Acoustical Activity and Other First-Order Spatial Dispersion Effects in Crystals*

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It is demonstrated phenomenologically that as a result of first-order spatial dispersion an "acoustical activity" of transverse acoustic waves, the analog of optical activity, arises in certain crystal classes. Crystals which are optically active are also found to be acoustically active. Furthermore, in the case of propagation along high-symmetry axes, the effect manifests itself, as in the case of optical activity, as a simple rotation of the plane of polarization of transverse acoustic waves. Acoustic effects of first-order spatial dispersion which have no optical analog are also treated. Acoustical activity can also be inferred from the transformation properties of the acoustic phonons, and the acoustical activity of crystals may thereby be derived from phonon-dispersion curves. An estimate of the magnitude of the acoustical activity of tellurium is so obtained. The effects of first-order spatial dispersion on transverse-optical phonons and the optical properties which arise from them are also considered. Practical problems involved in the observation of acoustical activity are discussed.

1. INTRODUCTION

ALTHOUGH optical activity is a well-established phenomenon, its acoustical analog has, to our knowledge, not been previously investigated. The effect most often associated with optical activity, which is exhibited by crystals lacking certain symmetry elements, is the rotation of the plane of polarization of light propagating along optic axes. This rotation results from a decomposition of the linearly polarized light into right and left circularly polarized modes which propagate coherently with different velocities and superpose at any point in the crystal to form a wave linearly polarized at a different angle. In the case of propagation along directions other than optic axes, the light propagates as right and left ellipitical polarized modes having different velocities.

Similar considerations should apply to transverse-acoustic waves. For crystals lacking certain symmetry elements, we would expect the crystal to respond differently to left and right circularly (or elliptically) polarized acoustic waves. Furthermore, we would expect that, in the case of propagation along "acoustic axes," there would be a rotation of the plane of polarization of linearly polarized transverse waves.

Optical activity is known to result from first-order spatial dispersion contributions to the dielectric constant. Acoustical activity, correspondingly, should result from first-order spatial dispersion contributions to the elastic constants. We present here a discussion of the effects of the first-order spatial dispersion of the elastic constants and its effects on the propagation of acoustic waves with specific application to acoustical activity.

2. SPATIAL DISPERSION

A. Electromagnetic Waves

Before proceeding with a discussion of the propagation of acoustic waves, let us review the effects of spatial dispersion on the propagation of light waves. The macroscopic linear response of a crystal to a light wave is described by the dielectric constant, which relates the electric displacement **D** to the electric field **E**. For most cases, the dielectric constant is a function of frequency only and does not depend on the wave vector. A dependence of the dielectric constant on wave vector occurs when the **D** at a given point depends on the **E** not only at that point, but at neighboring points as well, i.e., the response is nonlocal.[1] Formally, one expresses this dependence by writing the functional form of the dielectric constant as $\epsilon_{ij}(\omega,\mathbf{k})$, and the dependence of the dielectric constant on the wave vector $\mathbf{k}$ is known as spatial dispersion. When the magnitude of the nonlocal part of the dielectric constant is small, $\epsilon_{ij}(\omega,\mathbf{k})$ may be expanded in a power series in $\mathbf{k}$, namely,

$$\epsilon_{ij}(\omega,\mathbf{k}) = \epsilon_{ij}(\omega) + ig_{ijl}(\omega)k_l + h_{ijlm}(\omega)k_lk_m + \cdots. \quad (2.1)$$

Optical activity arises from the first-order terms $ig_{ijl}(\omega)k_l$, and the tensor g_{ijl} is called the optical gyrotropic tensor.

Because of time-reversal invariance and causality, $\epsilon_{ij}(\omega)$ is symmetric, i.e., $\epsilon_{ij}(\omega) = \epsilon_{ji}(\omega)$. [This is a general property which holds for any set of linear-response terms connecting conjugate intensive and extensive parameters F_i and X_i, respectively (such as D_i and E_i), whose contribution to the Hamiltonian has the form $\sum_i \int X_i(\mathbf{r})F_i(\mathbf{r})d^3\mathbf{r}$.[2]] Since the sign of $\mathbf{k}$ is reversed when time is reversed, the obvious generalization in the presence of spatial dispersion is $\epsilon_{ij}(\omega,\mathbf{k}) = \epsilon_{ji}(\omega, -\mathbf{k})$. It follows from this that the third-rank coefficient g_{ijl}

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[1] A. A. Rukhadze and V. P. Silin, Usp. Fiz. Nauk. 74, 223 (1961) [English transl.: Soviet Phys.—Usp. 4, 459 (1961)].

of the first-order term in the expansion of $\epsilon_{ij}(\omega,\mathbf{k})$ has the property $g_{iji}(\omega) = -g_{jil}(\omega)$. In transparent regions of the spectrum, where the absorption of light is negligible, $\epsilon_{ij}(\omega,\mathbf{k})$ is Hermitian, i.e., $\epsilon_{ij}{}^{*}(\omega,\mathbf{k}) = \epsilon_{ij}(\omega,\mathbf{k})$.[2] Under these conditions $g_{iji}(\omega)$ is real.

Optical activity cannot take place in crystals containing symmetry elements such as a center of inversion, or mirror planes perpendicular to, or containing, axes of threefold or higher symmetry, which transform left and right circularly polarized light into one another for all directions of propagation.[3] In other crystal classes, the effects of optical activity are present for light propagating in general directions, but, because of symmetry, are absent for certain propagation directions such as those in, or normal to, a mirror plane, or along a fourfold inversion axis. The symmetry elements also determine the direction dependence of the optical activity of waves propagating in different directions. The same results can be obtained by determining which coefficients g_{iji} vanish and which are related to each other under the various symmetry transformations.[4] On the basis of either procedure, one finds that optical activity does not occur in centrosymmetric crystals, nor does it occur in any cubic crystal which possesses reflection symmetry. The optic axis of a uniaxial crystal is one of threefold or higher symmetry. Therefore, light propagating along the optic axis of such a crystal cannot exhibit optical activity if the symmetry elements of the crystal include a mirror plane or an inversion axis. Simple rotation of the plane of polarization is, consequently, found only in the so-called "enantiomorphus" cubic and uniaxial crystals which lack mirror and inversion symmetry.

Let us take as an example the dielectric tensor of a low-symmetry uniaxial crystal, such as tellurium or quartz, which has a D_3 point-group symmetry. The dielectric tensor, to first-order terms in the spatial dispersion, is given by

$$\epsilon(\omega,k_3) = \begin{bmatrix} \epsilon_{11} & ig_{123}k_3 & 0 \\ -ig_{123}k_3 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{33} \end{bmatrix} \quad (2.2)$$

for wave propagation along the optic axis, taken along X_3. The propagation of light waves is described by the equation

$$E_i - n_i(\mathbf{n}\cdot\mathbf{E}) = (v^2/c^2)D_i = (v^2/c^2)\epsilon_{ij}E_j, \quad (2.3)$$

which is derived from Maxwell's equations. Here v is the phase velocity and $\mathbf{n}$ is the unit vector along the propagation direction. When $\mathbf{n}$ is along the optic axis

X_3 we find, on combining (2.2) and (2.3), that

$$\begin{bmatrix} E_1 \\ E_2 \\ 0 \end{bmatrix} = \frac{v^2}{c^2}\begin{bmatrix} \epsilon_{11} & ig_{123}k_3 & 0 \\ -ig_{123}k_3 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{33} \end{bmatrix}\begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}. \quad (2.4)$$

It is then simple to show, using standard methods, that the proper modes of propagation are the circularly polarized modes $E_{\pm} = E_x \pm E_y$, where the plus sign corresponds to left and the minus sign corresponds to right circularly polarized light.[5] Their phase velocities are given by

$$v_{\pm}{}^2 = c^2/\epsilon_{11} \pm g_{123}k_3 = c^2/n_{\pm}{}^2, \quad (2.5)$$

where $n_{\pm}$ are the corresponding refractive indices of the circularly polarized waves. If a linearly polarized wave propagating parallel to optic axis is incident on the crystal, it will decompose into right and left circularly polarized waves of equal amplitude. At a distance l from the incident surface, their phase difference is $(\omega l/c)(n_+ - n_-)$.[3] The resultant of the two waves at that point is a linearly polarized wave whose direction of polarization makes an angle of $(\omega l/2c)(n_+ - n_-)$ rad with respect to the polarization direction of the incident wave. This rotation of the plane of polarization is a direct consequence of the optical activity of the crystal.

B. Acoustic Waves

Let us now consider the analogous situation in acoustics. The macroscopic response of a crystal to an acoustic wave is determined by the compliance elastic constants. The elastic constants describe the linear relationship between the stress and the strain. Unlike $\mathbf{D}$ and $\mathbf{E}$, the stress T and strain $\mathscr{S}$ are not vectors, but rather second-order symmetric tensors. In full tensor notation they are therefore describable by two indices as T_{mn} and $\mathscr{S}_{pq}$. However, since the tensors are symmetric, the tensor components are independent of the order of these indices so that they may be equally well designated by a single index, in contracted form, as T_i and $\mathscr{S}_j$, respectively.[4] The compliance elastic constants can be written in a full notation as c_{mnpq}, or in a contracted notation as c_{ij}. In the case of static strains, the relationship between stress and strain in contracted notation takes the form $T_i = c_{ij}\mathscr{S}_j$, and there is an additional contribution to the free energy of the crystal of the form $V_0 T_i \mathscr{S}_i = V_0 c_{ij}\mathscr{S}_i \mathscr{S}_j$, where V_0 is the crystal volume. Only the symmetric part of c_{ij} contributes to the free energy. When the applied strain is not static, the resultant stress at any time can depend on the strain applied at the same time, or at any prior time. As long as the relationship between stress and strain is linear,

[2] L. D. Landau and E. M. Lifschitz, in *Statistical Physics*, translated by E. Pierels and R. F. Pierels (Pergamon Press, Ltd., Oxford, England, 1958), pp. 104ff.

[3] J. P. Mathieu, *Les Theories Moleculaires du Pouvoir Rotatoire Naturel* (Centre National de la Recherche Scientifique, Paris, 1946).

[4] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1957).

[5] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, Ltd., Oxford, England, 1964), 2nd ed., p. 30.

we may express this dependence by the relation

$$T_i(t) = \int_0^\infty c_{ij}(\tau)\mathcal{E}_j(t-\tau)d\tau. \qquad (2.6)$$

A free energy can no longer be defined. However, the applied strain contributes a term of the form $V_0 T_i \mathcal{E}_i$ to the Hamiltonian and this can be used to establish the time-reversal symmetry of c_{ij}.

$T_i(t)$ and $\mathcal{E}_j(t)$ can be described by an appropriate superposition of plane waves. Taking any one such wave, of frequency ω, we have the linear relationship $T_i(\omega) = c_{ij}(\omega)\mathcal{E}_j(\omega)$ between the stress and strain amplitudes of any such wave, where $c_{ij}(\omega)$ is given by

$$c_{ij}(\omega) = \int_0^\infty c_{ij}(t)e^{i\omega t}dt. \qquad (2.7)$$

Since this linear relationship exists, and since the stress and strain contribute a term to the Hamiltonian of the above form, it follows from causality and from the symmetry of such crystals under time-reversal invariance that $c_{ij}(\omega)$, like $\epsilon_{ij}(\omega)$, must be symmetric, i.e., $c_{ij}(\omega) = c_{ji}(\omega)$.

Up to this point we have assumed that the interaction between stress and strain is a local one. If the interaction is nonlocal, the elastic constants exhibit a dependence on wave vector and take the form $c_{ij}(\omega, \mathbf{k})$. Again from consideration of time-reversal invariance, one arrives at the relation $c_{ij}(\omega, \mathbf{k}) = c_{ji}(\omega, -\mathbf{k})$. On expanding $c_{ij}(\omega, \mathbf{k})$ in powers of $\mathbf{k}$, one obtains

$$c_{ij}(\omega, \mathbf{k}) = c_{ij}(\omega) + id_{ij,l}(\omega)k_l + e_{ij,lm}(\omega)k_l k_m + \cdots. \qquad (2.8)$$

The tensor $d_{ij,l}(\omega)$ may be called the acoustic gyrotropic tensor. It follows, as in the case of light waves, that $d_{ij,l}(\omega)$ is antisymmetric in the subscripts i and j, i.e., $d_{ij,l}(\omega) = -d_{ji,l}(\omega)$, and real in the absence of attenuation. Note, however, that $d_{ij,l}$ is actually a fifth-rank tensor d_{mnpql} and that the effect of symmetry on $d_{ij,l}$ differs from its effect on g_{ijl}.

We are now in a position to see how first-order spatial dispersion affects acoustic wave propagation. Acoustic propagation in a given direction does not depend on the complete set of elastic constants, but on a dynamical matrix $[\mathfrak{D}]$ containing certain of the elastic constants. The basic equation for propagation of an acoustic wave along the X_3 axis of a crystal is[6]

$$\mathfrak{D}_{jn}(\omega, k_3)u_n = c_{3j3n}(\omega, k_3)u_n = \rho v^2 u_j. \qquad (2.9)$$

In this equation $\mathbf{u}$ is the particle displacement, ρ is the density, v is the wave velocity, and $c_{3j3n}(\omega, k_3)$ is the appropriate set of elastic constants, written in full notation. For the case where the X_3 axis is an acoustic axis having threefold or higher symmetry, and in the absence of spatial dispersion, this equation takes the

⁶ P. C. Waterman, Phys. Rev. 113, 1240 (1959).

form

$$\begin{bmatrix} c_{2323} & 0 & 0 \\ 0 & c_{2323} & 0 \\ 0 & 0 & c_{3333} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \rho v^2 \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix}, \qquad (2.10)$$

and in contracted notation it takes the form

$$[\mathfrak{D}]\begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \begin{bmatrix} c_{44} & 0 & 0 \\ 0 & c_{44} & 0 \\ 0 & 0 & c_{33} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \rho v^2 \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix}. \qquad (2.11)$$

The matrix $[\mathfrak{D}]$ is the dynamical matrix describing acoustic-wave propagation along an acoustic axis. When the effects of spatial dispersion are taken into account (see Sec. 3) the dynamical matrix for optically active uniaxial and cubic crystals takes the form

$$[\mathfrak{D}] = \begin{bmatrix} c_{2323} & id_{13233}k_3 & 0 \\ -id_{13233}k_3 & c_{2323} & 0 \\ 0 & 0 & c_{3333} \end{bmatrix}$$

$$= \begin{bmatrix} c_{44} & id_{54,3}k_3 & 0 \\ -id_{54,3}k_3 & c_{44} & 0 \\ 0 & 0 & c_{33} \end{bmatrix} \qquad (2.12)$$

in full and contracted tensor notation, respectively. On substituting this expression into (2.9), one finds that the transverse modes are circularly polarized with phase velocities $v_\pm^2 = (1/\rho)(c_{44} \pm d_{54,3}k_3)$. In analogy with the optical case, the plane of polarization of an incident linearly polarized transverse-acoustic wave will be rotated by an angle $\phi = \frac{1}{2}\omega l[1/v_- - 1/v_+]$. To first order in $d_{54,3}k_3/c_{44}$ the angle is given by

$$\phi = \frac{1}{2}\omega^2 l\rho \; d_{54,3}/c_{44}^2. \qquad (2.13)$$

3. ACOUSTICAL ACTIVITY IN VARIOUS CRYSTAL CLASSES

The dependence of $d_{ij,l}$ on crystal symmetry is more complicated than that of g_{ijl} since $d_{ij,l}$ is a fifth-rank tensor whereas g_{ijl} is a third-rank tensor. We have seen, however, that the effect of first-order spatial dispersion on a transverse-acoustic wave propagating along a crystal direction of threefold or higher symmetry is similar to its effect on a light wave propagating along such directions, the dynamical matrix being especially simple in such cases. For the present, we restrict our attention to acoustic propagation along axes of threefold or higher symmetry and along cubic [100] axes, which, because of symmetry, must be acoustic axes. It is clear from (2.12), which applies to cubic, trigonal, hexagonal, and tetragonal crystals that only components of the form $d_{i3l33}(i, l=1, 2, 3)$ contribute to acoustical activity along an acoustic axis. The coefficient d_{13233} (or $d_{54,3}$) couples transverse modes with one another, while d_{13333} (or $d_{53,3}$) and d_{23333} (or $d_{43,3}$) couple transverse modes to the longitudinal mode. Relationships between the coefficients may be found by consideration of crystal symmetry, using methods described in standard texts.[4] It is easily shown that all coefficients must be zero in centrosymmetric crystal classes. In all uniaxial

classes the coefficients d_{13333} and d_{23333} are zero, so that there is no coupling of transverse to longitudinal modes.

Table I summarizes which noncentrosymmetric uniaxial classes, respectively, can or cannot exhibit acoustical activity for sound waves propagating along the acoustic axis. The coefficient d_{13233} must vanish in the latter classes.[7]

There are two acoustic axes in cubic crystals, namely, [001] and [111], so that two sets of coefficients must be considered. These sets are related, and in fact it is convenient to calculate the entire set of d_{ijklm} coefficients. There are three noncentrosymmetric crystal classes, T, T_d, and O. In class T the nonvanishing coefficients, referred to the cubic crystal axes, are (in contracted notation)

$$(1)\quad d_{14,1}=d_{25,2}=d_{36,3},$$
$$(2)\quad d_{15,2}=d_{26,3}=d_{34,1},$$
$$(3)\quad d_{16,3}=d_{24,1}=d_{35,2},$$
$$(4)\quad d_{45,3}=d_{56,1}=d_{64,2}.$$

In class O, set (1) is zero and set $(2)=-$set (3) i.e., $d_{15,2}=-d_{16,3}$. In class T_d, set (4) is zero, and set $(2)=$set (3), i.e., $d_{15,2}=d_{16,3}$.

For a transverse wave propagating along [100] axes, the acoustical activity is determined by the coefficients of set (4). Consequently, a rotation of the plane of polarization may be expected in classes T and O, but not in class T_d. No coupling between transverse and longitudinal modes results from any of these coefficients.

For transverse waves propagating along a [111] direction, the coefficient responsible for acoustic activity is[7]

$$d'_{45,3}=\tfrac{1}{9}[3d_{15,2}-3d_{16,3}-2d_{45,3}], \quad (3.1)$$

where we have referred $d'_{45,3}$ to a coordinate system (x'_1, x'_2, x'_3) along the crystalline [11$\bar{2}$], [1$\bar{1}$0], and [111] axes, respectively. This term may be nonvanishing in crystal classes T and O, but must be zero in class T_d so that acoustical activity does not occur in the latter class. Furthermore, since the [111] axis is one of threefold symmetry, there will be no coupling of the transverse modes to the longitudinal mode in any of these classes.

In summary, we note that for waves propagating along an acoustic axis, acoustical activity will be observable in crystal classes possessing axes of threefold

[7] D. L. Portigal, Ph.D. thesis, University of Pennsylvania, 1967 (unpublished).

or higher symmetry which do not have mirror planes or inversion axes. The same classes are the ones that will show optical activity for light waves propagating along an optic axis. Also, note that in the absence of spatial dispersion the transverse and longitudinal waves propagating along these axes are pure modes, and that first-order spatial dispersion does not mix the longitudinal mode with the transverse modes.

Although the coefficients responsible for acoustical activity along the high-symmetry axes are zero in a T_d-type crystal, such crystals do have two nonvanishing sets of first-order spatial dispersion coefficients which apparently contribute terms in the dynamical matrix for waves propagating in general directions, in contrast with the optical case, where no such coefficients appear. It is of interest to understand how these coefficients might affect the polarization of sound wave. It is not difficult to show that these coefficients do not couple polarization components which are normal to the propagation direction. The argument is as follows: If, as above, we consider the set of "transformed" coefficients d'_{ijlmn} for propagation along a general direction designated as X'_3, coupling of the transverse polarization components must involve the coefficient d'_{13233}. However, since $d'_{13233}=-d'_{23133}$, we can equally represent this coefficient as a component of a fourth-rank pseudotensor d'_{ijlm} such that $d'_{i3j33}=\delta_{ij3}d'_{3333}$, where δ_{ijl} is the unit antisymmetric tensor. Referring this pseudotensor to the crystal axes, $d'_{3333}=a_{3i}a_{3j}a_{3l}a_{3m}d_{ijlm}=d_{ijlm}n_in_jn_ln_m$, where the a_{3i} are the direction cosines of the wave vector with respect to the crystal axes, and $\mathbf{n}$ is a unit vector along the propagation direction. Only terms in d_{ijlm} that are completely symmetric in i, j, l, and m will contribute to this sum. In class T, this pseudotensor is equivalent to the elastic tensor with the additional requirement that the components are symmetric in the indices. The only nonzero components are therefore $d_{1111}=d_{2222}=d_{3333}$ and $d_{1122}=d_{1133}=d_{2233}=d_{1212}=d_{1313}=d_{2323}$. However, in class T_d there is an additional mirror symmetry, which causes these components to be zero. Consequently, in T_d crystals, first-order spatial dispersion terms do not couple transverse-polarization components. They do couple longitudinal components, and lead to modes in which the polarization vector "rolls" along the direction of propagation. This aspect of wave propagation warrants further study.

4. FIRST-ORDER SPATIAL-DISPERSION EFFECTS ON PHONON-DISPERSION CURVES

First-order spatial dispersion also determines the form of the phonon-dispersion curves. For example, one may expect a splitting of the degeneracy of transverse waves propagating along symmetry directions corresponding to acoustic axes, e.g., [100] and [111] directions in the case of cubic crystals, and the [001] axes of uniaxial crystals.

The effect of spatial dispersion manifests itself in the transformation properties of the acoustic phonons. In acoustically active crystals the transverse phonons which are degenerate at $k=0$ become nondegenerate at finite k along acoustic axes. These nondegenerate states, moreover, have characteristic right and left circular polarization. This is a very general situation, which may be best illustrated by example. For this purpose let us again consider tellurium as a simple case.

In tellurium there are three atoms per unit cell, so there will be nine branches in the ω-versus-k curves. Three of these branches are the acoustic and the other six are the optic branches. Any phonon mode having wave number k will transform under the same symmetry operations as k. These operations form a group, and each mode will transform as some representation of that group. In general, modes belonging to different representations will have distinct frequencies, although accidental degeneracies will exist at isolated points in the Brillouin zone. In tellurium, there are six symmetry operations divided into three classes at the center of the zone. The first class is the identity operation E. The second class is composed of 120° and 240° rotations about the threefold screw axis of the crystal. The third class is composed of twofold rotations about three equivalent binary axes normal to the threefold axis. Its Brillouin zone is a hexagonal prism, whose long axis is one of threefold symmetry.[8] Therefore, at the center of the Brillouin zone, i.e., at $k=0$, the phonon spectrum is represented by three irreducible representations, Γ_1, Γ_1', and Γ_2, having a character table shown in Table II. The longitudinal acoustic mode transforms as Γ_1',[8] whereas the transverse modes, being degenerate at $k=0$, must transform as Γ_2.

The symmetry properties of a phonon propagating along the trigonal axis will be described by the symmetry properties of a general point along the threefold axis of the Brillouin zone. This point is symmetric only under the operations E, and 120° and 240° rotations about the threefold axis, each of which forms a distinct class. Due to screw symmetry the character table is complicated.[8] However, in the long-wavelength limit it takes a very simple form, as seen in Table III. As $k \to 0$, we have the compatability relations $\Delta_1 \to \Gamma_1$ or Γ_1'; Δ_2 and $\Delta_3 \to \Gamma_2$. Therefore Δ_1 is the longitudinal mode and Δ_2 and Δ_3 are the transverse modes propagating along the trigonal axis.

At $k=0$, the degenerate transverse normal modes

TABLE II. D_3 character.

	E	$C_3 C_3^2$	$C_2^1 C_2^2 C_2$
Γ_1	1	1	1
Γ_1'	1	1	−1
Γ_2	2	−1	0

[8] M. Hulin, Ann. Phys. (N. Y.) 8, 641 (1963); J. Phys. Chem. Solids Suppl. 21, 135 (1965).

TABLE III. Δ Axis character.

($\omega = \exp\frac{2}{3}\pi i$)		
Δ_1	1	1	1
Δ_2	1	ω	ω^*
Δ_3	1	ω^*	ω

involve equal displacement of all atoms in the unit cell in the plane normal to the trigonal axis. For small k, the normal modes should not differ too greatly from the $k=0$ modes. However, since Δ_2 and Δ_3 are distinct at nonzero k, the modes are nondegenerate. Moreover, the normal modes in the Δ_2 and Δ_3 representation must be, respectively, multiplied by ω and ω^* under a 120° rotation about the trigonal axes, and by ω^* and ω under a 240° rotation. In the Δ_2 representation these conditions are satisfied only by the mode in which all atoms in the cell move with the right-handed circular polarization. In the Δ_3 representation, the conditions are satisfied only if all atoms move with left-handed polarization. Consequently, there are two distinct circularly polarized modes at nonzero k, which become degenerate when $k \to 0$. Thus the existence of acoustical activity can be inferred from the symmetry properties of phonon-dispersion curves. The phonon-dispersion curves of tellurium have been taken as an example, but similar arguments will apply to all classes of trigonal or higher symmetry in which acoustical activity may occur.

It should be possible, of course, to obtain the magnitude of the acoustical activity along acoustic axes from experimental or theoretical phonon-dispersion curves. No neutron scattering measurements seem to have been made on crystals which may exhibit acoustical activity. However, Hulin[8] has calculated theoretical phonon-dispersion curves for tellurium which can be used to obtain a theoretical estimate of the acoustical activity of transverse waves propagating along the trigonal axis of tellurium. Hulin's calculations are based on a model involving three force constants. The force constants used in these calculations are based on older values of the elastic constants, and differ on the average by 10% from force constants calculated from the latest values of the elastic constants. The phonon frequencies of each acoustic branch were calculated at the Brillouin-zone edge and the midpoint of the Δ branches. The shape of the curves joining the calculated points was deduced from general symmetry requirements, and from elastic wave theory.[9] Using Hulin's curves (Fig. 1), one finds that the mean velocity $\bar{v}$ of the two transverse modes at the midpoint of the Δ branches is essentially equal to the transverse velocity at $\Gamma(k=0)$. The fractional splitting of the velocities of the two branches at the midpoint of the acoustic Δ branches is found to be $(v_+ - v_-)/\bar{v} = 0.18$. The symmetric splitting of the velocities of the two circularly polarized branches is con-
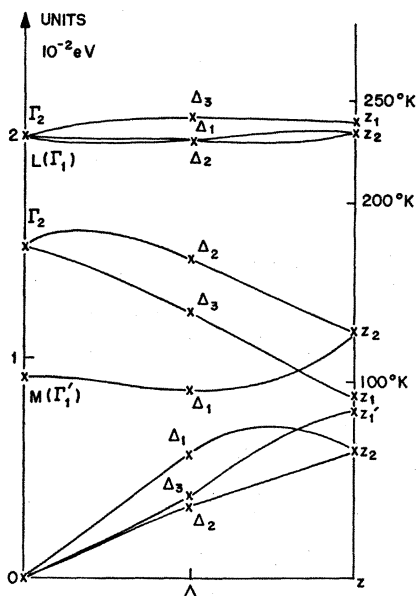
[9] M. Hulin (private communication).

FIG. 1. Theoretical phonon-dispersion curves for tellurium along the ternary axis [after M. Hulin, J. Phys. Chem. Solids Suppl. **21**, 135 (1965)].

sistent with the simple theory of acoustical activity based on a first-order expansion of the elastic constants in powers of k, and implies that the simple first-order expansion of the elastic constant is physically meaningful even at the midpoint of the Δ branch of tellurium. From the expansion for the velocity difference of the two modes, we find that the relevant acoustical activity constant $d_{45,3}$ is 1.7×10^{-3} cgs units. This leads, for example, to a circular birefrigence $(v_{+}-v_{-})/\bar{v}$ of 10^{-4} at 1 Gc/sec, or a rotation of the plane of polarization of about 165°/cm at that frequency.

Note that the transverse-optical branches of acoustically active crystals will also split into modes of right- and left-handed symmetry at points ($k>0$) along the acoustic axes. In tellurium there are two sets of such modes which have Γ_2 symmetry at $k=0$ and which have Δ_2 and Δ_3 symmetry at points along the trigonal axes. Hulin's curves (Fig. 1) show that the transverse-optical branches have a well-defined splitting along Δ. The splitting is, in fact, rather large for the lower frequency branches. The optical modes are both infrared and Raman-active, and their splitting may be observable in either the infrared-absorption spectra or the Raman-scattering spectra. The splitting of the right- and left-handed polarized transverse-optical modes may also lead to an observable contribution to the far-infrared optical activity of tellurium.

5. PRACTICAL ASPECTS

Since the rotation of the plane of polarization increases as the square of the frequency, any attempts to observe this effect should be carried out at as high a frequency as possible. On the other hand, the attenuation of acoustic waves also increases rapidly with frequency, and establishes an upper limit to the frequency which varies from material to material. An order-of-magnitude estimate of the rotation per unit length, ϕ/l, may be obtained by noting that $(v_{+}-v_{-})/\bar{v}$ is or order $ka/2\pi$,[10] where a is comparable to the lattice constant. On this basis, ϕ/l is of the order of 1 rad/cm when the acoustic frequency is about one gigacycle. This estimate is in agreement with that obtained for tellurium from the theoretical phonon-dispersion curves.

Note, however, that the effect of acoustical activity can be masked by accidental *linear* birefringence that is associated with crystal defects. A similar effect can result from misalignment of the wave vector relative to the acoustic axis. This effect of misalignment is particularly serious for a trigonal acoustic axis, since in this situation the linear birefringence varies directly with the misalignment angle, whereas it varies as the square of the misalignment angle along axes of higher symmetry.[6] In tellurium, for example, 0.5° misalignment results in a linear birefrigence of 2×10^{-3},[7] which is an order of magnitude greater than the estimated circular birefringence 1×10^{-4} at 1 Gc/sec, so that either the frequency must be increased, or the misalignment angle decreased, by an order of magnitude for measurements to be feasible.

Lack of collimation of the incident beam constitutes another serious limitation to the observation of acoustical activity. Again, the effect will be particularly large along a trigonal acoustic axis, since, as a result of internal conical refraction, the intensity of the circularly polarized ("collimated") modes can be appreciably lower than that of the linearly polarized "background" modes.[7] In the case of acoustic waves, diffraction may well be the major source of "lack of collimation."

6. CONCLUSION

It was shown that due to first-order spatial dispersion an acoustical activity can occur in crystals which exhibit optical activity. Moreover, it was demonstrated that the magnitude of the acoustical-activity coefficients of a given crystal might be deduced from experimental or theoretical phonon-dispersion curves. The practical problems involved in the observation of acoustical activity were analyzed. Other interesting effects of first-order spatial dispersion on the propagation of acoustic waves in general directions were considered. Finally, the effects of first-order spatial dispersion on the transverse-optical vibration modes, and the optical properties arising from them, were also pointed out.

[10] L. D. Landau and E. M. Lifschitz, *Electrodynamics of Continuous Media*, translated by J. B. Sykes and J. S. Bell (Pergamon Press, Ltd., Oxford, England, 1958), p. 337.