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Elastic-Wave Formulation for Electroelastic Waves in Unbounded Piezoelectric Crystals

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The equations describing the elastic behavior of plane-wave disturbances in an infinite piezoelectric crystal are reduced in form to those of a purely elastic medium in the quasistatic approximation. The internal energy of the piezoelectric solid is expressed as one elastic-type term, and an alternative expression for the elastic energy flux yields the combined elastic and electric energy flux on replacing the elastic constant c^E with the stiffened "constants" c^{kD} without introducing $\vec{\nabla} \times \vec{H} = \vec{D}$ and $\vec{P} = \vec{E} \times \vec{H}$. Similarly, the electric displacement is expressed in terms of the strain variables alone by means of modified piezoelectric "constants" e^{kD}. Properties of this "stiffened-elastic" formalism and of the usual mechanical-electrical formulation are the same, and the two formulations are discussed in relation to each other. The elastic-propagation properties of piezoelectrics are describable by a ray or wave surface, which exists in terms of the c^{kD}, and the techniques of variational elasticity carry over to piezoelectrics. The positive definiteness of the c^{kD} is asserted for an arbitrary direction to realize physical stability and, whereas no new limiting restrictions among material constants obtain, their use in Rayleigh–Ritz procedures assures its monotonic convergence. The symmetry and transformation properties of the c^{kD} show that, whereas their symmetry is lower than that of the c^E, their centrosymmetric nature requires only the centrosymmetric crystal groups to describe the elastic properties of piezoelectric crystals. Various stiffened-elastic properties are numerically evaluated for an arbitrary nonpure mode and symmetry-related directions for α-quartz (class 32), $LiNbO_3$ ($3m$), CdS ($6mm$), $Ba_2NaNb_5O_{15}$ ($2mm$), $Bi_{12}GeO_{12}$ (23), and GaAs ($\bar{4}3m$). The work offers a simplified approach to characterizing bulk and surface elastic-wave properties of electroelastic waves in piezoelectric crystals and of modally analyzing particular classes of piezoelectric structures.

I. INTRODUCTION

In describing the elastic behavior of piezoelectric crystals, the customary procedure is to use the strain-induced stress plus the electric-field-induced stress for the total stress in Newtons equation of motion for distributed media.[1–4] As appropriate, traveling-wave solutions are assumed and the wave-propagation properties calculated for the particular direction chosen. For purely elastic crystals, piezoelectric contributions to the stress are, by definition, not considered and one obtains the formalism for (infinite) purely elastic vibrating crystals. As pointed out by Borgnis,[5] the theory is referred to as Christoffel theory by many, but is initially due to G. Green.

The Green–Christoffel theory has been the basis of many analyses and results. It is of interest and practical value to carry over many of these to the vibrating piezoelectric solid. Attempts to do this would be justified by the formal reduction and correspondence of the piezoelectric equations of motion to those of the theory of elasticity.[6,7] Such a correspondence is completed in Sec. III after briefly introducing and reviewing linear piezoelectric theory in Sec. II. A relation giving the electric displacement within this correspondence is also given in Sec. III. The existence of the ray or wave surface for piezoelectrics is discussed in Sec. IV. In Sec. V the variational-elasticity formalism is extended to piezoelectric media and the monotonic convergence of the Rayleigh–Ritz expansion is shown to follow from the assertion of the positive definiteness of the potential energy. Relations among the material constants owing to this positive definiteness are explored in Sec. VI. The transformation and symmetry properties of the coefficients in the potential energy are developed in Sec. VII and the centrosymmetric symmetry groups are shown to describe the symmetry of the elastic properties for crystals of the piezoelectric crystal classes. Included are numerical calculations for piezoelectric crystals of various symmetry classes.

II. THEORY, INTRODUCTION, AND REVIEW

Indicial and symbolic notation is used. Indices run from 1 to 3 unless otherwise stated and the summation over repeated index pairs is understood. Differentiation of g_r with respect to x_i is shown as $g_{r,i}$, and with respect to k_i as g_{r,k_i}. The scalar φ differentiated with respect to x_i is shown as $\varphi_{,i}$. $\vec{k}$ is the wave normal vector, k its magnitude, $\hat{k}$ its unit direction, and k_i its ith component. Cross and dot product symbols are used as needed for clarity. Exponentials are suppressed when their presence is not significant and the meanings of other symbols are clear from their context or are explained. The notation, which is commonly accepted, is that of Tiersten,[3,8] Auld,[4] and Holland

and EerNisse,[9] and many others.

In piezoelectric media, the following equations apply[3,4,8]:

$$\rho\ddot{u}_i = \tau_{ij,j} \quad , \tag{1}$$

where

$$\tau_{ij} = c^E_{ijmn} S_{mn} - e_{ijr} E_r \ , \tag{2}$$

$$D_l = e_{lmn} S_{mn} + \epsilon^s_{lr} E_r \ , \tag{3}$$

$$S_{mn} = \tfrac{1}{2}(u_{m,n} + u_{n,m}) \ . \tag{4}$$

The absence of free electric charge requires

$$\vec{\nabla} \cdot \vec{\mathrm{D}} \equiv D_{l,l} = 0 \ , \tag{5}$$

and for electromagnetic disturbances propagating at or near the velocity of sound where magnetic induction may be neglected

$$\vec{\nabla} \times \vec{\mathrm{E}} = 0 \ . \tag{6}$$

Equation (6), which is the essence of the "quasistatic approximation,"[8] permits writing

$$\vec{\mathrm{E}} \equiv -\vec{\nabla}\ \varphi \equiv -\vec{\varphi} \quad . \tag{7}$$

φ is the scalar quasistatic electric-field potential. From the chosen forms of the constituitive equations (2) and (3), the internal energy function for the system is

$$2U = S_{ij}\tau_{ij} + E_l D_l = c^E_{ijmn} S_{ij} S_{mn} + \epsilon^s_{lr} E_l E_r \ , \tag{8}$$

which is positive definite. On consideration of the time rate of change of total energy in an arbitrary volume, the outward energy flux across the bounding surface in the j direction $-P_j$ is

$$\int -P_j\, dS_j \equiv \int_S (\tau_{ij}\dot{u}_i - \varphi \dot{D}_j)\, dS_j = \frac{\partial}{\partial t}\int_V (\rho \dot{u}_j^2 + U)\, dV \ . \tag{9}$$

Equation (5) states that any electric charge which may exist is induced, and the zero divergence of Eq. (3) says that any electric field or charge supporting this field is induced by the elastic strain, and conversely, according to

$$-\epsilon^s_{lr} E_{r,l} = e_{lmn} S_{mn,l} \ . \tag{10}$$

In terms of the potential introduced in Eq. (7), this becomes

$$\epsilon^s_{lr}\, \varphi_{,rl} = e_{lmn} S_{mn,l} \ , \tag{11}$$

which quantitatively states the relation between the induced potential and the strain, and couples the elastic displacement and potential disturbance together into a single electroelastic disturbance. For a disturbance of the plane-wave form,

$$u_m = u_{m0} e^{i(\omega t - k_i x_i)} \ , \tag{12}$$

$$\varphi = \varphi_0 e^{i(\omega t - k_i x_i)} \ , \tag{13}$$

the following relations can be derived:

$$\epsilon^{sk}\varphi = -e_{lmn} S_{mn,l} = -e_{lmn} u_{m,ln} = e_{lmn} k_l k_m u_n \ , \tag{14}$$

where $\epsilon^{sk} = \epsilon^s_{pq} k_p k_q$. The amplitude of the potential part of the wave in terms of the amplitudes u_{m0} of the elastic-displacement part of the wave is

$$\varphi_0 = \frac{e_{lmn} k_l k_n u_{m0}}{\epsilon^{sk}} \quad . \tag{15}$$

(Note that the subscript zero refers to the amplitude of u_m and φ and does not indicate a component or a unit vector.)

With Eq. (13), Eq. (7) yields the electric field components as

$$E_r = -\ \varphi_{,r} = ik_r\varphi = ik_r\varphi_0 e^{i(\omega t - k_i x_i)} \ . \tag{16}$$

The quantity $i\varphi$ is identical to Auld's[4] C and, of course, the same conclusion may be drawn—that the induced electric field part of the wave is parallel to the propagation direction $\vec{\mathrm{k}}$. Additional useful expressions for E_r result on multiplying each expression for φ in Eq. (14) by ik_r, or on symbolically differentiating each term with respect to x_r to obtain $S_{mn,ln}$, $u_{m,nlr}$, and $u_{m,r}$ and then changing sign; the intermediate expression

$$E_r = \frac{-k_r(k_l e_{lmn} u_{m,n})}{\epsilon^{sk}} = \frac{-k_r(k_l e_{lmn} S_{mn})}{\epsilon^{sk}} \tag{17}$$

is the equivalent of Auld's Eq. (29).

Note that $D_{l,l} = 0$ implies that $\vec{\mathrm{D}}$ is normal to $\vec{\mathrm{k}}$, for differentiating Eq. (3) yields $D_{l,l} = D_l k_l$ and, as $\vec{\mathrm{E}}$ is parallel to $\vec{\mathrm{k}}$, $\vec{\mathrm{D}}$ is perpendicular to $\vec{\mathrm{E}}$. (The conclusions regarding the orientations of $\vec{\mathrm{k}}$, $\vec{\mathrm{E}}$, and $\vec{\mathrm{D}}$, are the same as Auld's and are reached without introducing $\vec{\nabla} \times \vec{\mathrm{H}} = \dot{\vec{\mathrm{D}}}$, as he has done.)

The well-known fact that the piezodielectrically stiffened elastic constants may be used in place of c^E in the Green–Christoffel equations follows from differentiating Eq. (2) with respect to x_j, replacing $-E_{r,j}$ with $k_r(k_l e_{lmn} S_{mn})/\epsilon^{sk}$ from Eq. (17), and of course using Eq. (1). The intermediate result

$$\tau_{ij,j} = \left(c^E_{ijmn} + \frac{e_{ijr} k_r e_{mnp} k_p}{\epsilon^{sk}} \right) S_{mn,j} \equiv c^{kD}_{ijmn} S_{mn,j} \tag{18}$$

implies

$$\tau_{ij} = c^{kD}_{ijmn} S_{mn} \tag{19}$$

and defines the stiffened elastic "constants" c^{kD}. The latter can be directly derived from Eq. (2) [on replacing E_r from Eq. (17)].

The foregoing is intended as both a brief review and a starting point, except perhaps for Eqs. (19) (which is an explicit statement of a piezodielectrically stiffened stress-strain law with directionally dependent constants for piezodielectric materials) and (15), both of which may not have been so expressed previously. In the following section, the potential energy function and the energy-flow equation are expressed in terms of the c^{kD} and the strain variables. Finally, the electric displacement is expressed in terms of the strain variables and, as it turns out, modified piezoelectric constants e^{kD}_{lmn}.

III. CORRESPONDENCE

The form of Eq. (19) and the existence of Eq. (17) both suggest expressing the internal energy function, Eq. (8), in terms of strain variables alone. This follows directly, and

$$2U = c^{kD}_{ijmn} S_{ij} S_{mn} \,, \tag{20}$$

a result which could be taken as justification for obtaining U by multiplying Eq. (19) by S_{ij}. Actual justification includes the fact that $\vec{D}$ and $\vec{E}$ are perpendicular (i.e., $E_l D_l = 0$) for the internal energy is the sum $\tau_{ij} S_{ij} + E_l D_l$. Physical stability requires the positive definiteness of U. The restrictions this places on c^{kD}, c^E, e, and ϵ^s and some other properties of the c^{kD} will be examined later.

Next, we consider the substitution of c^{kD} for c^E in the expression for elastic energy flux to obtain the energy flux for the piezoelectric medium. Clearly, $-P_j = c^E_{ijmn} S_{mn} \dot{u}_i \equiv \tau^E_{ij} \dot{u}_j$ does not yield $-P_j = \tau_{ij} \dot{u}_i - \varphi \dot{D}_j$ [from Eq. (5)], and vice versa, under the exchange $c^E \longleftrightarrow c^{kD}$. The form which naturally admits such a substitution is based upon two facts: (1) that, for undamped elastic plane waves propagating in an anisotropic medium, the velocity $\vec{v}$, at which energy is propagated is given by the envelope of planes perpendicular to the radius vector of the phase velocity surface,[10] or, equivalently, by the normal to the inverse velocity or slowness surface,[11,12] and (2) that the elastic flux is in the direction of this normal.[13] The scalar function connecting the two is the energy density of the elastic plane wave for the particular direction of propagation. An expression for $\vec{v}_g$ which yields the to-be-derived result most easily is the well-known $\vec{v}_g = \partial\omega/\partial\vec{k}$, and the energy density is $\rho\omega^2 u_i^2$, their product being the energy flux. For time-averaged quantities and normalized displacement, $u_{i0}^2 = 1$,

$$-P_j = \rho\omega^2 \frac{\partial\omega}{\partial k_j} = \tfrac{1}{2}\rho\omega \frac{\partial\omega^2}{\partial k_j} \,. \tag{21}$$

For the elastic case $\rho\omega^2 = c^E_{ijmn} u_{i0} u_{m0} k_j k_n$ follows from Eqs. (1), (2), and (12) with all e_{ijr} coefficients zero. Equation (21) yields $-P_j = \tau^E_{ij} \dot{u}_j$. For piezoelectric materials, $\rho\omega^2 = c^{kD}_{ijmn} u_{i0} u_{m0} k_j k_n$, and Eq. (21) yields

$$-2P_s = 2\omega c^{kD}_{ijms} u_{i0} u_{m0} k_j + \omega c^{kD}_{ijmn,k_s} u_{i0} u_{m0} k_j k_n \,, \tag{22}$$

where

$$c^{kD}_{ijmn,k_s} = \frac{\partial}{\partial k_s} \frac{e_{ijr} k_r e_{mnp} k_p}{\epsilon^s_{ab} k_a k_b}$$

$$= 2\left(\frac{e_{ijs} e_{mnp} k_p}{\epsilon^s_{ab} k_a k_b} - \frac{e_{ijr} k_r e_{mnp} k_p \epsilon^s_{sq} k_q}{(\epsilon^s_{ab} k_a k_b)^2} \right) . \tag{23}$$

Whereas the termwise construction of Eq. (9) follows from Eq. (22), Eq. (22) is easily obtained by using a form of Eq. (9),

$$-P_s = c^{kD}_{imjs} S_{ij} \dot{u}_m - \varphi \dot{D}_s \,, \tag{24}$$

where φ is $ik_l e_{lmn} S_{mn} / \epsilon^s_{ab} k_a k_b$ from Eq. (14), $\dot{D}_s$ is obtained from differentiating Eq. (3), and E_r is from Eq. (16). Clearly, Eq. (22) also yields the elastic energy flux for purely elastic materials on $c^{kD} \rightarrow c^E$, for the last term becomes zero. That the term is perpendicular to the propagation direction may be seen on forming and evaluating

$$k_s \frac{\partial}{\partial k_s} \left(c^{kD}_{ijmn} \right) ,$$

which is zero. Thus, with the correspondence of Eqs. (22) and (24) completed, Eq. (22) may be formally expressed in terms of the c^{kD} and S_{pq} as

$$-P_s = c^{kD}_{ijms} S_{ij} \dot{u}_m - \tfrac{1}{2} c^{kD}_{ijmn,k_s} S_{ij} \dot{S}_{mn} \tag{25a}$$

or

$$-P_s = c^{kD}_{ijms} S_{ij} \dot{u}_m - \tfrac{1}{4} c^{kD}_{ijmn,k_s} \overline{S_{ij} \dot{S}_{mn}} \tag{25b}$$

or

$$-P_s = \left(c^{kD}_{ijms} + \tfrac{1}{2} i k_n c^{kD}_{ijmn,k_s} \right) S_{ij} \dot{u}_m \,. \tag{25c}$$

The derivation depends upon Eq. (21) extended to piezodielectric materials. It does not depend upon the addition of an electromagnetic energy flux and an electrically stiffened elastic energy flux, i.e., upon the idea of these fluxes as independent entities,[2,14] nor does it depend upon the addition of independent elastic and electrical energy terms[2] if Eq. (20) [instead of (8)] is accepted at the outset. The fact that the last term of Eqs. (24) and (25) may be identified with the quantity $\vec{E} \times \vec{H}$,[4,8,15] the electromagnetic energy flux or Poynting vector, does not of itself support the concept of an electromagnetic energy flux within the quasistatic approximation. In order to do this, the introduction of a magnetic field accompanying the electroelastic disturbance by means of $\vec{\nabla} \times \vec{H} = \dot{\vec{D}}$ is necessary. Such an identification is convenient; the formalism and its properties have been established without invoking $\vec{\nabla} \times \vec{H} = \dot{\vec{D}}$.

What has been shown so far is a common formalism which describes the elastic behavior of piezoelectric and elastic materials. In order to describe the piezoelectric effect, the phenomenological equation describing the electric displacement must be carried over. In this formulation, where the strain variables are considered to be the independent ones, E_r in Eq. (3) is eliminated as before and the electric displacement becomes

$$D_l = \left(e_{lmn} - \frac{e_{amn}k_a \epsilon^s_{lb} k_b}{\epsilon^{sk}}\right) S_{mn} \equiv e^{kD}_{lmn} S_{mn} \,. \qquad (26)$$

On forming the divergence of Eq. (26), $D_{l,l} = 0$ results, as required. This directly follows on summing over the double index l, which results when k_l appears as a multiplying factor after differentiating S_{mn}.

In summary, the formalism consists of the following:

$$\rho \ddot{u}_i = \tau_{ij,j} \,, \qquad (1)$$

$$\tau_{ij} = c^{kD}_{ijmn} S_{mn} \,, \qquad (19)$$

$$D_l = e^{kD}_{lmn} S_{mn} \,, \qquad (26')$$

$$S_{mn} = \tfrac{1}{2}(u_{m,n} + u_{n,m}) \,, \qquad (4)$$

$$c^{kD}_{ijmn} = c^E_{ijmn} + \frac{e_{ijr}k_r e_{mnp}k_p}{\epsilon^s_{cd}k_c k_d} \,, \qquad (18')$$

$$e^{kD}_{lmn} = e_{lmn} - \frac{e_{amn}k_a \epsilon^s_{lb}k_b}{\epsilon^s_{cd}k_c k_d} \,, \qquad (26')$$

$$2U = c^{kD}_{ijmn} S_{ij} S_{mn} \,, \qquad (20)$$

$$-P_s = c^{kD}_{ijms} S_{ij} \dot{u}_m - \tfrac{1}{2} c^{kD}_{ijmn,k_s} S_{ij} \dot{S}_{mn} \,, \qquad (25a)$$

$$\int_s -P_j \, dS_j = \frac{\partial}{\partial t} \int_V (\rho \dot{u}_j^2 + U) \, dV \,. \qquad (9')$$

The potential part of the wave disturbance, given by Eq. (13), exists physically but does not enter the formalism as an independent variable. The potential may be modified to take into account a constant external potential φ'' and electric field E_i' by writing $\varphi = \varphi_0 e^{i(\omega t - k_i x_i)} + E_i' x_i + \varphi''$ without changing the validity of the formalism. $D_{l,l} = 0$ is a property of the system.

IV. GENERAL PROPAGATION PROPERTIES IN PIEZODIELECTRIC MEDIA

The propagation of elastic waves in anisotropic media has been examined[10,12,16-18] in terms of three surfaces—the phase-velocity surface, the inverse-phase-velocity (or slowness) surface, and the wave (or ray or energy-transport or group-velocity) surface—and the interrelationship of these surfaces developed. These relationships carry over in toto for the case of electroelastic wave propagation in piezodielectric materials. The positive definiteness of the c^{kD}, necessary for physical stability, ensures the reality of the roots of the characteristic equation associated with Eqs. (1), (19), and (12), and consequently of the reality of the three sheets of the phase-velocity surface $F(\vec{v}) = 0$ and of the slowness surface $G(\vec{s}) = 0$, where $\vec{s} \equiv s\vec{1} = (k/\omega)\vec{1} = (1/v)\vec{1}$. The polar reciprocal nature of the slowness and group-velocity surfaces may be seen to remain on forming $-k_s p_s$. This yields $(k_s/\omega)(-P_s/\rho\omega^2) = 1$, which is readily recognizable as $\vec{s} \cdot \vec{v}_g = 1$, the statement of polar reciprocity of the slowness and group-velocity surfaces. [The multiplication of this equation by the scalar v yields $\vec{1} \cdot \vec{v}_g = v$. This is the basis for the statement that the group-velocity surface is the envelope of planes perpendicular to radius vectors of length v. Alternatively, because these radius vectors are clearly the vectors from the origin of the phase-velocity surface $F(\vec{v}) = 0$ to points on it, $\vec{1} \cdot \vec{v}_g = v$ is also the basis for the statement that the group-velocity or envelope surface is the (first) negative pedal surface to the phase-velocity surface. The pedal surface $P(x_i) = 0$ of the surface $S(x_i) = 0$ is the set of points determined by the planes tangent to S and the perpendiculars to each of them from a common origin. S is called the negative pedal of P. See p. 352 of Ref. 10.]

Compared to those for purely elastic media, these surfaces for piezodielectrics are more complicated because the c^{kD} are themselves functions of direction through the stiffening contributions. Since the piezoelectric constants are involved, the general symmetry features of the surfaces would appear to be that associated with a piezoelectric crystal class. Nevertheless, as shall be seen after examination of the symmetry properties of the c^{kD}, the over-all symmetry conforms to the same symmetry groups as for purely elastic media, and methods of analysis developed for elastic media should, in general, be valid for piezoelectrically stiffened elastics. Whether a simple replacement of the c^E by the c^{kD} is all that would be involved (an unlikely situation in general) must be determined by an examination of each particular method of analysis and of the problem to be analyzed. For example, such a replacement would not necessarily yield directions of pure mode propagation[5,19] and of internal and external conical refraction[17,18,20] of piezodielectrics. Considered in the next section is the amenability of the c^{kD} formalism to the techniques of variational calculus.

V. APPLICABILITY TO VARIATIONAL TREATMENT OF PIEZODIELECTRICS

The variational calculus is used to approximate the normal modes of linearly elastic and piezodielectric structures.[8,9] For the former, only the c^E are involved. For the latter, the formalism is expressed, in terms of the c^E, e, and ϵ^s, and Holland and EerNisse[9] (HE) themselves have pointed out that the potential energy term[8] (actually the electric enthalpy) in the Lagrangian is not positive definite for the unbounded configuration and consequently that the monotonic convergence of Rayleigh–Ritz procedures based upon it is not assured.[9] The resolution of this difficulty is considered in the context of the "kD" formulation. The reader is referred to their presentation of variational-elasticity theory and to their variational treatment of piezoelectric problems for review and notation, as these are the basis of the following discussion.

In variational-elasticity theory, arbitrary variations in the displacement functions δu_i are considered. These, in turn, may require modification of the c^{kD} coefficients insofar as the variations introduce departures from the plane-wave form of the u_i for which the c^{kD} are defined. This is not the case, however, since the variations in the u_i are related to variations in the coefficients of the trial functions

$$\delta u_i = \sum_{\alpha=1}^{S_m} \delta B^{(\alpha)} U_i^{(\alpha)} .$$

Also, the $U_i^{(\alpha)}$ are pointwise complete, such as the set of functions $\cos mx$ (see p. 99 of Ref. 9), and because the c^{kD} depend upon the propagation direction and not the harmonic of the trial function, the c^{kD} remain unchanged. With this stipulation, the equations of variational-elasticity theory for unbounded media apply for unbounded piezoelectric solids on replacing the c^E by the c^{kD}. The approximate results obtained (the resonant frequencies and modal displacement patterns for particular electrodeless piezoelectric structures) should be comparable to those which obtain for similar structures from HE's variational treatment of the infinite piezoelectric medium, for which it is not explicit that the electric enthalpy term is positive definite. With the former procedure, however, the potential energy term of the Lagrangian, $u_{i,j} c_{ijmn}^{kD} u_{m,n}$, has been asserted to be positive definite (on physical grounds), thus assuring monotonic convergence.

The use of stiffened coefficients in the variational treatment of three-dimensional piezoelectric structures of arbitrary shape, electrode configuration, and external force distribution is also possible. In such cases, information about the modal potential distribution may be obtained from $D_{i,i} = 0$, which must hold for each mode ν. Specifically, after variationally evaluating the $A^{(\nu)}$ of $u_i = \sum_\nu A^{(\nu)} u_i^{(\nu)}$, $\varphi^{(\nu)}$ follows from Eq. (14). For problems where the finite frequency potential φ'' must be included, EerNisse has pointed out that the $A^{(\nu)}$ obtained from solving the variational problem with the c^{kD} are no longer suitable.[21] Ways to meet this limitation and to extend further the use of the c^{kD} in variational and other procedures have not been explored.

VI. POSITIVE DEFINITENESS OF c^{kD}

Already noted is the positive definiteness of the internal energy[8] $2U = c_{ijmr}^E S_{ij} S_{mn} + \epsilon_{rl}^s E_r E_l$, a condition which must exist for a vibrationally stable solid. In the form of U expressed by Eq. (20), the c^{kD} array must be positive definite for an arbitrary direction of propagation. For the case of the positive definite c^E, the tensor components are related among themselves and zero for each of the applicable symmetry classes by setting the determinants of the principal minors to be greater than zero. The components of the c^{kD} array can be similarly treated for each of the piezoelectric crystal classes. The resulting inequality relations are not particularly useful, because the number of independent c^{kD} components is generally much larger than that for the c^E tensor and, ultimately, the resulting relations are expressible in terms of the c^E, e, and ϵ^s components. For symmetry class 32, some typical expressions are, using the 2-to-1 index contraction,

$11 \longleftrightarrow 1, \quad 22 \longleftrightarrow 2, \quad 33 \longleftrightarrow 3,$

$23\text{-}32 \longleftrightarrow 4, \quad 13\text{-}31 \longleftrightarrow 5, \quad 12\text{-}21 \longleftrightarrow 6 ;$

$$\left(\frac{e_{11}^2}{c_{66}^E} + \epsilon_{11}^s\right) l_1^2 + \epsilon_{11}^s l_2^2 + \epsilon_{33}^s l_3^2 > 0 ,$$

$$\left(\frac{e_{11}^2}{c_{11}^E - (c_{14}^E)^2/c_{44}^E} - \frac{2e_{11}e_{14}}{c_{11}^E c_{44}^E/c_{14}^E - c_{14}^E} + \frac{e_{14}^2}{c_{44}^E - (c_{14}^E)^2/c_{11}^E} + \epsilon_{11}^s\right) l_1^2 + \left(\frac{e_{14}^2}{c_{44}^E} + \epsilon_{11}^s\right) l_2^2 + \epsilon_{33}^s l_3^2 > 0 .$$

Whereas for convenient choices of the propagation direction $\vec{l}$ such as (1, 0, 0) and (1, 1, 0) the individual coefficients of the $l_i l_j$ may be isolated or combined and compared to zero, the relations obtained are the same as those which derive from the 9×9 array which expresses U in terms of the c^E, e, $-e^T$, and ϵ^s, where $-e^T$ is the negative transpose of the e subarray.[22] Because e and $-e^T$ appear in this array, the relations do not restrict the size of the coefficients which describe elastic, piezoelectric, and dielectric effects in terms of one another. This is compatible with the accepted independent nature of these effects.

VII. TRANSFORMATION AND SYMMETRY PROPERTIES OF c^{kD} AND e^{kD}

The apparent simplicity of the formalism is offset by the directional dependence of the c^{kD} and e^{kD}. The elements of the c^{kD} array no longer have the property of a tensor in that they do not represent a linear transformation of a strain to stress[23] for plane stress waves of arbitrary propagation direction (and referring to them as a "tensor"[4] is inappropriate). Accordingly, identity relations among the c^{kD} components cannot be obtained from the application of coordinate transformations, which are invariant for a crystal symmetry class, and, as shall be explicitly shown later, the addition of the nonzero stiffening contributions to identically zero c_{pq}^E and the addition of unequal contributions to identically equal c_{pq}^E are not infrequent.

The transformation properties of the c^{kD} depend on those of the c^{E} and the stiffening contributions. Those of the former are known, and, in the Appendix, the stiffened contributions are shown to have the transformation rule of a fourth-rank tensor. Like the c^{E}, they are invariant with respect to inversion through the origin. Thus, the c^{kD} are centrosymmetric and the seven crystal systems which describe the symmetry of the elastic properties of an elastic crystal do the same for a piezodielectric crystal. This is so in the face of the identically nonzero piezoelectric constants of the noncentrosymmetric classes and is due to the occurrence of the piezoelectric constants in the c^{kD} and in the characteristic equation only as products of even parity: $e_{ijr}e_{mnp}$.

In general, identically nonzero piezoelectric constants lead to the already mentioned nonzero and unequal contributions to the c^{E}. The c^{kD} array for class 32 (α-quartz) takes the form shown in Table I. The expressions for the stiffened constants are listed in Table II, and for special directions such as (1, 1, 0), (1, 0, 0), and (0, 0, 1) further simplification results. For most other symmetry classes, where more than two piezoelectric coefficients exist, equivalent symmetry tables and expressions would reveal fewer relations. Notwithstanding the existence of a different c^{kD} array for each piezoelectric symmetry class, with its apparent reduction in symmetry, the higher symmetry of the seven crystal systems for purely elastic media apply, as already shown. An analytic demonstration of this, which keeps track of the apparent symmetry-reducing terms and accounts for their cancellation or invariance under the symmetry operations of the crystal class, must be performed for each class and use must be made of the symmetry classes' restrictions on the c^{E}, e, and ϵ^{s}. Such a proof being beyond the scope of this paper, numerical counterexamples were sought from among representative noncentrosymmetric classes and none were found.

The calculations are outlined in Table III. Initially, an arbitrary direction of propagation ($\phi = 3°$, $\theta = 30°$) was chosen which was neither a pure-mode direction nor one for which the stiffened contributions to the c^{kD} were accidentally identically zero. Specific elastic properties calculated are the polar and azimuthal angles of the eigen- or vibration vector (ϕ_A, θ_A), the sense of which is of course arbitrary, the direction of energy flux given by (ϕ_P, θ_P), which is sensewise unique, the phase velocity, and the group velocity. Also calculated are the magnitude and direction of $\vec{D}$ whose sense depends upon the sense of the eigenvector. These quantities were again numerically evaluated for a second direction of propagation, which in all cases was obtained from the first by an inversion through the origin of the crystal coordinate system. The procedure was repeated for other directions which are symmetrically equivalent for each of the seven crystal groups that describe elastic effects, but nonequivalent for each of the piezoelectric crystal classes. The symmetry element tested for each direction is also listed and is with reference to the first, or identity, direction. For example, trigonal crystal class 32 of α-quartz does not have mirror planes perpendicular to its twofold rotation axes, where the centrosymmetric trigonal group, which is class $\bar{3}m$, does.[24] One such plane would be the longitudinal plane at $\phi = 30°$, and the reflected direction corresponding to (ϕ, θ) = (3°, 30°) is (57°, 30°). For the two directions considered, the table shows that the calculated energy flux directions are also related by reflection in a mirror plane at $\phi = 30°$, suggesting that the symmetry of class $\bar{3}m$, not 32, prevails. The directions of vibration and displacement are similarly related, but to within an arbitrary reversal of direction, and vector magnitudes v and v_g are equal.

TABLE I. Indices for c_{pq}^{lD} array of class 32 for arbitrary $\hat{l}$. Underlined symbols denote a stiffened contribution inconsistent with unstiffened symmetry. $c_{pq}^{lD} = c_{qp}^{lD}$.

11	12	13	14	$-\underline{25}$	$-\underline{26}$
	11	13	-14	$\underline{25}$	$\underline{26}$
		33	0	0	0
			44	$\underline{45}$	$-\underline{25}$
				$\underline{55}$	$\underline{56}$
					$\underline{66}$

TABLE II. c_{pq}^{lD} expressed in terms of c_{pq}^{E} and stiffened contributions, class 32.

$$\epsilon^{sl} = \epsilon_{ab}^{s} l_a l_b$$
$$c_{11}^{lD} = c_{11}^{E} + e_{11}^{2} l_1^{2}/\epsilon^{sl}$$
$$c_{12}^{lD} = c_{12}^{E} - e_{11}^{2} l_1^{2}/\epsilon^{sl}$$
$$c_{66}^{lD} = c_{66}^{E} + e_{11}^{2} l_2^{2}/\epsilon^{sl}$$
$$c_{p3}^{lD} = c_{p3}^{E}$$
$$c_{14}^{lD} = c_{14}^{E} + e_{11} e_{14} l_1^{2}/\epsilon^{sl}$$
$$c_{44}^{lD} = c_{44}^{E} + e_{14}^{2} l_1^{2}/\epsilon^{sl}$$
$$c_{25}^{lD} = \quad + e_{11} e_{14} l_1 l_2/\epsilon^{sl}$$
$$c_{45}^{lD} = \quad - e_{14}^{2} l_1 l_2/\epsilon^{sl}$$
$$c_{55}^{lD} = c_{44}^{E} + e_{14}^{2} l_2^{2}/\epsilon^{sl}$$
$$c_{26}^{lD} = \quad + e_{11}^{2} l_1 l_2/\epsilon^{sl}$$
$$c_{56}^{lD} = c_{14}^{E} + e_{11} e_{14} l_2^{2}/\epsilon^{sl}$$

Whereas the absence of a numerical counterexample from among the few cases examined does

TABLE III. Evaluation of some elastic and electrical properties of selected piezoelectrics at related propagation directions. Blank spaces denote values equivalent or equal to first nonblank entry in column scanning upward. Angles are measured in degrees, velocity in 10^3 m/sec, and D in C/m^2. Values of the c^E, e, and ϵ^S used are those compiled in Surface Wave Velocities, Vol. I of Microwave Acoustic Handbook, edited by A. J. Slobodnik, Jr. and E. D. Conway (Air Force Cambridge Research Laboratories, Bedford, Mass., 1970) (unpublished), and are referenced to the published literature as follows: quartz, Ref. 25; $LiNbO_3$, Ref. 26; CdS, Ref. 27; $Ba_2NaNb_5O_{15}$, Ref. 28; $Bi_{12}GeO_{20}$, Ref. 29; GaAs, Ref. 30. These data are not necessarily the latest but are adequate for this purpose of the table.

Material (crystal class) (symmetry)	Propagation direction (ϕ, θ)	Vibration direction (ϕ_A, θ_A)	Energy flux direction (ϕ_P, θ_P)	Phase velocity V	Group velocity V_g	Electric displacement direction (ϕ_D, θ_D)	Electric displacement magnitude $\lvert D \rvert$	Symmetry operation verified
α-Quartz	3,30	162.29,145.64	−18.33,35.36	6.578	6.741	−129.37,68.74	0.0655	identity
(32)	−177,150		161.67,144.64			50.63,111.26		inversion
(trigonal)	−57,150	−77.11,145.64	−78.33,144.64			170.63,111.26		$\bar{3}\perp x_3$
	57,30	−102.29,145.64	78.33,35.36			9.37,111.26		$m\perp 2$
$LiNbO_3$	3,30	−176.80,153.65	1.13,28.33	7.227	7.231	161.48,61.76	1.679	identity
($3m$)	−177,150		−178.87,151.67			−18.52,118.24		inversion
(trigonal)	−57,150	−56.80,153.65	−58.87,153.67			101.48,118.24		$\bar{3}\parallel x_3$
	−3,150	−3.20,153.65	1.13,151.67			−161.48,118.24		$2\parallel x_1$
CdS	3,30	−177,153.02	3,24.78	4.303	4.321	3,120	0.2909	identity
($6mm$)	−177,150		−177,155.22			−177,60		inversion
(hexagonal)	3,150	3,153.02	3,155.20			3,60		$m\perp x_3$
	−3,150	−3,153.02	−3,155.20			−3,60		$2\parallel x_1$
$Ba_2NaNb_5O_{15}$	3,30	3.17,37.76	3.35,34.74	5.879	5.899	−177.60,60.00	3.052	identity
($mm2$)	−177,150		−176.65,145.26			2.40,120.00		inversion
(orthorhombic)	−3,150	176.83,37.72	−3.35,145.26			177.60,120.00		$2\parallel x_2$
	3,150	−176.83,37.72	3.35,145.26			−177.60,120.00		$m\perp x_3$
$Bi_{12}GeO_{20}$	3,30	−177.15,155.31	2.92,22.35	3.442	3.473	−90.81,87.80	0.578	identity
(23)	−177,150		−177.08,157.65			89.19,92.20		inversion
(cubic)	177,30	−2.85,155.31	177.08,22.35			90.81,92.20		$m\perp x_1$
	−3,30							$m\perp x_2$
	3,150							$m\perp x_3$
	87,30							$m\parallel\langle 1,1,0\rangle$
	93,30							$4\parallel x_3$
	1.73,119.96	1.31,114.66	1.20,112.32			−87.80,89.19		$\bar{3}\parallel\langle 1,1,1\rangle$
GaAs	3,30	−176.48,143.41	3.75,37.99	5.145	5.195	89.19,92.20	0.1464	identity
($\bar{4}3m$)	−177,150		−176.25,142.01			−90.81,87.80		inversion
(cubic)	−3,30							$m\perp x_2$
	3,150							$m\perp x_3$
	87,150							$2\parallel\langle 1,1,0\rangle$
	93,30							$4\parallel x_3$
	1.73,119.96	−177.39,53.49	2.92,127.89			−87.80,89.19		$\bar{3}\parallel\langle 1,1,1\rangle$

not constitute a proof that none exists—the proof is the centrosymmetric nature of the transformation rule derived—the examples demonstrate that, at least for the materials and directions considered, the contributions which outwardly appear to reduce symmetry do not. These contributions are to be distinguished from morphic effects,[24] which may indeed reduce symmetry, and their existence provides the means whereby the values of the piezoelectric constants are customarily evaluated in conjunction with obtaining the elastic constants.[25–30]

By similar analysis, the symmetry and transformation properties of the modified piezoelectric constants e^{kd} may be developed. Their symmetry is lower than that of the ordinary piezoelectric constants, and whereas they too are not a tensor, their transformation rule is that of a third-rank tensor. Because, in the examples given, the strains S_{mn} are calculated for symmetry-related propagation directions, their symmetry is given by the centrosymmetric groups, and consequently the symmetry of the electrical displacements $D_l = e^{kD}_{lmn} S_{mn}$ is also that of the centrosymmetric groups, as Table III shows. In order that $D_{l,l} = 0$, Eq. (26) requires the e^{kD} to have the property $k_l e^{kD}_{lmn} \equiv 0$ for arbitrary and nonzero S_{mn}. That they do indeed have this property follows from their definition, as Eq. (26) clearly shows.

Constants similar to the orientation-dependent c^{kD} and e^{kD} have been obtained[2,31] for rotated coordinate systems where one of the axes is along the propagation direction. Here, the coordinate system is fixed along crystallographic axes. While functions of $\vec{k}$ or $\vec{l}$, the coefficients depend on $k_i/k \equiv \hat{l}_i$ to zero degree, thus not raising the degree of the equations of elasticity for piezodielectrics. Their use in calculating elastic properties is warranted, be they bulk or surface wave properties.

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APPENDIX: TRANSFORMATION RULE FOR STIFFENING CONTRIBUTION TO ELASTIC CONSTANTS

Recall the fact that, for an orthogonal coordinate transformation represented by $x_i = a_{ij} x'_j$, the k_i and the constants transform as

$$k_t = a_{tt''} k'_{t''} , \tag{A1}$$

$$\epsilon^s_{cd} = a_{cc'} a_{dd'} \epsilon^{s'}_{c'd'} , \tag{A2}$$

$$e_{ijr} = a_{ii'} a_{jj'} a_{rr'} e'_{i'j'r'} . \tag{A3}$$

The transformation rule of the stiffened contribution

$$e_{ijr} k_r e_{mns} k_s / \epsilon^s_{cd} k_c k_d \tag{A4}$$

is obtained from a factorwise substitution according to Eqs. (A1)–(A3). One obtains

$$\frac{(a_{ii'} a_{jj'} a_{rr'} e'_{i'j'r'})(a_{rr''} k'_{r''})(a_{mm'} a_{nn'} a_{ss'} e'_{m'n's'})(a_{ss''} k'_{s''})}{(a_{cc'} a_{dd'} \epsilon^s_{c'd'})(a_{cc''} k'_{c''})(a_{dd''}{}_{d''})} . \tag{A5}$$

Associate direction cosine pairs of like left position subscripts such as $a_{cc'} a_{cc''}$, whose sum over c is 1 for $c' = c''$ and zero otherwise for orthonormal transformations. Summing over c and all other repeated indices d, s, and r, reduces Eq. (A5) to

$$\frac{(a_{ii'} a_{jj'})(e'_{i'j'r'} k'_{r'})(a_{mm'} a_{nn'})(e'_{m'n's'} k'_{s'})}{\epsilon^{s'}_{c'd'} k'_{c'} k'_{d'}} . \tag{A6}$$

On commuting the remaining direction cosines to the left, the transformation rule for a fourth-rank quantity becomes obvious. Symbolically,

$$\left(\frac{[ke][ek]}{[k\epsilon^s k]}\right)_{ijmn} = a_{ii'} a_{jj'} a_{mm'} a_{nn'} \times \left(\frac{[k'e'][e'k']}{[k'e'k']}\right)_{i'j'm'n'} .$$

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Theory of Inelastic Neutron Scattering from Orientationally Disordered Molecular Crystals, with Particular Application to ND_4Br and ND_4Cl

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It is argued that the enhancement and narrowing of several single-phonon peaks observed in the Raman scattering on NH_4Br as the transition temperature is approached should also appear in the inelastic diffuse neutron scattering. Whereas the expression for the Raman scattering cross section contains several unknown parameters (i.e., the components of the Raman tensor), all of the major parameters in the neutron scattering cross section are known. Diffuse inelastic scattering from ammonium chloride is also discussed. The results of this paper should be at least qualitatively applicable to other orientationally disordered molecular crystals such as ice and $NaNO_2$ and to some magnetic systems.

I. INTRODUCTION

There has recently been a good deal of both theoretical and experimental work on Raman scattering by NH_4Br and NH_4Cl.[1-7] The tetrahedral-symmetry ammonium ion occupies the body-centered position in the CsCl lattice structure of these compounds, and thus is able to take on two possible orientations.[1,2] Below 243 °K in NH_4Cl, all the NH_4^+ ions have the same orientation, above 243 °K they are disordered.[2] Below 235 °K, the NH_4^+ ions in NH_4Br order such that in a row of NH_4^+ ions along one of the crystallographic axes (call it the c axis) all NH_4^+ ions have the same orientation, and neighboring rows have opposite orientation.[1,2] In Refs. 1, 3, and 5, it was found that in NH_4Br in the vicinity of the ordering temperature there are a couple of phonon peaks in the Raman-scattering spectrum whose intensities are enhanced and whose widths decrease as we approach the transition temperature in either direction. This was explained as being due to coupling of these modes with the short-range order. A mathematical foundation has recently been given for this mechanism.[6] Although this model explains the enhancement effect, it does not explain one of the polarization selection rules that occurs below the transition temperature, namely, that the mode at 56 cm^{-1} only occurs for incident and scattered light polarized along the c axis.[5] This effect could be due to changes in the Raman tensor (i.e., derivatives of the polarizability) which occur as the crystal orders. Such effects were not considered in Ref. 6. In this paper, it will be shown that the enhancement effects observed in Raman scattering should also show up in a diffuse-inelastic-neutron-scattering spectrum, which comes about as a result of ammonium-ion disorder. The integrated cross section of this effect is estimated to be an order of magnitude smaller than that of the nondiffuse inelastic scattering. The effect is interesting in itself, and also, since the derivatives of the polarizability tensor do not enter the neutron scattering cross section, neutron-scattering experiments should give a direct test of the mechanism proposed in Ref. 6 to explain the Raman scattering experiments. If, as in the model of Ref. 7, all short-range order is neglected, the Raman