Lower Symmetry of the Elastic and Piezoelectric Tensors

D. F. Nelson

Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

(Received 3 November 1987)

A long-wavelength lattice-dynamical calculation of the elastic and piezoelectric tensors that does not use the adiabatic approximation yields linear coupling to rotation as well as to strain in dynamic interactions. This leads in the general anisotropic case to 45 independent elastic components (rather than 21 as believed for over a century) and to 27 independent piezoelectric components (rather than 18). The new coupling should be observable at temperatures close to a second-order phase transition where a zone-center soft mode has fallen into the hypersonic region.

PACS numbers: 62.20.Dc, 03.40.Dz, 63.20.Dj, 77.60.+v

From the beginning of the formulation of the modern theory of elasticity by Cauchy in the 1820's, there was controversy over whether there were 15 or 21 independent components of the stiffness tensor c_{ijkl} in a general anisotropic (triclinic) crystal, until the experiments of Voigt in the late 1880's gave strong support to theories of 21 independent components.[1] Except for one challenge by Laval[2] in the 1950's, which was refuted by Lax,[3] 21 has been the accepted number ever since.

In this Letter, I derive that there can be 45 independent stiffness components in a general anisotropic crystal. The derivation is based on lattice dynamics in the long-wavelength limit but does not invoke the adiabatic approximation by which the inertial effects of the optic modes are usually ignored. I show that the optic-mode inertial effects cause a linear elastic coupling to rotations, as well as to strains. I believe that these inertial effects will make measurable contributions to stiffness components of crystals when the frequency of a zone-center soft mode driving a second-order phase transition has dropped into the hypersonic region.

Some time ago we examined the total stress tensor of a dielectric crystal possessing all long-wavelength modes (optic and acoustic) of mechanical motion in interaction with the electromagnetic field, including questions of uniqueness.[4,5] We showed that the total spatial-frame stress tensor t_{ij}^{T}, when properly defined, consists of the symmetric Maxwell stress tensor m_{ij} of the vacuum electric field $\mathbf{E}$ and the vacuum magnetic induction field $\mathbf{B}$, of the flow material momentum $-\rho\dot{x}_i\dot{x}_j$ (also a symmetric quantity), where $\mathbf{x}$ is the spatial (center-of-mass) position and ρ is the spatial (deformed) mass density, and of the elastic stress tensor t_{ij}^{E}, an asymmetric quantity. The latter tensor was shown[6] to be the entire stress tensor entering the spatial-frame[7] center-of-mass (elasticity) equation when body forces are put into the form of an electric force acting on the dielectric (bound) charge and a Lorentz force acting on the dielectric (bound) current.[8]

The antisymmetric part of the elastic stress tensor, and hence of the total stress tensor, was shown[9] to create a torque that is balanced by a change in the internal angular momentum density $\mathbf{l}$ of the optic modes:

$$J^{-1}d(Jl_i)/dt=\epsilon_{ijk}t_{kj}^{T}=\epsilon_{ijk}t_{kj}^{E}, \tag{1}$$

where J is the Jacobian of the transformation from material $\mathbf{X}$ to spatial $\mathbf{x}$ coordinates, d/dt is a total (material) time derivative, and ϵ_{ijk} is the permutation symbol. Thus, the usual requirement that the antisymmetric part of the stress tensor vanish to ensure angular momentum conservation is not relevant to a medium represented by a manifold of N vector matter continua (N is the number of particles per primitive unit cell), $N-1$ of which lead to $3N-3$ optic modes, and one of which produces the three acoustic modes.

The elastic stress tensor t_{ij}^{E} was shown[10] to be expressible as

$$t_{ij}^{E}=t_{ij}^{\Pi}+\frac{1}{J}\sum_{\nu=1}^{N-1}m^{\nu}\dot{y}_i^{T\nu}y_j^{T\nu}, \tag{2}$$

with t_{ij}^{Π} given by

$$t_{ij}^{\Pi}=\frac{1}{J}\frac{\partial(\rho^0\Sigma)}{\partial E_{BC}}x_{i,B}x_{j,C}=t_{ji}^{\Pi}, \tag{3}$$

where all Π_A^{ν} are held constant during differentiation. Here $\mathbf{y}^{T\nu}$ is one of $N-1$ vector internal coordinates[11] that are closely related to optic-mode coordinates, m^{ν} is the material-frame mass density associated with the ν internal coordinate, $\rho^0\Sigma$ is the stored energy per unit material-frame (undeformed) volume, $E_{BC}=\frac{1}{2}(x_{k,B}x_{k,C}-\delta_{BC})$ is the Green finite strain tensor, $\Pi_A^{\nu}=X_{A,i}y_i^{T\nu}-Y_A^{\nu}$ is a rotationally invariant measure of the internal coordinate, and $x_{i,B}=\partial x_i/\partial X_B$. The (total) internal coordinate $\mathbf{y}^{T\nu}=\mathbf{Y}^{\nu}+\mathbf{y}^{\nu}$ consists of a constant or spontaneous part $\mathbf{Y}^{\nu}$ present in the natural (unperturbed) state of the crystal and a part that varies from external influences (e.g., strains or electric fields). Equation (2) shows that the antisymmetric part of t_{ij}^{E} is not only an internal coordinate or optic-mode effect, but also that it is only a dynamic effect. Thus, the static stress tensor is perfectly symmetric. In other words, the antisymmetric part is always dispersive. Furthermore, it can be sur-

mised from the time derivatives in Eq. (2) that the antisymmetric part of t_{ij}^E will be measurably large only for acoustic-wave frequencies near an optic-mode resonant frequency. To bring such a resonant frequency near to the accessible acoustic region will probably require the use of a soft mode whose frequency approaches zero at a second-order phase transition.

To evaluate the generalized stiffness tensor and piezoelectic stress tensor explicitly requires (1) the use of the stored energy written to bilinear order,

$$\rho^0\Sigma=\sum_{\nu\mu}{}^{20}M_{AB}^{\nu\mu}\Pi_A^\nu\Pi_B^\nu+\sum_\nu{}^{11}M_{ABC}^\nu\Pi_A^\nu E_{BC}+{}^{02}M_{ABCD}E_{AB}E_{CD}, \tag{4}$$

where the ${}^{mn}M$ are expansion constants having tensor indices as subscripts, internal-coordinate designations as postsuperscripts, and mnemonic notation ($mn=20,11,02$) indicating the fields to which they couple as presuperscripts; (2) the solution of the internal-motion equations,

$$m^\nu\ddot{y}_i^{T\nu}=q^\nu E_i-\frac{\partial(\rho^0\Sigma)}{\partial\Pi_C^n}X_{C,i}, \tag{5}$$

for a harmonic excitation (angular frequency ω), where q^ν is the charge density associated with the ν internal motion; and (3) the linearization of Eq. (2).[12] For the display of the result, it is convenient to transform from the vector internal coordinates to the scalar normal (optic) mode coordinates[13] by

$$\eta^k=\sum_\nu(m^\nu)^{1/2}n_j^{k\nu}y_j^\nu; \tag{6}$$

a similar relation between N^k, the spontaneous part of the normal coordinate, and $\mathbf{Y}^\nu$; and

$$2\sum_\nu{}^{20}M_{jl}^{\nu\mu}n_j^{k\nu}(m_\nu m^\mu)^{-1/2}=\Omega_k^2n_l^{k\mu}. \tag{7}$$

Here $\mathbf{n}^{k\nu}$ ($\nu=1,2,\ldots,N-1$; $k=1,2,\ldots,3N-3$) are the optic-mode orthonormal eigenvectors, and Ω_k are the transverse optic-mode frequencies.

The result of this calculation is

$$t_{ij}^E=c_{ijab}(\omega)u_{a,b}-e_{hij}(\omega)E_h, \tag{8}$$

where

$$c_{ijab}(\omega)=2\,{}^{02}M_{ijab}-\sum_k\frac{{}^{11}N_{ij}^k\,{}^{11}N_{ab}^k}{\Omega_k^2-\omega^2}+\omega^2\sum_{km}\sum_\nu\frac{{}^{11}N_{ij}^kn_a^{k\nu}n_b^{m\nu}N^m}{\Omega_k^2-\omega^2}$$
$$+\omega^2\sum_{km}\sum_\nu\frac{{}^{11}N_{ab}^kn_i^{k\nu}n_j^{m\nu}N^m}{\Omega_k^2-\omega^2}-\omega^2\sum_{kmn}\sum_{\nu\mu}\frac{\Omega_k^2}{\Omega_k^2-\omega^2}N^nn_i^{k\nu}n_j^{n\nu}n_a^{k\mu}n_b^{m\mu}N^m, \tag{9}$$

$$e_{hij}(\omega)=-\sum_k\frac{c_h^k\,{}^{11}N_{ij}^k}{\Omega_k^2-\omega^2}+\omega^2\sum_{km}\sum_\nu\frac{c_h^kn_i^{k\nu}n_j^{m\nu}N^m}{\Omega_k^2-\omega^2}, \tag{10}$$

and for compactness I use

$${}^{11}N_{ab}^k=\sum_\nu n_j^{k\nu}\,{}^{11}M_{jab}^\nu(m^\nu)^{-1/2}, \tag{11}$$

$$c_j^k=\sum_\nu q^\nu n_j^{k\nu}(m^\nu)^{-1/2}. \tag{12}$$

Note that for $\omega\neq0$,

$$c_{jiab}(\omega)\neq c_{ijab}(\omega)=c_{abij}(\omega)\neq c_{abji}(\omega), \tag{13}$$

$$e_{hij}(\omega)\neq e_{hji}(\omega), \tag{14}$$

which leads in the most general anisotropic case to 45 independent components of the stiffness tensor $c_{ijab}(\omega)$ and 27 independent components of the piezoelectric stress tensor $e_{hij}(\omega)$. Because of this generalized symmetry the displacement gradient $u_{a,b}=\partial u_a/\partial x_b$, not the infinitesimal strain, is the correct independent variable. The displacement gradient is a sum of infinitesimal strain, $u_{a,b}=(u_{a,b}+u_{b,a})/2$, plus an infinitesimal rotation, $u_{[a,b]}=(u_{a,b}-u_{b,a})/2$. Note that terms in $c_{ijab}(\omega)$ and $e_{hij}(\omega)$ that give new antisymmetric contributions are proportional to ω^2 as expected from the derivatives appearing in Eq. (2). It should also be noted that all such terms depend directly on N^m, the spontaneous or constant parts of the optic-mode coordinates. That such quantities exist is readily shown by the calculation of the spontaneous polarization of a pyroelectric or ferroelectric crystal. The result,

$$P_j^s=\sum_\nu q^\nu Y_j^\nu=\sum_k c_j^kN^k, \tag{15}$$

would not exist without the existence of N^k, or equivalently of the spontaneous part $\mathbf{Y}^\nu$ of the internal coordinates.

I wish to emphasize that the above derivation of lowered symmetry of the elastic and piezoelectric tensors is based on accepted lattice dynamics of real crystals. It obtains a new result through (a) the lack of use of the adiabatic approximation and (b) the recognition that optic-mode coordinates have, in general, spontaneous parts. In contrast, the Laval proposal,[2] while having some predictions in common with this work, was based on hypothetical noncentral forces created by the charge density of valence and conduction electrons. The existence of the noncentral forces was believed unrelated to the use or lack of use of the adiabatic approximation. For the latter reason the Lax refutation[3] of the Laval proposal invoked the adiabatic approximation. Clearly the purely electronic motions envisaged in the Laval model are appropriately handled by that approximation.

For these reasons I regard the present derivation as quite distinct from the Laval speculation. Furthermore, I note that the use of the adiabatic approximation in the Lax refutation makes it inapplicable to the present work.

Lastly, one should note that an underdamped zone-center soft mode has been observed in chloranil at a frequency of about 2 cm^{-1}=60 GHz[14] at a temperature slightly below the second-order phase transition. Since acoustic waves at frequencies of order of 30 GHz can be studied by Brillouin scattering, the terms proportional to $\omega^2/(\Omega_s^2-\omega^2)$, where s denotes the soft mode, should be measurably large. On the other hand, I do not believe that the acoustic velocity anomalies observed very near or below the commensurate-incommensurate phase transition in $BaMnF_4$ by Fritz[15] and in $RbH_3(SeO_3)_2$ by Esayan *et al.*[16] result from this mechanism. For one thing the frequencies of measurement, 4 to 30 MHz in Ref. 15 and 15 to 90 MHz in Ref. 16, are very low. Secondly, the incommensurate phase possesses a helical structure modulation that may produce a measurable acoustic activity effect[17,18] which modifies the acoustic velocity through a fifth-rank tensor term. However, an explanation based on wave-vector dispersion[19] has not proven successful,[20] nor has a model based on phasons.[21]

I wish to acknowledge useful conversations with J. F. Scott concerning the anomalies near commensurate-incommensurate phase transitions.

---

[1]For a historical review, see A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Cambridge Univ., Cambridge, 1927; reprinted by Dover, New York, 1944), 4th ed., pp. 1–31.

[2]J. Laval, C. R. Acad. Sci. (Paris) **232**, 1947 (1951), and **238**, 1773 (1954), and in *L'Etat Solide, LX^e Congres de Physique Solvay* (Stoops, Bruxelles, 1951), p. 273.

[3]M. Lax, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagan, 1963,* edited by R. F. Wallis (Pergamon, Oxford, England, 1965), p. 583. This paper gives quite a complete referencing of the controversy.

[4]D. F. Nelson and M. Lax, Phys. Rev. B **13**, 1770 (1976).

[5]D. F. Nelson, *Electric, Optic, and Acoustic Interactions in Dielectrics* (Wiley, New York, 1979), pp. 134–141.

[6]Nelson, Ref. 5, pp. 129–131.

[7]The present discussion is being carried out in the spatial (as distinct from material) description so as to make direct contact with the equations of Ref. 5. Since we are dealing with *linear* elasticity and piezoelectricity, the same result is found in both spatial and material descriptions. Only when spatial- and material-description results differ, as in nonlinear effects, should the material description be used since it is in that frame that measurements are typically made.

[8]It has been pointed out, correctly, that the electromagnetic equations can be used to shift portions of the body forces into divergence of stress forces and thus that there is no single or unique division between these two types of forces. However, I wish to point out that expressing the body forces as a sum of electric plus Lorentz forces is a natural and readily interpretable choice and leads to the stress tensor t_{ij}^E appearing in the elasticity equation to depend *only* on the *mechanical* coordinates of optic and acoustic modes and to be the elastic stress tensor that appears directly in the total stress tensor. Clearly, this represents a very important division between stress and body forces.

[9]Nelson, Ref. 5, pp. 146–149.

[10]Nelson, Ref. 5, pp. 131–132.

[11]Nelson, Ref. 5, pp. 77–80.

[12]The electric and Lorentz body forces give no linear terms to the center-of-mass or elasticity equation.

[13]Nelson, Ref. 5, pp. 204–205.

[14]D. M. Hanson, J. Chem. Phys. **63**, 5046 (1975).

[15]I. J. Fritz, Phys. Lett. **51A**, 219 (1975).

[16]S. Kh. Esayan, V. V. Lemanov, N. Manatkulov, and L. A. Shuvalov, Kristallografiya **26**, 1086 (1981) [Sov. Phys. Crystallogr. **26**, 619 (1981)].

[17]A. S. Pine, Phys. Rev. B **2**, 2049 (1970).

[18]J. Joffrin and A. Levelut, Solid State Commun. **8**, 1573 (1970).

[19]V. Dvorak and S. K. Esayan, Solid State Commun. **44**, 901 (1982).

[20]J. F. Scott, in *Nonlinearity in Condensed Matter,* edited by A. R. Bishop *et al.* (Springer-Verlag, Berlin, 1987), p. 320.

[21]R. J. Gooding and M. B. Walker, Phys. Rev. B **35**, 6831 (1987).