's, where in Pb Te, if I remember correctly, the frequencies are an order of magnitude lower than for bismuth. Thus in the dynamical behavior of these crystals as well one sees evidence for the static instability of the simple cubic structure. This suggests a very interesting experiment. In the (SnGe)Te system, above the temperature range of stability of the arsenic structure, where the NaCl structure is stable, the transition frequency between "static" and high frequency behavior should occur at very low frequencies as one approaches the transition temperature. Indeed, in principle it would go through zero if the transition were second order. One should look for this experimentally.

G. A. Baraff (addressed to M. H. Cohen): 1) Can the large asymmetry between the left-hand and right-hand force constants be understood in terms of the incipient instability you mentioned? 2) Do your band structure calculations, when reinterpreted in terms of orbitals, show the large asymmetry between bonds binding nearest planes and bonds binding next nearest planes, implied by Yarnell's explanation of the left-right force constant asymmetry?

Cohen: The answer to both questions is *yes.* Indeed, the extreme case of tightly bound, loosely bound alternate layers would give a very much larger ratio of force constants than that reported by Dr. Yarnell. The sort of factor of 2 ratio is what one might expect on a distorted simple cubic picture, although I don't think any calculations have been done which would substantiate my conclusion. In other words, the theory of force constants is in such a primitive state at the present time that one can only argue on the basis of prejudices rather than sound theory.