General closed-form expressions for acoustic waves in elastically anisotropic solids

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By solving the Christoffel equations, general closed-form expressions are obtained for the phase and group velocities and displacement eigenvectors of arbitrarily directed acoustic waves in elastically anisotropic solids. The relationship of these general results to expressions that hold in symmetry directions is shown, and applications to phonon focusing and the determination of acoustic axes and extrema of the phase velocity are discussed. Methods for extracting the elastic constants and orientation of a crystal from measured sound velocities are outlined.

I. INTRODUCTION

The propagation of acoustic waves in elastically anisotropic solids is governed by a set of three linear equations known as the Christoffel equations. The characteristic equation relates the velocity v, the direction of the wave, and the elastic constants of the medium, and is cubic in v^2. These equations occupy a pre-eminent position in the field of crystal acoustics, and their solution is required for a wide variety of purposes from ultrasonic and light-scattering experiments to calculations on phonon focusing and other thermodynamic effects.

Considerable simplification to the equations comes about when the wave normal lies along a crystal symmetry direction. In general, the secular equation for these directions factors into a term which is linear in v^2 and one which is quadratic. Simple expressions for the velocities thus result, and in many cases these are easily reversed to obtain the elastic constants from measured velocities. This aspect of the problem is dealt with briefly in Kittel's "Introduction to Solid-State Physics,"[1] and, even in specialist monographs on crystal acoustics,[2,3,4] there is a heavy emphasis on the symmetry directions. However, there are many situations in which the solution of the characteristic equation is required for arbitrary crystallographic directions. Although a number of general relationships between the phase and group velocities and displacement eigenvectors have been uncovered, it has been the practice in the past to leave the solution of the characteristic equation for arbitrary directions to numerical[5] or approximational[6] methods. The hexagonal system is a special case, since its characteristic equation can always be factored,[7] and the solution for the cubic system has recently been discussed by this author.[8]

The general method of solution presented here, which yields closed-form expressions for the phase velocity and related quantities, has many advantages both from a computational point of view and also because of the perspective on acoustic anisotropy that it provides. Some of the areas of current interest where this method could be of immediate use are ballistic heat-pulse propagation[9,10] and other phonon-focusing effects,[11] relaxation of paramagnetic[12] and paraelectric centers,[13] charge-density waves,[14] vibrational effects on x rays,[15] second sound,[16] Akhiezer damping of sound waves,[17] and the measurement of elastic constants using nonaligned crystals.[18] In fact, there are potential applications in virtually any effect connected with long-wavelength phonons or acoustic waves in crystals.

The main thrust of this paper hinges around three invariants T, G, and H of the Christoffel matrix. In Sec. II the equations of motion are briefly reviewed and the implicit relationship between the velocity and these three invariants is established. The role crystal symmetry plays in shaping the precise form of T, G, and H is discussed here and in more detail in the Appendix. In Sec. III the trigonometric method is used for solving the characteristic equation for v^2, and the solution is discussed in the context of acoustic anisotropy, special directions, the group velocity, and phonon focusing. Section IV deals with the solution of the Christoffel equations when the wave vector lies in a symmetry direction. This aspect of the problem has been discussed by a number of authors, and the intention here is merely to present the essential results in a simple and concise form and show their relationship to the general solution. Finally, in Sec. V methods are described for determining the orientation and elastic constants of crystals from velocities measured in arbitrary crystallographic directions.

II. EQUATIONS OF MOTION

The equations of motion for elastically anisotropic solids have been reviewed by a number of

authors.[2-4] We will confine our attention here to ideal Hooke's Law behavior, neglecting body forces, body torques, dissipative processes, and nonlinear or dispersive phenomena. A disturbance in such a medium is represented by a set of position- and time-dependent particle displacements $u_r(x_i,t)$ which are related by the equations

$$\rho\frac{\partial^2 u_r}{\partial t^2}=C_{rlsm}\frac{\partial^2 u_s}{\partial x_l\partial x_m}, \tag{1}$$

where ρ is the density of the medium and C_{rlsm} are the second-order elastic constants. A plane monochromatic wave $u_r=U_r\exp[i(k_ix_i-\omega t)]$ is a solution to the above equations, subject to the frequency ω, wave vector $\vec{k}=(k_i)$, and amplitudes U_r satisfying the conditions

$$(C_{rlsm}k_lk_m-\rho\omega^2\delta_{rs})U_s=0. \tag{2}$$

On dividing through by k^2, Eq. (2) takes on the form

$$(\Gamma_{rs}-\rho v^2\delta_{rs})U_s=0, \tag{3}$$

where $v=\omega/k$ is the phase velocity and $\Gamma_{rs}=C_{rlsm}n_ln_m$ is the Christoffel matrix which depends, through the wave normal $\vec{n}=(n_i)$, on the direction of $\vec{k}$ but not on its magnitude. Using the contracted Voigt notation for the elastic constants,[19] the Christoffel coefficients are, in the most general case, given by[2]

$$\begin{aligned}
\Gamma_{11}&=C_{11}n_1^2+C_{66}n_2^2+C_{55}n_3^2+2C_{56}n_2n_3+2C_{15}n_3n_1+2C_{16}n_1n_2,\\
\Gamma_{22}&=C_{66}n_1^2+C_{22}n_2^2+C_{44}n_3^2+2C_{24}n_2n_3+2C_{46}n_3n_1+2C_{26}n_1n_2,\\
\Gamma_{33}&=C_{55}n_1^2+C_{44}n_2^2+C_{33}n_3^2+2C_{34}n_2n_3+2C_{35}n_3n_1+2C_{45}n_1n_2,\\
\Gamma_{23}=\Gamma_{32}&=C_{56}n_1^2+C_{24}n_2^2+C_{34}n_3^2+(C_{23}+C_{44})n_2n_3+(C_{36}+C_{45})n_3n_1+(C_{25}+C_{46})n_1n_2,\\
\Gamma_{13}=\Gamma_{31}&=C_{15}n_1^2+C_{46}n_2^2+C_{35}n_3^2+(C_{36}+C_{45})n_2n_3+(C_{13}+C_{55})n_3n_1+(C_{14}+C_{56})n_1n_2,\\
\Gamma_{12}=\Gamma_{21}&=C_{16}n_1^2+C_{26}n_2^2+C_{45}n_3^2+(C_{25}+C_{46})n_2n_3+(C_{14}+C_{56})n_3n_1+(C_{12}+C_{66})n_1n_2.
\end{aligned} \tag{4}$$

From the form of Eq. (3) we see that $\vec{U}=(U_s)$ must be an eigenvector of Γ_{rs} and that ρv^2, the corresponding eigenvalue, is determined by the characteristic equation

$$|\Gamma_{rs}-\rho v^2\delta_{rs}|=0. \tag{5}$$

This is a cubic equation for ρv^2 which, because of the symmetry of Γ_{rs} with respect to interchange of r and s, has three real roots. The requirement for crystal stability ensures that Γ_{rs} is a positive definite matrix and hence the three eigenvalues are positive.

The cubic equation is converted into a more convenient form for solution by carrying out a linear transformation that eliminates the quadratic term. On making the replacement

$$3\rho v^2=S+T, \tag{6}$$

where

$$T=\Gamma_{rr} \tag{7}$$

is the trace of Γ, one arrives at the following equation for S:

$$|\Lambda_{rs}-S\delta_{rs}|=0, \tag{8}$$

where

$$\Lambda_{rs}=3\Gamma_{rs}-T\delta_{rs}. \tag{9}$$

The eigenvectors are unaffected by this operation. On expanding the determinant in Eq. (8) the following cubic equation for S results:

$$S^3-3GS-2H=0. \tag{10}$$

The coefficient of the quadratic term is equal to the trace of Λ, which is zero, while the other two coefficients are given by

$$3G=\Lambda_{12}^2+\Lambda_{23}^2+\Lambda_{31}^2-\Lambda_{22}\Lambda_{33}-\Lambda_{33}\Lambda_{11}-\Lambda_{11}\Lambda_{22}, \tag{11}$$

and

$$2H=|\Lambda|=\Lambda_{11}\Lambda_{22}\Lambda_{33}+2\Lambda_{12}\Lambda_{23}\Lambda_{31}-\Lambda_{11}\Lambda_{23}^2-\Lambda_{22}\Lambda_{31}^2-\Lambda_{33}\Lambda_{12}^2. \tag{12}$$

The quantities T, G, and H play a central role in the developments that follow. They are invariants of the Christoffel tensor (matrix) or, more precisely, T is the first invariant of Γ while $-3G$ and $2H$ are the second and third invariants, respectively, of Λ. This terminology refers to the fact that the three quantities are unaltered by an orthogonal transformation of the coordinate system that the elastic constants and wave normal are referred to. It is apparent from their generating equations that T, G, and H are homogeneous functions of degree 1, 2, and 3, respectively, in the elastic constants C_{ij} and of degree 2, 4, and 6, respectively, in the components of $\vec{n}$.

A. Symmetry considerations

Equation (10) has three real roots S_0, S_1, and S_2 which, through Eq. (6), yield the three velo-

cities v_0, v_1, and v_2. An important representation for the three invariants, provided by these quantities, is[4]

$$T=\rho(v_0^2+v_1^2+v_2^2)\,, \tag{13}$$

$$3G=-(S_0S_1+S_1S_2+S_2S_0)\,, \tag{14}$$

and

$$2H=S_0S_1S_2\,. \tag{15}$$

Since the three velocities and hence S_0, S_1, and S_2 are crystal properties, they are unaltered when any crystal symmetry operation is applied either to the medium or to the measurement. It follows from the last three equations that, as functions of the wave direction or normal $\vec{n}$, T, G, and H must therefore be invariant under the symmetry operations of a crystal. The Christoffel coefficients Γ_{rs} do not individually exhibit this property, but in the way they are combined in Eqs. (7), (11), and (12), functions with the crystal symmetry result. Inversional symmetry is present in the equations of motion even for those crystals which do not possess a center of inversion. This is obvious from the fact that the Γ_{rs} are quadratic functions of the components of $\vec{n}$. The appropriate crystal classification scheme is therefore by Laue groups. The Appendix contains a fuller discussion of the effects of crystal symmetry and the form that Λ, T, G, and H take under the various Laue groups.

B. Piezoelectric coupling

In piezoelectric media, i.e., crystals which lack a center of inversion, there is a coupling between the strain field and the electric field, and as a result an acoustic wave is accompanied by a disturbance in the electromagnetic field. This effect can be described in terms of a piezoelectrical stiffening of the elastic constants.[2,20] In place of the tensor elastic constants C_{rlsm} in the Christoffel equations, one uses a set of quantities

$$C'_{rlsm}=C^E_{rlsm}+\frac{e_{rlp}n_pe_{smq}n_q}{(\epsilon^s_{\alpha\beta}n_\alpha n_\beta)}\,,$$

where C^E_{rlsm} is the elastic-stiffness tensor at constant electric field, e_{ijk} is the piezoelectric stress tensor, and $\epsilon^s_{\alpha\beta}$ is the permittivity tensor at constant strain. These new stiffnesses are no longer material constants since they depend on the direction $\vec{n}$ of the wave as well. Moreover, nonvanishing components of C'_{rlsm} may occur even where crystal symmetry dictates that the corresponding components of C^E_{rlsm} are zero. Nevertheless, one can still form the functions T, G, and H, which determine the velocities, and these functions still reflect the Laue-group symmetry and are homogeneous in the components of $\vec{n}$.

III. GENERAL SOLUTION

A. Phase velocities

In most calculations concerned with acoustic waves in crystals the phase velocities play a vital role. Once the phase velocities are known as a function of direction, there are straightforward procedures for obtaining the displacement eigenvectors, group velocities, and other quantities of interest. For general directions in hexagonal crystals and for symmetry directions in other crystals the problem of calculating the phase velocities is simplified by the fact that the characteristic equation can be factored, and a number of velocity expressions have been derived that serve for these special cases. Waterman[21] has developed perturbation formulas applicable to near-symmetry directions, which are useful in treating beam-divergence effects in ultrasonics. Except for crystals of cubic and hexagonal symmetry, there do not appear before now to have been any published exact analytic velocity expressions that apply to arbitrary crystallographic directions.

The practice in the past has been mainly to use numerical methods applied to specific crystals.[5] In the case of cubic crystals Orth[6] has developed a Taylor-series expansion for the velocity, and wide use has been made,[22] in thermodynamic calculations, of finite sums of Kubic harmonics to represent certain functions of the velocities. Other methods of approximation have been discussed by Fedorov.[4]

Since the velocity equation is a cubic, its solution can be expressed in terms of radicals. There is, however, much advantage to be gained by employing the trigonometric[23] form of solution. This has been done recently for cubic crystals by this author,[8] and we generalize the method here to all crystals. Since the quadratic term is absent, the roots of Eq. (10) are given simply by

$$S_j=2G^{1/2}\cos(\psi+\tfrac{2}{3}\pi j)\quad(j=0,1,2)\,, \tag{16}$$

where

$$\psi=\tfrac{1}{3}\arccos(H/G^{3/2})\,, \tag{17}$$

and hence from Eq. (16),

$$3\rho v_j^2=T+2G^{1/2}\cos(\psi+\tfrac{2}{3}\pi j)\,. \tag{18}$$

Three velocities are generated as the polarization index j takes on the values 0, 1, and 2. Equations (17) and (18) together with the expressions for T, G, and H given in the Appendix constitute an exact general closed-form solution for the ve-

locity. Physical requirements, as pointed out in the Sec. II, dictate that for any direction $\vec{n}$ there are three positive values of v_j^2. The three roots of Eq. (10) are therefore all real and hence the discriminant $108(G^3-H^2)$ is positive.[23] It follows that G is necessarily positive and $|H/G^{3/2}| \leq 1$ so that ψ is real. For H positive $0<\psi<\pi/6$ while for H negative $\pi/6<\psi<\pi/3$.

A convenient way of representing the three velocities is shown in Fig. 1. Because of the limits on ψ and the fact that T and $2G^{1/2}$ are necessarily positive, v_0 is always the largest velocity, v_1 the smallest, and v_2 the intermediate one. This allows the identification, as a rule, of v_0 as the quasilongitudinal, v_1 as the slow quasitransverse, and v_2 as the fast quasitransverse velocities. Tellurium dioxide[2] and the pseudocrystalline material spruce wood[3] provide rare exceptions to this rule. In these rare cases the classification of modes as longitudinal or transverse can lead to inconsistencies, but the assignment of the velocities v_0, v_1, and v_2 in the way described above is free of any ambiguities. As far as symmetry planes are concerned, where there is a crossover between a pure T and a mixed-mode velocity curve, the label v_1 is attached to the mode which happens to be slowest in any particular direction and not to the character of the mode.

In the isotropic limit, T and $2G^{1/2}$ are constants and $\psi=0$ so that the three velocities are independent of direction, and the two transverse velocities are identical. For the majority of crystals ψ, while depending on direction, remains small and there is still a clear distinction between the quasilongitudinal velocity on one hand and the two quasitransverse velocities on the other. It is only for exceptionally anisotropic crystals that ψ ever exceeds $\pi/6$.

A direction in a crystal in which the two transverse velocities are equal is defined as an acoustic axis. Such directions are determined by the condition $\psi=0$, i.e., $H/G^{3/2}=1$. A T and L mode coincide in velocity when $\psi=\pi/3$, i.e., $H/G^{3/2}=-1$. The condition for degeneracy of either kind is therefore $H^2=G^3$.

Since v_j^2 is a homogeneous function of degree 1 in the elastic constants, the solution may also be written in the form

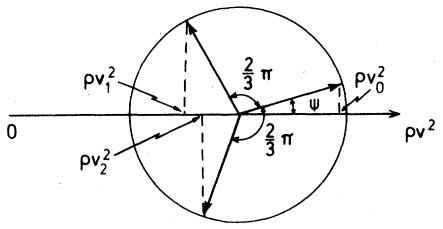

FIG. 1. "Phasor" diagram for representing the three values of ρv_j^2. The circle is centered a distance $\frac{1}{3}T$ along the ρv^2 axis, and has radius $\frac{2}{3}G^{1/2}$.

$$\frac{3\rho}{C_0}v_j^2 = T_0 + 2G_0^{1/2}\cos(\psi+\tfrac{2}{3}\pi j)\,, \tag{19}$$

$$\psi = \tfrac{1}{3}\arccos(H_0/G_0^{3/2})\,, \tag{20}$$

where C_0 is any one of, or a suitable combination of, elastic constants and T_0, G_0, and H_0 are homogeneous functions of degree zero in the elastic constants. In this way the solution can be made to effectively depend on one fewer elastic parameter than before. For example, drawing on results from the Appendix, it is convenient in the case of cubic symmetry to take $C_0=C_2=C_{11}-C_{44}$. Setting $C_3=K/C_2$ we find that

$$T_0 = \frac{C_1}{C_2}n^2\,, \tag{21}$$

$$G_0 = n^4 - 3C_3(2-C_3)P\,, \tag{22}$$

and

$$H_0 = n^6 - \tfrac{9}{2}C_3(2-C_3)Pn^2 + \tfrac{27}{2}C_3^2(3-2C_3)Q\,. \tag{23}$$

These results show that the relative variation of v_j^2 with direction depends only on the single parameter $C_3=(C_{11}-C_{12}-2C_{44})/(C_{11}-C_{44})$, which can be used to characterize the elastic anisotropy of a cubic crystal. At the same time, $C_1/3\rho$ is the mean-square velocity and C_2/ρ is a measure of the separation between the L and T squared velocities.

B. Displacement eigenvectors

With the velocities determined, the displacement eigenvectors may be found by means of Eqs. (3) and (9) and are

$$U_{j1}:U_{j2}:U_{j3} = \frac{\alpha_1}{S_j-\Lambda_{11}+\alpha_1^2}:\frac{\alpha_2}{S_j-\Lambda_{22}+\alpha_2^2}:\frac{\alpha_3}{S_j-\Lambda_{33}+\alpha_3^2}\,, \tag{24}$$

where

$$\alpha_1 = \left(\frac{\Lambda_{12}\Lambda_{13}}{\Lambda_{23}}\right)^{1/2},\quad \alpha_2 = \left(\frac{\Lambda_{12}\Lambda_{23}}{\Lambda_{13}}\right)^{1/2},\quad \text{and } \alpha_3 = \left(\frac{\Lambda_{13}\Lambda_{23}}{\Lambda_{12}}\right)^{1/2}.$$

Only the ratios of the components of $\vec{U}$ are determined in this way. If one or more of the off-diagonal elements of Λ are zero, then the α's cannot be defined. The most likely reason for this happening is that $\vec{n}$ lies in a symmetry direction. In this case $\vec{U}$ may be determined by the methods described in Sec. IV.

The eigenvectors are independent of the trace T of Γ_{rs} and are unaffected by a scale change which alters all the elastic constants in the same proportion. Thus in the case of cubic symmetry one finds that

$$U_{j1}:U_{j2}:U_{j3}=\frac{n_1}{T_j-3C_3n_1^2}:\frac{n_2}{T_j-3C_3n_2^2}:\frac{n_3}{T_j-3C_3n_3^2}, \tag{25}$$

where

$$T_j=1+2G_0^{1/2}\cos(\psi+\tfrac{2}{3}\pi j).$$

As can be seen from this result, the only one of the three elastic constants that influences the eigenvectors is the anisotropy parameter C_3. This notable property of C_3 is not shared by the widely used Zener anisotropy factor[24] $\eta=2C_{44}/(C_{11}-C_{12})$.

C. Ray or group velocity

The ray velocity is an important physical attribute of any acoustic wave. This is the velocity at which energy is transported in the wave and it is required for interpreting phenomena in ultrasonics and phonon transport, etc. Except in special circumstances the ray velocity does not coincide either in magnitude or in direction with the phase velocity.

The group velocity is the velocity of the modulation envelope of a wave packet composed of waves of slightly differing values of $\vec{k}$ and ω, and is given by

$$\vec{V}_j=\nabla_{\vec{k}}\omega_j(\vec{k}),\quad V_{j\alpha}=\frac{\partial\omega_j}{\partial k_\alpha}, \tag{26}$$

while the ray velocity is obtained from the acoustic Poynting vector. However, in the absence of dissipation the distinction between these two velocities disappears, and Eq. (26) provides a convenient computational route for obtaining this velocity.

Using the fact that v_j is a homogeneous function of degree 1 in the components of $\vec{n}$ and that $\omega_j=kv_j$, Eq. (26) is readily converted to[4]

$$V_{j\alpha}=\frac{\partial v_j}{\partial n_\alpha}=\frac{1}{2v_j}\frac{\partial v_j^2}{\partial n_\alpha}. \tag{27}$$

Since $3\rho v_j^2=T+S_j$, it follows that

$$V_{j\alpha}=\frac{1}{6\rho v_j}\left(\frac{\partial T}{\partial n_\alpha}+\frac{\partial S_j}{\partial n_\alpha}\right). \tag{28}$$

On differentiating Eq. (16) one obtains

$$\frac{\partial S_j}{\partial n_\alpha}=\frac{S_j}{2G}\frac{\partial G}{\partial n_\alpha}+\frac{2G^{1/2}\sin(\psi+\frac{2}{3}\pi j)}{3(1-G^{-3}H^2)^{1/2}}\times\left(G^{-3/2}\frac{\partial H}{\partial n_\alpha}-\tfrac{3}{2}G^{-5/2}H\frac{\partial G}{\partial n_\alpha}\right). \tag{29}$$

A simpler but equivalent expression for $\partial S_j/\partial n_\alpha$ results if implicit differentiation is used in conjunction with the equation

$$\Omega(S_j,n_1,n_2,n_3)=S_j^2-3GS_j-2H=0. \tag{30}$$

By this route one obtains

$$\frac{\partial S_j}{\partial n_\alpha}=\left(S_j\frac{\partial G}{\partial n_\alpha}+\frac{2}{3}\frac{\partial H}{\partial n_\alpha}\right)\Big/(S_j^2-G). \tag{31}$$

The differentiation of T, G, and H with respect to n_α is straightforward using the expressions for these quantities provided in the Appendix.

The calculation of the group velocity is in some cases simplified by the use of spherical polar coordinates. The wave vector is specified here by $\vec{k}=(k,\theta,\phi)$, and using the fact that $\omega_j=kv_j=kv_j(\theta,\phi)$, the radial and angular components of $\vec{V}_j$ are given by

$$V_{jk}=\frac{\partial\omega_j}{\partial k}=v_j, \tag{26a}$$

$$V_{j\theta}=\frac{1}{k}\frac{\partial\omega_j}{\partial\theta}=\frac{\partial v_j}{\partial\theta}, \tag{26b}$$

and

$$V_{j\phi}=\frac{1}{k\sin\theta}\frac{\partial\omega_j}{\partial\phi}=\frac{1}{\sin\theta}\frac{\partial v_j}{\partial\phi}. \tag{26c}$$

These can be projected onto the Cartesian axes to give

$$V_{j1}=v_j\sin\theta\cos\phi+\frac{\partial v_j}{\partial\theta}\cos\theta\cos\phi-\frac{\partial v_j}{\partial\phi}\frac{\sin\phi}{\sin\theta}, \tag{27a}$$

$$V_{j2}=v_j\sin\theta\sin\phi+\frac{\partial v_j}{\partial\theta}\cos\theta\sin\phi+\frac{\partial v_j}{\partial\phi}\frac{\cos\phi}{\sin\theta}, \tag{27b}$$

and

$$V_{j3}=v_j\cos\theta-\frac{\partial v_j}{\partial\theta}\sin\theta. \tag{27c}$$

The group velocity can also be described in terms of spherical coordinates, i.e., $\vec{V}_j=(V_j,\Theta_j,\Phi_j)$, where

$$V_j=(V_{j1}^2+V_{j2}^2+V_{j3}^2)^{1/2}, \tag{28a}$$

$$\tan\Theta_j=(V_{j1}^2+V_{j2}^2)^{1/2}/V_{j3}, \tag{28b}$$

and

$$\tan\Phi_j=V_{j2}/V_{j1}. \tag{28c}$$

The differentiation of v_j with respect to θ and ϕ is done in the same way as for n_α, making use of the appropriate expressions provided in the Appendix.

D. Extrema of the phase velocity

In order to find the extremal values of the phase velocity $v_j(n_1,n_2,n_3)$ subject to the constraint $n^2=n_1^2+n_2^2+n_3^2=1$ we use the method of Lagrange multipliers which immediately leads to the set of three simultaneous equations

$$\frac{\partial v_j}{\partial n_\alpha}=\mu n_\alpha, \quad \alpha=1,2,3 \tag{32}$$

where μ is an undetermined multiplier. The above equations express the individual components of the equation

$$\vec{V}_j=\mu\vec{n}\ . \tag{33}$$

The extrema of v_j thus correspond to directions in which the group velocity is parallel to $\vec{n}$ and therefore coincides with the phase velocity. Conical points require separate treatment due to the fact that two of the velocities are degenerate and $\partial v/\partial n_\alpha$ is not well defined.

Disregarding solutions that require special values for the elastic constants, one has in the case of cubic symmetric the following extremal directions:

(i) [100] directions for all three modes;
(ii) [110] directions for all three modes;
(iii) pure T mode for $\vec{n}$ perpendicular to any [100] direction;
(iv) L mode in any [111] direction, the pure T modes form conical points in these directions;
(v) directions of the form

$$n_x^2=n_y^2=\tfrac{1}{2}(1-n_z^2)=\frac{2-C_3}{8-5C_3}$$

for the quasi-T mode.

This again highlights the role played by C_3. These conclusions are in agreement with the corresponding results of Levelut.[25]

E. Phonon focusing

A general feature of elastically anisotropic solids is that thermal-phonon group velocities tend to aggregate more around some directions than others. This effect, known as phonon focusing, can exert a considerable influence on the boundary-limited conduction of heat[11] and the ballistic propagation of heat pulses[9] through crystals. Recent experiments by Hensel and Dynes[26] and Northrop and Wolfe[27] have brought to light remarkable directional anisotropy in the phonon flux emanating from a localized heat source in Ge. Behavior no less complex is to be expected in many, if not most, crystals.

The effect is conveniently treated as follows. A distribution of phonons of polarization j and wave vectors contained within a cone of solid angle $\delta\Omega_n$ about the direction $\vec{n}$ propagate with group velocities spread over a solid angle $\delta\Omega_v$ about the direction of $\vec{V}_j(\vec{n})$. A measure of the associated enhancement of the phonon flux in the direction of $\vec{V}_j$, or phonon focusing in this direction, is the phonon amplification factor

$$A_j=\frac{\delta\Omega_n}{\delta\Omega_v}. \tag{34}$$

This quantity depends on the curvature of the inverse velocity surface and thus requires second derivatives of v_j for its evaluation. Maris[10] has established an expression for A_j that can be put in the following form:

$$A_j^{-1}=\frac{1}{V_j^3}\left|\left[\left(\vec{n}_1\cdot\frac{\partial\vec{V}_j}{\partial\vec{n}}\right)\times\left(\vec{n}_2\cdot\frac{\partial\vec{V}_j}{\partial\vec{n}}\right)\right]\cdot\vec{V}_j\right|, \tag{35}$$

where $\vec{n}_1$ and $\vec{n}_2$ are any two unit vectors which are perpendicular to each other and to $\vec{n}$. A number of derivatives of the form

$$\frac{\partial V_{j\alpha}}{\partial n_\beta}=\frac{1}{6\rho v_j}\left(\frac{\partial^2 T}{\partial n_\alpha\partial n_\beta}+\frac{\partial^2 S_j}{\partial n_\alpha\partial n_\beta}\right)-\frac{V_{j\alpha}V_{j\beta}}{v_j} \tag{36}$$

are encountered in this expression. The second term in the above equation may be obtained through implicit differentiation using Eq. (30). The result is

$$\frac{\partial^2 S_j}{\partial n_\alpha\partial n_\beta}=\left(-2S_j\frac{\partial S_j}{\partial n_\alpha}\frac{\partial S_j}{\partial n_\beta}+\frac{\partial S_j}{\partial n_\alpha}\frac{\partial G}{\partial n_\beta}+\frac{\partial S_j}{\partial n_\beta}\frac{\partial G}{\partial n_\alpha}+S_j\frac{\partial^2 G}{\partial n_\alpha\partial n_\beta}+\frac{2}{3}\frac{\partial^2 H}{\partial n_\alpha\partial n_\beta}\right)\Big/(S_j^2-G). \tag{37}$$

Philip and Viswanathan[28] have pointed out that in terms of spherical coordinates, A_j is given by (the modulus signs are this author's)

$$A_j^{-1}=\left|J_j\sin\Theta_j/\sin\theta\right|, \tag{35a}$$

where

$$J_j=\frac{\partial(\Theta_j\Phi_j)}{\partial(\theta,\phi)}=\frac{\partial\Theta_j}{\partial\theta}\frac{\partial\Phi_j}{\partial\phi}-\frac{\partial\Theta_j}{\partial\phi}\frac{\partial\Phi_j}{\partial\theta} \tag{35b}$$

is the Jacobian of the transformation relating the variables (Θ_j,Φ_j) and (θ,ϕ). The calculation of A_j by this method entails the evaluation of the second derivatives of v_j with respect to θ and ϕ, which is done in the same way as the differentiation with respect to n_α and n_β.

The presence of folds in one or more sheets of the ray surface, a common feature in many

crystals, can result in the phonon flux in a given direction consisting of more than just one component for each polarization. All of these components will, in general, be associated with different wave normals and will be traveling at different speeds. Thus with suitable time resolution one can expect to observe the various components of a propagating heat pulse separating into individual pulses.

The edges of the folds in the ray surface are associated with points on the inverse velocity surface where the Gaussian curvature is zero. These points give rise to singularities in the phonon-amplification factor. Because the detector will necessarily have a finite angular resolution one would, of course, expect to observe peaks rather than singularities. A useful way of portraying the combined phonon amplification is shown in Fig. 2, in which the $j=1$ and the $j=2$ modes of Ge are represented. These diagrams have been generated by taking a uniform net of wave-vector directions [separated by 0.5° for Figs. 2(a) and 2(b) and by 0.25° for Fig. 2(c)], calculating the directions of the associated group velocities, and plotting these in a polar projection. Only the results for the irreducible sector defined by $n_z \geq n_x \geq n_y \geq 0$ are displayed in order to avoid repetition. It should be pointed out that many of the ray vectors lying in this sector are associated with wave vectors located outside this sector.

Several features of these diagrams are worth discussing. The folding edges of the ray surface show up clearly as lines of accumulation of the directional points, and correspond to the lines of infinite phonon amplification calculated by Northrop and Wolfe.[27] All the main features in the experimental integrated TA phonon-intensity pattern of Ge obtained by these authors are reflected in Fig. 2. The features marked 1, 2, 3, 4, and 5 in Fig. 2 correspond, in the experimental data of Hensel and Dynes,[26] respectively, to peaks in the phonon intensity 5° and 7° from [001], 2° from [011], and ±5.5° on either side of the [111] direction. The $j=1$ and $j=2$ inverse velocity surfaces make contact in the [111] direction giving rise to a circular cone of internal refraction, and this accounts for the region around this direction for the $j=2$ mode which is devoid of ray vectors.

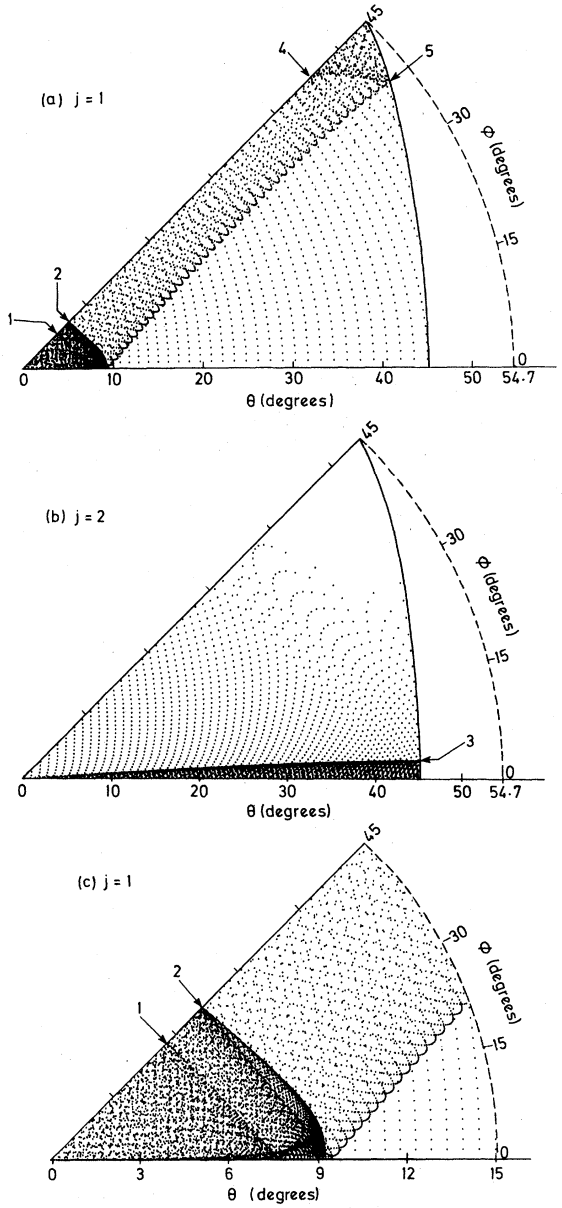

FIG. 2. Combined phonon amplification for each of the transverse modes of Ge, calculated using the elastic constants (Ref. 27) $C_{11}:C_{12}:C_{44}=1.0:0.38:0.52$. (a) $j=1$ mode and (b) $j=2$ mode. (c) Region near $\theta=0$ in (a) enlarged.

IV. SOLUTION IN SYMMETRY DIRECTIONS

The application of the results of the preceding section to symmetry directions is not entirely straightforward. A stumbling block in the form of vanishing denominators is in some cases encountered. While steps can be taken to overcome these obstacles, it is more convenient to use a different approach right from the start.

In the past most treatments of acoustic waves in crystals have dwelled heavily on the symmetry directions, and the principal results in this area have been reviewed in the books by Fedorov,[4] Musgrave,[3] and Auld.[2] The approach outlined below contains some novel elements and serves to complement the results of the preceding section.

Concerning acoustic waves, the key element that is present for any symmetry direction is the mirror plane. In the context of Laue groups, all threefold, fourfold, and sixfold axes lie in symmetry planes and twofold axes lie either in or perpendicular to symmetry planes. These may be simulated mirror planes, as in the case of the groups TII and RII. By analyzing the most general situation in which a mirror plane can occur, which corresponds to monoclinic symmetry, we will derive expressions for the phase velocity and other quantities which can be specialized to any symmetry direction in any crystal.

We will suppose the mirror plane to be perpendicular to the x_3 direction. For $\vec{n}$ lying in the plane, one of the modes has its displacement vector perpendicular to this plane, while the other two modes have their displacements in the plane. The same consideration applies when $\vec{n}$ is perpendicular to a mirror plane. Because this eigenvector which is parallel to the x_3 direction must satisfy Eq. (2) it follows that $\Gamma_{13}=\Gamma_{23}=0$, and the characteristic equation is, therefore,

$$\begin{vmatrix} \Gamma_{11}-\rho v^2 & \Gamma_{12} & 0 \\ \Gamma_{12} & \Gamma_{22}-\rho v^2 & 0 \\ 0 & 0 & \Gamma_{33}-\rho v^2 \end{vmatrix} = 0 . \tag{38}$$

Expanding the determinant one obtains

$$(\rho v^2-\Gamma_{33})[\rho^2 v^4-\rho v^2(\Gamma_{11}+\Gamma_{22})+\Gamma_{11}\Gamma_{22}-\Gamma_{12}^2]=0 . \tag{39}$$

The factor which is linear in ρv^2 yields the root

$$\rho v_0^2=\Gamma_{33} , \tag{40}$$

while the quadratic factor provides the other two roots:

$$2\rho v_{1,2}^2=\Gamma_{11}+\Gamma_{22}\pm[(\Gamma_{11}-\Gamma_{22})^2+4\Gamma_{12}^2]^{1/2} . \tag{41}$$

These results are consistent with the general velocity expressions discussed in the preceding section, although the numbering is different. This can be seen as follows: With Λ_{13} and Λ_{23} being zero, and using the fact that $\Lambda_{rr}=0$, the equation determining ψ takes on the form

$$\cos 3\psi = 4\cos^3\psi - 3\cos\psi = H/G^{3/2} = \frac{\frac{1}{2}\Lambda_{33}(\Lambda_{11}\Lambda_{22}-\Lambda_{12}^2)}{[\frac{1}{3}(\Lambda_{33}^2+\Lambda_{12}^2-\Lambda_{11}\Lambda_{22})]^{3/2}} . \tag{42a}$$

This cubic equation for $\cos\psi$ readily factors to yield

$$\cos\psi=\frac{\Lambda_{33}}{2G^{1/2}} , \tag{42b}$$

and therefore

$$\sin\psi=\frac{[(\Lambda_{11}-\Lambda_{22})^2+4\Lambda_{12}^2]^{1/2}}{2(3^{1/2})G^{1/2}} , \tag{42c}$$

or another two roots for which ψ differs from the above value by $\pm\frac{2}{3}\pi$. Any of the three roots, in conjunction with Eq. (18), leads to Eqs. (40) and (41).

The associated displacement eigenvectors are $\vec{U}_0=(0,0,1)$ and $\vec{U}_{1,2}=(p,q,0)$, where

$$\frac{q}{p}=\frac{\rho v_{1,2}^2-\Gamma_{11}}{\Gamma_{12}} . \tag{43}$$

All three are pure modes when $\vec{n}$ lies along a rotational axis in the mirror plane.

In the symmetry plane the Christoffel coefficients for the monoclinic group are

$$\begin{aligned} \Gamma_{11}&=C_{11}n_1^2+C_{66}n_2^2+2C_{16}n_1n_2 , \\ \Gamma_{22}&=C_{66}n_1^2+C_{22}n_2^2+2C_{26}n_1n_2 , \\ \Gamma_{33}&=C_{55}n_1^2+C_{44}n_2^2+2C_{45}n_1n_2 , \\ \Gamma_{12}&=C_{16}n_1^2+C_{26}n_2^2+(C_{12}+C_{66})n_1n_2 , \end{aligned} \tag{44}$$

so that in terms of the azimuthal angle ϕ where $n_1=\cos\phi$ and $n_2=\sin\phi$ we have that

$$\rho v_0^2=C_{55}\cos^2\phi+C_{44}\sin^2\phi+2C_{45}\cos\phi\sin\phi , \tag{45}$$

$$\begin{aligned} 2\rho v_{1,2}^2=&(C_{11}+C_{66})\cos^2\phi+(C_{22}+C_{66})\sin^2\phi+2(C_{16}+C_{26})\cos\phi\sin\phi \\ &\pm\{[(C_{11}-C_{66})\cos^2\phi+(C_{66}-C_{22})\sin^2\phi+2(C_{16}-C_{26})\cos\phi\sin\phi]^2 \\ &+4[C_{16}\cos^2\phi+C_{26}\sin^2\phi+(C_{12}+C_{66})\cos\phi\sin\phi]^2\}^{1/2} , \end{aligned} \tag{46}$$

and

$$\frac{q}{p}=\frac{\rho v_{1,2}^2-(C_{11}\cos^2\phi+C_{66}\sin^2\phi+2C_{16}\cos\phi\sin\phi)}{[C_{16}\cos^2\phi+C_{26}\sin^2\phi+(C_{12}+C_{66})\cos\phi\sin\phi]} . \tag{46a}$$

For $\vec{n}$ perpendicular to the symmetry plane, i.e., in the x_3 direction, we have $\Gamma_{11}=C_{55}$, $\Gamma_{22}=C_{44}$, $\Gamma_{33}=C_{33}$, and $\Gamma_{12}=C_{45}$ so that

$$\rho v_0^2=C_{33} , \tag{47}$$

$$2\rho v_{1,2}^2=(C_{44}+C_{55})\pm[(C_{55}-C_{44})^2+4C_{45}^2]^{1/2} , \tag{48}$$

and

$$\frac{q}{p}=\frac{\rho v_{1,2}^2-C_{55}}{C_{45}}. \tag{49}$$

These results are simplified somewhat if the freedom to rotate the x_1 and x_2 axes in the symmetry plane is used to eliminate C_{45}.[4]

For $\vec{n}$ lying in the symmetry plane, but not along a threefold axis, the group velocity also lies in this plane. The conical-refraction effects that take place along threefold axes have been dealt with elsewhere[4] and will not be discussed here. With the x_3 component of $\vec{V}$ thus determined, the other two components may be obtained using Eq. (27). In this way for the pure T mode v_0 we obtain

$$V_{0\alpha}=\frac{1}{2\rho v_0}\frac{\partial\Gamma_{33}}{\partial n_\alpha}\quad(\alpha=1,2). \tag{50}$$

For the other two modes we obtain the group velocity by implicit differentiation on the velocity equation

$$\Omega=\rho^2v_j^4-\rho v_j^2(\Gamma_{11}+\Gamma_{22})+\Gamma_{11}\Gamma_{22}-\Gamma_{12}^2=0. \tag{51}$$

The result is

$$V_{j\alpha}=-\frac{1}{2\rho v_j}\left[\left(\frac{\partial\Omega}{\partial n_\alpha}\right)\Big|\left(\frac{\partial\Omega}{\partial(\rho v_j^2)}\right)\right]$$

$$=\frac{\rho v_j^2(\partial/\partial n_\alpha)(\Gamma_{11}+\Gamma_{22})+(\partial/\partial n_\alpha)(\Gamma_{12}^2-\Gamma_{11}\Gamma_{22})}{2\rho v_j(2\rho v_j^2-\Gamma_{11}-\Gamma_{22})} \tag{52}$$

$$(\alpha=1,2;\ \ j=1,2).$$

Along twofold, fourfold and sixfold axes the group and phase velocities coincide, and the same is true for the L mode along a threefold axis.

The expressions derived above apply not only to monoclinic but in fact to any crystal system which contains a (001) mirror plane, and they are also easily adapted for other planes. The effect of additional symmetry elements is to simplify the elastic constant matrix by eliminating certain of the constants and introducing relationships between others.

Orthorhombic symmetry is distinguished from monoclinic by having $C_{45}=C_{16}=C_{26}=C_{36}=0$. The There are two additional mirror planes, the (100) and (010). To adapt the expressions for the (100) plane is simply a matter of interchanging the x_1 and x_3 axes which in the abbreviated subscript notation means interchanging $1\equiv11\rightleftharpoons33\equiv3$, $4\equiv23\rightleftharpoons21\equiv6$, while $2\equiv22$ and $5\equiv31$ are unaltered. Thus, for instance, $C_{12}\rightarrow C_{32}$ and $C_{66}\rightarrow C_{44}$, etc. If, following this, the x_2 and x_3 axes are interchanged, i.e., $2\equiv22\rightleftharpoons33\equiv3$ and $6\equiv12\rightleftharpoons13\equiv5$, then expressions pertaining to the (010) plane result.

The corresponding results for tetragonal symmetry are obtained from orthorhombic symmetry by setting $C_{22}=C_{11}$, $C_{23}=C_{13}$, and $C_{55}=C_{44}$. In addition there are two equivalent mirror planes perpendicular to the [110] and [1$\bar{1}$0] directions. The transformation here is not effected simply by an interchange of subscripts. A rotation of coordinate axes so that x_3' is perpendicular to one of these planes and x_1' lies along the fourfold axis transforms the elastic constant matrix to

$$C_{ij}'=\begin{pmatrix} C_{33} & C_{13} & C_{13} & 0 & 0 & 0\\ C_{13} & [\frac{1}{2}(C_{11}+C_{12})+C_{66}] & [\frac{1}{2}(C_{11}+C_{12})-C_{66}] & 0 & 0 & 0\\ C_{13} & [\frac{1}{2}(C_{11}+C_{12})-C_{66}] & [\frac{1}{2}(C_{11}+C_{12})+C_{66}] & 0 & 0 & 0\\ 0 & 0 & 0 & \frac{1}{2}(C_{11}-C_{12}) & 0 & 0\\ 0 & 0 & 0 & 0 & C_{44} & 0\\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix},$$

and it is these transformed constants that one enters into the monoclinic results.

The tetragonal results may be adapted for cubic symmetry by setting $C_{33}=C_{11}$, $C_{13}=C_{12}$, and $C_{66}=C_{44}$. There are no further inequivalent symmetry planes to consider.

In trigonal symmetry there are three equivalent symmetry planes, one of which is conventionally taken to be the (100) plane. For these planes and their perpendiculars one modifies the monoclinic results by carrying out the abreviated subscript interchange $1\rightleftharpoons3$ and $4\rightleftharpoons6$ and making use of the fact that $C_{34}=0$, $C_{22}=C_{11}$, $C_{23}=C_{13}$, $C_{55}=C_{44}$, $C_{56}=-C_{24}=C_{14}$, and $C_{66}=\frac{1}{2}(C_{11}-C_{12})$.

The hexagonal results are realized by setting $C_{14}=0$ in the trigonal results. Because of the rotational invariance of the equations of motion about the x_3 axis, the resulting expressions apply to any plane containing the x_3 axis.

V. DETERMINATION OF CRYSTAL ORIENTATION AND ELASTIC CONSTANTS FROM MEASURED PHASE VELOCITIES

A variety of experimental techniques such as ultrasonics and Brillouin scattering employ

acoustic waves to probe the elastic properties of crystals. The data provided by these techniques are, in the first instance, a set of measured velocities, and from this the elastic constants have to be determined. The algebra involved in extracting this information is greatly simplified if the waves are chosen to lie in crystal symmetry directions. In the past most investigators have in fact relied predominantly on measurements taken in these directions. The practical disadvantage of being limited in this way is that the crystals being investigated have to be faceted and aligned in special ways which is not always convenient or indeed even feasible. This is particularly true when the crystalline phases being studied exist only under extreme conditions of temperature or pressure. Fast-ion conductors[29] and inert-gas crystals[18] are two situations that might be cited.

A set of measured sound velocities in one or more arbitrary directions in a crystal contains information both on the elastic constants and on the location of these directions with respect to the crystallographic axes. One can use this information to determine the orientation of a crystal if the elastic constants are known, or to determine the elastic constants if the orientation is known, or even to determine both.

The orientation of a crystal is fully determined when two distinct directions in that crystal are identified. If the elastic constants are known, then from a measurement of the three phase velocities in some direction it is possible, within certain limits, to determine the location of that direction with respect to the crystallographic axes. The identification of this direction is most easily carried out by calculating T, G, and H by means of Eqs. (13), (14), and (15) and then making use of the expressions for these quantities given in the Appendix.

In the case of the tetragonal group $T\mathrm{I}$ the value of T determines $n_3^2=\cos^2\theta$. Since the polar angle θ is confined to the interval $0\leq\theta\leq\pi$, there are two possible values of θ which are the complements of each other. On substituting for $\cos^2\theta$ and $\sin^2\theta$ in the expression for either G or H, $\cos 4\phi$ is determined. This means that there are eight possible values of ϕ in the interval $0\leq\phi\leq 2\pi$. Overall, therefore, one arrives at 16 possible directions. For the holohedral point group 4/mmm these are all equivalent directions, but for the other point groups in this categroy, they separate into two nonequivalent sets, each consisting of eight equivalent directions and which are related by inversion. There are no purely mechanical means to distinguish between these two sets. By referring the elastic constants to the special axes for which $C_{16}=0$, the above method can also be applied to the group $T\mathrm{II}$. The 16 directions obtained form two distinguishable sets of eight equivalent directions. The correct set is determined when measurements in a second direction are done. However, in the case of the point groups 4 and $\bar{4}$ there remains the ambiguity associated with inversion.

For the rhombohedral group $R\mathrm{I}$, T again yields two complementary values of θ, or correspondingly, two equal and opposite values of $\cos\theta$. On substituting into G one obtains the values of $\cos\theta\sin 3\phi$. The positive value of $\cos\theta$ leads to six values of ϕ while the negative value of $\cos\theta$ leads to another six values, which are displaced by $\pi/3$ with respect to the former set. There are thus 12 possible directions. For the holohedral point group $\bar{3}m$ there are all equivalent directions, but for the other two point groups in this categroy the ambiguity of inversion remains. Applied to the rhombohedral group $R\mathrm{II}$ this method leads to two distinguishable sets of six equivalent directions. The ambiguity of inversion affects the point group 3.

In the case of the hexagonal system, only the direction of the x_3 axis can be determined and not that of the other two axes.

For cubic system, T is independent of direction while G yields the value of $P=n_1^2n_2^2+n_2^2n_3^2+n_3^2n_1^2$, and on substitution into H one obtains the value of $Q=n_1^2n_2^2n_3^2$. The normalization of $\vec{n}$ yields a third quantity $1=n_1^2+n_2^2+n_3^2$. It is apparent from the structure of these three quantities that n_1^2, n_2^2, and n_3^2 are the three roots[30] of the cubic equation $x^3-x^2+Px-Q=0$. Since the three roots can be permuted in six ways among n_1^2, n_2^2, n_3^2, and n_1, n_2, and n_3 can each be positive or negative, there are $6\times2\times2\times2=48$ possible directions. These are equivalent directions for the holohedral point group $m3m$, but for the other cubic point groups they separate into two or four sets, which are indistinguishable as far as the second-order elastic tensor is concerned.

For the orthorhombic group O, the expresion for T and the normalization condition $n^2=1$ can be used to eliminate two of the components of $\vec{n}$ from the expression for G. This results in a quadratic equation for the squared third component. One of the roots must be eliminated on the basis of its sign or compatibility with H. In this way one arrives at two equal and opposite values for each component of $\vec{n}$ and there are thus eight possible directions. These are equivalent directions for the point group mmm but separate into two sets, related by inversion, for the other two orthorhombic groups. The complexity of T, G, and H for the monoclinic and triclinic systems does not

favor the same simple approach as above, but in principle it should still be possible to determine the crystal orientation.

The determination of elastic constants from velocity data associated with selected symmetry directions has been discussed by a number of authors.[31] The evaluation can either be done using the velocity expressions given in Sec. IV or, where all three velocities in a given direction are known, from the three invariants of the Christoffel matrix. By judiciously selecting the directions of measurement the effect of various elastic constants can be suppressed and the algebra considerably simplified. In some cases ambiguities arise that can only be resolved by considerations of particle displacements[32] or thermodynamic constraints.[33] This concerns the sign of c for the group TI and the fact that for the group O, the sign of $b_1b_2b_3$ can be determined but not the signs of b_1, b_2, and b_3 individually.

Where the measured velocities are associated with arbitrary nonsymmetry crystallographic directions, except in the case of the hexagonal system, there are no simple "short-cuts" in determining the elastic constants. In the first place, these velocities depend on all the elastic constants so a step-by-step determination of individual C_{ij}'s is not possible. An even more serious obstacle is the high degree of the equations that occur. In the case of cubic symmetry an equation of degree 6 has to be solved in order to determine C_3. Head[34] has convincingly demonstrated in a recent publication that sextic equations of this sort are unlikely to be solvable in the classical Galoisian sense, and numerical methods are therefore necessary for extracting their roots. This problem persists through the lower-symmetry systems.

Since an explicit expression for the velocities has been obtained, it is a relatively simple matter to employ one of the standard fitting procedures to determine the elastic constants and any other unknown parameters there are. Where the number of measured velocities v_p is equal to the number of unknown parameters, and the approximate values $\mu_r^{(0)}$ of the parameters are known, one can generate a succession of improved values $\mu_r^{(n)}$ by means of the iteration equation

$$v_p^{(n)} + (\mu_r^{(n+1)} - \mu_r^{(n)}) \frac{\partial v_p^{(n)}}{\partial \mu_r} = v_p , \tag{53}$$

where $v_p^{(n)}$ and its derivatives are obtained using Eq. (18) and the values $\mu_r^{(n)}$ of the parameters. Where the number of measured velocities exceeds the number of unknown parameters, a least-squares–fitting procedure is appropriate. Where all three velocities are measured in each direction there is the choice of fitting either to the velocities or to the three invariants T, G, and H.

As an illustration we will calculate the elastic constants and orientation of a xenon crystal (crystal 1) studied by Gornall and Stoicheff.[18] The reader is referred to their paper for a description of the Brillouin scattering measurements carried out on this cubic crystal and for all other relevant details. The x-ray diffraction method that was used to determine the orientation of the crystal led to uncertainties of $\lesssim \pm 2°$ in the Euler angles relating the crystallographic axes to the laboratory reference frame, and this was estimated to influence the determination of the elastic constants by as much as ±15%. In contrast to this, the uncertainties in the Brillouin frequency shifts were all less than 1% and in many cases less than 0.1%. There is thus good reason here for treating the Euler angles as parameters rather than using the measured values of the these angles.

Using the program MINUIT developed by James and Roos,[35] we have carried out a least-squares fit with equal weighting give to all scattering data. Six parameters were employed, viz., C_{11}, C_{12}, C_{44}, θ, χ, and ϕ_0. The angles θ and χ were the two Euler angles that were fixed in the measurements and all recorded values of ϕ were presumed to need incrementing by an amount ϕ_0. The range of θ, χ, and ϕ_0 over which the search was conducted was confined only sufficiently to avoid

TABLE I. Experimental and calculated Brillouin spectra for xenon based on crystal 1 data provided by Gornall and Stoicheff (Ref. 18). The shifts $\nu_i^{(1)}$ have been calculated with the Euler angles treated as parameters and the shifts $\nu_i^{(2)}$ with these angles fixed at their measured values.

ϕ_i (deg)	Polarization index j	Observed ν_i (GHz)	Calculated $\nu_i^{(1)}$ (GHz)	Calculated $\nu_i^{(2)}$ (GHz)
169	0	3.463	3.460	3.444
179	0	3.517	3.514	3.504
189	0	3.545	3.547	3.542
199	0	3.555	3.552	3.553
209	0	3.530	3.532	3.538
219	0	3.492	3.494	3.503
229	0	3.454	3.452	3.460
239	0	3.415	3.422	3.426
169	1	1.583	1.577	1.598
179	1	1.493	1.474	1.490
189	1	1.383	1.411	1.415
199	1	1.426	1.418	1.410
209	1	1.488	1.484	1.469
219	1	1.552	1.556	1.545
229	1	1.568	1.568	1.564
239	1	1.515	1.519	1.519
229	2	1.959	1.947	1.945
239	2	2.027	2.036	2.039

equivalent orientations. The best fit obtained was with $C_{11}=3.026$, $C_{12}=1.942$, and $C_{44}=1.443$ in units of 10^{10} dyn/cm^2 and $\theta=26.0°$, $\chi=124.3°$, and $\phi_0=0.1°$, all three of the angles being within the bounds determined by x-ray diffraction. The calculated Brillouin frequency shifts $\nu_i^{(1)}$ are given in the fourth column of Table I. The rms deviation between these and the observed frequency shifts ν_i is 0.009 GHz. For comparison, the fifth column of Table I contains the best fit $\nu_i^{(2)}$ obtained when the angles were fixed at their mean measured values, viz., $\theta=26°$, $\chi=123°$, and $\phi_0=0°$. With the fitted values of the elastic constants $C_{11}=2.980$, $C_{12}=1.911$ and $C_{44}=1.472$ in units of 10^{10} dyn/cm^2 the rms deviation at 0.013 GHz is significantly larger than before.

For crystals belonging to the Laue groups TII and RII, the angle ϕ_0 defined in the Appendix would naturally be featured as one of the parameters in an analysis of the sort described above.

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APPENDIX

We consider here the form that Λ, T, G, and H take for the different crystal Laue groups. The defining equations for these quantities are combined with the expressions for the Christoffel coefficients so that the results are expressed directly in terms of the elastic constants and the wave direction $\vec{n}$. In this way T, G, and H are clearly seen to have the Laue group symmetry. Where not otherwise specified, the coordinate axes may be taken to be located in the conventional way with respect to the crystallographic directions.

Factors of $n^2=n_1^2+n_2^2+n_3^2$, where they occur, preserve the homogeneity of T, G, and H when these functions are expressed in terms of the components of $\vec{n}$, but are replaced by 1 when angular coordinates θ and ϕ are employed.

1. First tetragonal group TI (classes 422, 4mm, $\bar{4}$2m, and 4/mmm)

There are six independent nonzero elastic constants $C_{11}=C_{22}$, C_{33}, $C_{44}=C_{55}$, C_{66}, C_{12}, and $C_{13}=C_{23}$. We will also make use of the combinations $a=C_{33}-C_{44}$, $b=3(C_{12}+C_{66})$, $c=3(C_{13}+C_{44})$, $d=2C_{11}-C_{44}-C_{66}$, $e=2C_{66}-C_{11}-C_{44}$, $f=2C_{44}-C_{11}-C_{66}$, $g=3(C_{11}-C_{12}-2C_{66})$, $h=3(C_{11}+C_{12})$, $A_1=c^2+3af$, $A_2=e^2-df$, $A_3=a(f^2+2ed)-ec^2$, and $A_4=2(c^2-ah)$. In terms of these constants one readily establishes that

$$T=(C_{11}+C_{44}+C_{66})(n_1^2+n_2^2)+(C_{33}+2C_{44})n_3^2\,, \tag{A1}$$

$$\Lambda=\begin{pmatrix} dn_1^2+en_2^2-an_3^2 & bn_1n_2 & cn_1n_3 \\ bn_1n_2 & en_1^2+dn_2^2-an_3^2 & cn_2n_3 \\ cn_1n_3 & cn_2n_3 & fn_1^2+fn_2^2+2an_3^2 \end{pmatrix}, \tag{A2}$$

$$3G=3a^2n_3^4+A_1n_3^2(n_1^2+n_2^2)+A_2(n_1^2+n_2^2)^2-ghn_1^2n_2^2\,, \tag{A3}$$

and

$$2H=2a^3n_3^6+aA_1n_3^4(n_1^2+n_2^2)+A_3n_3^2(n_1^2+n_2^2)^2+def(n_1^2+n_2^2)^3+gfhn_1^2n_2^2(n_1^2+n_2^2)-gA_4n_1^2n_2^2n_3^2\,. \tag{A4}$$

These results may be expressed in terms of spherical polar coordinates θ and ϕ. Since $n_1=\sin\theta\cos\phi$, $n_2=\sin\theta\sin\phi$, and $n_3=\cos\theta$ we have that

$$T=(C_{11}+C_{44}+C_{66})\sin^2\theta+(C_{33}+2C_{44})\cos^2\theta\,, \tag{A5}$$

$$3G=3a^2\cos^4\theta+A_1\cos^2\theta\sin^2\theta+A_2\sin^4\theta-\tfrac{1}{8}gh\sin^4\theta(1-\cos4\phi)\,, \tag{A6}$$

and

$$2H=2a^3\cos^6\theta+aA_1\cos^4\theta\sin^2\theta+A_3\cos^2\theta\sin^4\theta+def\sin^6\theta+\tfrac{1}{8}gfh\sin^6\theta(1-\cos4\phi)-\tfrac{1}{8}gA_4\sin^4\theta\cos^2\theta(1-\cos4\phi)\,. \tag{A7}$$

The fourfold symmetry about the x_3 axis and the various symmetry planes of this tetragonal group are evident in these results. It is worth noting that the azimuthal angle ϕ occurs in relatively few of the terms, all of which contain g as a factor. The condition $g=0$ therefore renders the equations

of motion transversely isotropic, i.e., invariant under rotations about the x_3 axis.

2. Second tetragonal group *T*II (classes 4, $\bar{4}$, and 4/m)

The four symmetry planes containing the x_3 axis are absent from this group, and there is one further independent elastic constant $C_{16} = -C_{26}$. The natural orientation of the x_1 and x_2 axes in the remaining plane is no longer prescribed by symmetry and this freedom of choice can be used to eliminate C_{16}.[4] The angle ϕ_0 through which the axes have to be rotated about the x_3 direction in order to remove C_{16} from the elastic constant matrix is given by

$$\tan 4\phi_0 = \frac{4C_{16}}{C_{11} - C_{12} - 2C_{66}} . \tag{A8}$$

This does not alter the fact that seven parameters are still needed to fully characterize the second-order elastic tensor, but it does allow the results of the preceding subsection to be applied unaltered to this group as well.

3. First rhombohedral group *R*I (classes 32, 3m, and $\bar{3}$m)

There are six independent elastic constants $C_{11} = C_{22}$, C_{33}, C_{12}, $C_{13} = C_{23}$, $C_{44} = C_{55}$, and $C_{14} = -C_{24} = C_{56}$, while $C_{66} = \frac{1}{2}(C_{11} - C_{12})$. We also make use of the constants a, b, c, d, e, and f defined previously and $B_1 = c^2 + 3af + 36C_{14}^2$, $B_2 = e^2 - df + 9C_{14}^2$, $B_3 = a(c^2 + 3af - 72C_{14}^2)$, $B_4 = a(f^2 + 2ed) - ec^2 + 9(a - 4f + 4c)C_{14}^2$, $B_5 = 2ab - c(a+c)$, and $B_6 = ce + fb - 9C_{14}^2$. For this group T is the same as before, i.e.,

$$T = T_{\text{tetrag}} , \tag{A9}$$

while

$$\Lambda = \Lambda_{\text{tetrag}} + 3C_{14} \begin{pmatrix} 2n_2n_3 & 2n_3n_1 & 2n_1n_2 \\ 2n_3n_1 & -2n_2n_3 & (n_1^2 - n_2^2) \\ 2n_1n_2 & (n_1^2 - n_2^2) & 0 \end{pmatrix} , \tag{A10}$$

$$3G = 3a^2n_3^2 + B_1n_3^2(n_1^2 + n_2^2) + B_2(n_1^2 + n_2^2)^2 - 6C_{14}(b+c)n_3n_2(n_2^2 - 3n_1^2) , \tag{A11}$$

$$3G = 3a^2\cos^4\theta + B_1\cos^2\theta\sin^2\theta + B_2\sin^4\theta + 6C_{14}(b+c)\cos\theta\sin^3\theta\sin 3\phi , \tag{A12}$$

and

$$2H = 2a^3n_3^6 + B_3n_3^4(n_1^2 + n_2^2) + B_4n_3^2(n_1^2 + n_2^2)^2 + def(n_1^2 + n_2^2)^3 + 6C_{14}B_5n_3^3n_2(n_2^2 - 3n_1^2)$$
$$+ 6C_{14}B_6n_3n_2(n_1^2 + n_2^2)(n_2^2 - 3n_1^2) - 9dC_{14}^2[n_1(n_1^2 - 3n_2^2)]^2 - 9eC_{14}^2[n_2(n_2^2 - 3n_1^2)]^2 , \tag{A13}$$

$$2H = 2a^3\cos^6\theta + B_3\cos^4\theta\sin^2\theta + B_4\cos^2\theta\sin^4\theta + \text{def}\sin^6\theta - 6C_{14}B_5\cos^3\theta\sin^3\theta\sin 3\phi$$
$$- 6C_{14}B_6\cos\theta\sin^5\theta\sin 3\phi - 9dC_{14}^2\sin^6\theta\cos^2 3\phi - 9eC_{14}^2\sin^6\theta\sin^2 3\phi . \tag{A14}$$

The threefold symmetry about the x_3 axis and the presence of the three symmetry planes containing the x_3 axis as well as the absence of a perpendicular symmetry plane are evident in these results. Those terms into which ϕ enters contain C_{14} as a factor, and therefore $C_{14} = 0$ is the condition for transverse isotropy.

4. Second rhombohedral group *R*II (classes 3 and $\bar{3}$)

The symmetry planes are missing from this group and as a consequence there is an additional independent elastic constant $C_{15} = -C_{25} = -C_{46}$. There is also flexibility in choosing the orientation of the x_1 and x_2 axes.[4] A rotation about the x_3 axis by an angle ϕ_0 given by

$$\tan\phi_0 = -C_{15}/C_{14} \tag{A15}$$

will eliminate this additional constant and the results of the preceding subsection becomes applicable to this group.

5. Hexagonal groups *H*I and *H*II (all hexagonal classes)

The elastic constant matrix for both these groups is the same and corresponds to the matrix for the *T*I group with $C_{66} = \frac{1}{2}(C_{11} - C_{12})$, i.e., $g = 0$ or to that for the *R*I group with $C_{14} = 0$. The characteristic equation is thus independent of ϕ, and as is well known, it can be factored to yield velocities which depend only on the polar coordinate θ.

6. Cubic groups *C*I and *C*II (all cubic classes)

There are only three independent elastic constants $C_{11} = C_{22} = C_{33}$, $C_{44} = C_{55} = C_{66}$, and $C_{12} = C_{13}$

$=C_{23}$. This can be treated as a special case of tetragonal symmetry. We adapt the TI results by setting $C_1=C_{11}+2C_{44}$, $a=d/2=-e=-f=C_2=C_{11}-C_{44}$, $g/3=K=C_{11}-C_{12}-2C_{44}$, $b=c=3(C_2-K)$, and $h=3(2C_2-K)$. In terms of C_1, C_2, and K we have

$$T=C_1n^2\,, \tag{A16}$$

$$\Lambda=\begin{pmatrix} C_2(3n_1^2-n^2) & 3(C_2-K)n_1n_2 & 3(C_2-K)n_1n_3 \\ 3(C_2-K)n_1n_2 & C_2(3n_2^2-n^2) & 3(C_2-K)n_2n_3 \\ 3(C_2-K)n_1n_3 & 3(C_2-K)n_2n_3 & C_2(3n_3^2-n^2) \end{pmatrix}, \tag{A17}$$

$$G=C_2^2n^4-3K(2C_2-K)P\,, \tag{A18}$$

and

$$H=C_2^3n^6-\tfrac{9}{2}C_2K(2C_2-K)Pn^2+\tfrac{27}{2}K^2(3C_2-2K)Q\,, \tag{A19}$$

where

$$P=n_1^2n_2^2+n_2^2n_3^2+n_3^2n_1^2=\sin^4\theta\sin^2\phi\cos^2\phi+\cos^2\theta\sin^2\theta$$

and

$$Q=n_1^2n_2^2n_3^2=\sin^4\theta\cos^2\theta\sin^2\phi\cos^2\phi\,.$$

The condition for elastic isotropy is that $K=C_{11}-C_{12}-2C_{44}=0$. When this is satisfied, T, G, and H are all constants and furthermore $G^3=H^2$.

7. Orthorhombic group O (classes 222, mm2, and mmm)

There are nine nonzero elastic constants C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23}. We also make use of the combinations $b_1=3(C_{23}+C_{44})$, $b_2=3(C_{13}+C_{55})$, $b_3=3(C_{12}+C_{66})$, $d_1=2C_{11}-C_{55}-C_{66}$, $e_1=2C_{66}-C_{11}-C_{55}$, $f_1=2C_{55}-C_{11}-C_{66}$, $d_2=2C_{66}-C_{22}-C_{44}$, $e_2=2C_{22}-C_{44}-C_{66}$, $f_2=2C_{44}-C_{22}-C_{66}$, $d_3=2C_{55}-C_{33}-C_{44}$, $e_3=2C_{44}-C_{33}-C_{55}$, and $f_3=2C_{33}-C_{44}-C_{55}$. In the case of this group we have

$$T=(C_{11}+C_{55}+C_{66})n_1^2+(C_{22}+C_{44}+C_{66})n_2^2+(C_{33}+C_{44}+C_{55})n_3^2\,, \tag{A20}$$

$$\Lambda=\begin{pmatrix} d_1n_1^2+d_2n_2^2+d_3n_3^3 & b_3n_1n_2 & b_2n_1n_3 \\ b_3n_1n_2 & e_1n_1^2+e_2n_2^2+e_3n_3^2 & b_1n_2n_3 \\ b_2n_1n_3 & b_1n_2n_3 & f_1n_1^2+f_2n_2^2+f_3n_3^3 \end{pmatrix}, \tag{A21}$$

$$3G=(d_jd_k-e_jf_k)n_j^2n_k^2+b_1^2n_2^2n_3^2+b_2^2n_3^2n_1^2+b_3^2n_1^2n_2^2\,, \tag{A22}$$

and

$$2H=d_ie_jf_kn_i^2n_j^2n_k^2+2b_1b_2b_3n_1^2n_2^2n_3^2-b_1^2d_in_i^2n_2^2n_3^2-b_2^2e_in_i^2n_3^2n_1^2-b_3^2f_in_i^2n_1^2n_2^2\,. \tag{A23}$$

8. Monoclinic group M (classes 2, m, and 2/m)

For this group there are 13 independent nonzero elastic constants. Taking the x_3 direction to be along the diad axis, the eight vanishing elastic constants are C_{14}, C_{15}, C_{24}, C_{25}, C_{34}, C_{35}, C_{46} and C_{56}. Rotation of the x_1 and x_2 axes in the symmetry plane can be used to eliminate one of the remaining constants. Because of the low degree of symmetry there is little advantage to be gained from developing the expanded forms of T, G, and H. For numerical purposes they may be obtained from Eqs. (4), (7), (9), (11), and (12).

9. Triclinic group N (classes 1 and $\bar{1}$)

All 21 elastic constants are nonzero and independent, although one may use the 3 degrees of freedom in orienting the coordinate axes to eliminate three of them. No general expanded formulae for T, G, and H will be given, but as with the previous group, they can be obtained numerically.

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