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Linear elasticity and piezoelectricity in pyroelectrics

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We present a new, first-principles theory of linear elasticity and piezoelectricity in pyroelectrics, materials including ferroelectrics, which possess a spontaneous polarization. The constitutive relations for the polarization, the electric displacement, the magnetic intensity, and the total stress are found to contain linear terms proportional to either the spontaneous polarization $\vec{P}^S$ or the spontaneous elecüc field $\vec{E}^S$. The terms involving $\vec{P}^S$ are found to cancel from the differential equations and boundary conditions when $\vec{P}^S$ is homogeneous. If $\vec{P}^S$ is not homogeneous, linear terms proportional to spatial derivatives of $\vec{P}^S$ remain in the Maxwell equations. The terms involving $\vec{E}^S$ lead to a new effective piezoelectric stress tensor of lower symmetry than the normal piezoelectric stress tensor, because it can couple to rotation as well as to strain. The terms involving $\vec{E}^S$ also produce a new effective elastic stiffness tensor of lower symmetry than the usual stiffness tensor in that it can couple to both strain and rotations. The reduced symmetry allows it to have as many as 45 different components instead of the usual 21.

I. INTRODUCTION

In a preceding paper[1] we presented a theory of long-wavelength electrodynamics of elastic pyroelectrics valid for arbitrary nonlinearities in the constitutive relations pertaining to electromagnetic, acoustic, and internal vibrations. In this paper we will linearize the theory and present its implications for linear elasticity and piezoelectricity in crystalline pyroelectrics. A partial summary[2] of this work has already been presented. The results of this paper will apply to pyroelectrics of any symmetry class, of any degree of anisotropy, and having any number of particles (ions and electrons) per unit cell. The term pyroelectric is used here to mean any material possessing a permanent electric dipole moment (spontaneous polarization). As such it includes ferroelectrics, which are reversible pyroelectrics, that is, pyroelectrics whose spontaneous polarization can be reversed with the application of a sufficiently strong electric field.

Pyroelectricity was discovered long before piezoelectricity and, in fact, motivated the discovery of the latter in 1880 by the Curie brothers.[3] Early phenomenological theories of piezoelectricity including that of Voigt[4] of 1890 were believed to apply to pyroelectrics as well as to nonpyroelectric piezoelectrics. This belief persists to the present day as evidenced in many places in the literature.[5–7]

This belief is surprising since the spontaneous polarization could be reasonably expected to create indirect piezoelectric effects. It is easy to conceive of two such effects. First, since the spontaneous polarization is a dipole moment per unit volume, a volume change from a simple compression should give a piezoelectriclike effect. Similarly, a rotation of a volume element, such as is present in a shear wave, should produce a piezoelectriclike effect by rotating the spontaneous polarization.

Reasoning such as this motivated the development of the general theory of the preceding paper[1] and its linearization presented here. We have, in fact, found the two effects just mentioned and several more. Motion of the spontaneous polarization enters the equations explicitly as a contribution to the dielectric current and hence to the magnetic intensity $\vec{H}$. These effects cause the constitutive relations of $\vec{D}$ (and also the linear polarization $\vec{P}$) and $\vec{H}$ to possess *linear* terms depending explicitly on the spontaneous polarization $\vec{P}^S$. The constitutive equations we derive thus differ markedly from the traditional ones of Voigt. Further we find that the spontaneous polarization explicitly enters the boundary condition for the normal component of the dielectric displacement $\vec{D}$ in *linear* terms caused by the deformation of the surface area and surface normal. The spontaneous polarization also enters the boundary condition for the tangential components of the magnetic intensity $\vec{H}$ caused by the motion of the surface.

It is natural to expect that new constitutive equations would necessitate a reinterpretation of past measurements of piezoelectricity in pyroelectrics. It thus came as a considerable surprise to find that the new constitutive equations are in complete accord with the interpretation traditionally given to various piezoelectric measurements when the spontaneous electric field has been cancelled by extrinsic surface charge. Among the latter are the measurement of a voltage across electrodes on a crystal resulting from an applied stress, measurement of a deformation resulting from an applied voltage, measurement of resonant frequencies of piezoelectric plates, and measurement of the piezoelectric stiffening of the elastic constants by ultrasonic-wave velocity observations. Though this theory supports the traditional interpretation of measurements it does not support all aspects of the Voigt theory. We, in fact, show that the Voigt theory has been in agreement with experiments only because of two compensating errors in the theory.

Our theory handles the spontaneous electric field $\vec{E}^S$ and spontaneous polarization as separate quantities, leaving their relation to be determined in the particular situation considered. This distinction is needed because, though the spontaneous polarization of a crystal always exists, its spontaneous electric field may be cancelled out by extrinsic surface charge. Such charge results either from a small bulk or surface conductivity of the crystal or from attraction of charge from the surrounding atmosphere. A spontaneous electric field can, on the other hand, exist for a time of the order of the dielectric relaxation time of the crystal plus ambience.

For these reasons we are led to consider two situations: one with the spontaneous electric field cancelled by extrinsic surface charge, and one with the spontaneous electric field present. The former case we have discussed in the preceding paragraphs; the latter is a new extension of the theory of piezoelectricity and elasticity of pyroelectrics. We find interesting new contributions to the stiffness tensor and the piezoelectric stress tensor which depend upon $\vec{E}^S$ and which have different interchange symmetries compared to the conventional tensors representing these phenomena. The new piezoelectric tensor contribution is antisymmetric upon interchange of the two tensor indices that couple to the displacement gradient. This means that the new contribution couples to rotation and not to strain. The new stiffness-tensor contribution possesses only interchange symmetry between the two pairs of indices; it possesses no symmetry upon interchange within either pair. This means that the new contribution couples to both strain and rotation. We emphasize that the new effects are intrinsic effects since a pyroelectric crystal in its natural state possesses a spontaneous electric field.

The paper is organized as follows: In Sec. II we record those results from the general treatment of the preceding paper that are needed here. Since piezoelectricity involves only frequencies low compared to internal resonances which are typically in the infrared, we adiabatically eliminate the internal coordinates from the equations in Sec. III. Sections IV and V then present the linearized electromagnetic and elastic equations, respectively. Section VI follows with a discussion of the linearized stress tensor.

Section VII considers the quasielectrostatic approximation of the dynamical equations. This approximation, valid when the electromagnetic wavelength is long compared to the crystal size, is a useful simplification and is usually valid for piezoelectric calculations. However, we will show that first-order corrections to this approximation which involve the magnetic intensity $\vec{H}$ have linear terms depending on the spontaneous polarization. This necessitates a careful consideration of $\vec{H}$ field effects in piezoelectricity of pyroelectrics. Section VIII considers the spontaneous electric field caused by the spontaneous polarization and its cancellation by extrinsic surface charge. The extrinsic surface charge determined in this discussion is of importance to a correct application of boundary conditions. Section IX discusses the various boundary conditions at the linear level. Section X considers the implications of this work on acoustic-wave propagation. Section XI summarizes the main conclusions and compares this work with the traditional theory of Voigt and with the recent work of Baumhauer and Tiersten.[7]

II. DYNAMICAL EQUATIONS

We will record in this section the general dynamical equations derived in the preceding paper[1] for nonconducting, nonmagnetic pyroelectrics having arbitrary symmetry, structural complexity, and nonlinearity. The Maxwell charge and current equations are

$$\frac{\vec{\nabla}\times\vec{B}}{\mu_0} - \epsilon_0 \frac{\partial \vec{E}}{\partial t} = \vec{j}^D , \tag{2.1}$$

$$\epsilon_0 \vec{\nabla}\cdot\vec{E} = q^D , \tag{2.2}$$

where $\vec{E}$ is the electric field, $\vec{B}$ is the magnetic induction, $\vec{j}^D$ is the dielectric (bound) current, and q^D the dielectric (bound) charge, the latter two quantities being given to electric dipole order by

$$\vec{j}^D \equiv \frac{\partial \vec{P}}{\partial t} + \vec{\nabla}\times\left(\vec{P}\times\frac{d\vec{x}}{dt}\right) , \tag{2.3}$$

$$q^D \equiv -\vec{\nabla}\cdot\vec{P} \tag{2.4}$$

(mks units are used).

The polarization is defined by

$$\vec{P}(\vec{z}, t) \equiv \sum_\nu{}' q^\nu \left(\frac{\vec{y}^{T\nu}(\vec{X}, t)}{J(\vec{X}, t)}\right)_{\vec{z}=\vec{x}(\vec{X}, t)} , \tag{2.5}$$

where $\vec{y}^{T\nu}$ ($\nu = 1, 2, \ldots, N-1$; N being the number of particles per unit cell) are internal coordinates, q^ν is the charge density associated with the νth internal coordinate, $\vec{x}(\vec{X}, t) \equiv \vec{y}^{T0}(\vec{X}, t)$ is the center-of-mass position, $\vec{z}$ is the spatial coordinate system coordinate vector, $\vec{X}$ the center-or-mass designation in the material coordinate system, $J(\vec{X}, t) \equiv \det(\partial x_i / \partial X_A) \equiv \det x_{i,A}$ is the Jacobian of the transformation, and the prime on the sum indicates the exclusion of the $\nu = 0$ (center-of-mass) term. The polarization has a spontaneous part given by

$$P_i^S \equiv \delta_{iA} \sum_\nu{}' q^\nu Y_A^\nu , \tag{2.6}$$

where $\vec{Y}^\nu$ is the spontaneous part of $\vec{y}^{T\nu}$ given by

$$y_i^{T\nu} = \delta_{iA} Y_A^\nu + y_i^\nu \quad (\nu = 0, 1, 2, \ldots, N-1) . \tag{2.7}$$

Here we have used the convention that tensor components referred to the spatial coordinate system are denoted by lower-case Latin letters and components referred to the material coordinate system are denoted by upper-case Latin letters. Equation (2.7) for $\nu = 0$ becomes

$$x_i = \delta_{iA} X_A + u_i , \tag{2.8}$$

since $Y_A^0 \equiv X_A$ and $y_i^0 \equiv u_i$. The vector $\vec{u}$ is the conventional displacement vector. The dielectric displacement $\vec{D}$ and magnetic field $\vec{H}$ are given in terms of the other fields by

$$\vec{D} \equiv \epsilon_0 \vec{E} + \vec{P} , \tag{2.9}$$

$$\vec{H} \equiv \frac{\vec{B}}{\mu_0} - \vec{P} \times \frac{d\vec{x}}{dt} . \tag{2.10}$$

The remaining Maxwell equations are

$$\vec{\nabla} \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0 , \tag{2.11}$$

$$\vec{\nabla} \cdot \vec{B} = 0 . \tag{2.12}$$

The pyroelectric crystal is represented by N dynamical vector equations, one for the center-of-mass motion and $N-1$ for the internal vibrations. They are

$$\rho \ddot{x}_i = (t_{ij}^y + \mathcal{E}_i P_j)_{,j} + q^D E_i + (\vec{j}^D \times \vec{B})_i , \tag{2.13}$$

$$m^\nu \ddot{y}_i^\nu = q^\nu \mathcal{E}_i - \frac{\partial \rho^0 \Sigma}{\partial y_i^{T\nu}} \quad (\nu = 1, 2, \ldots, N-1) . \tag{2.14}$$

Here m^ν is the mass associated with the νth internal coordinate, $\rho \equiv J^{-1} \rho^0$ is the deformed (spatial coordinate system) mass density, ρ^0 the undeformed (material coordinate system) mass density, t_{ij}^y is the local stress tensor defined by

$$t_{ij}^y \equiv \rho \frac{\partial \Sigma}{\partial x_{i,A}} x_{j,A} , \tag{2.15}$$

with the $\vec{y}^{T\mu}$ held fixed during the differentiation and the effective electric field $\vec{\mathcal{E}}$ is

$$\vec{\mathcal{E}} \equiv \vec{E} + \frac{d\vec{x}}{dt} \times \vec{B} . \tag{2.16}$$

The stored energy per unit mass, Σ, is given as a polynomial expansion

$$\rho^0 \Sigma = {}^{(0,1)}K_{AB} E_{AB} + {}^{(0,2)}K_{ABCD} E_{AB} E_{CD} + \sum_\mu{}' {}^{(1,0)}K_A^\mu \Lambda_A^\mu + \sum_{\mu\nu}{}' {}^{(2,0)}K_{AB}^{\mu\nu} \Lambda_A^\mu \Lambda_B^\nu + \sum_\mu{}' {}^{(1,1)}K^\mu_{ABC} \Lambda_A^\mu E_{BC} + \cdots , \tag{2.17}$$

where the measure of finite strain E_{AB} is defined by

$$E_{AB} \equiv \tfrac{1}{2}(C_{AB} - \delta_{AB}) , \tag{2.18}$$

$$C_{AB} \equiv x_{i,A} x_{i,B} , \tag{2.19}$$

and the invariant measures Λ_A^μ of the internal displacements are defined by

$$\Lambda_A^\mu \equiv (R_{iA} - \delta_{iA}) \delta_{iB} Y_B^\mu + R_{iA} y_i^\mu \quad (\mu \neq 0) , \tag{2.20}$$

R_{iA} being the finite rotation tensor given by

$$R_{iA} \equiv x_{i,B} (C^{-1/2})_{BA} , \tag{2.21}$$

and the ${}^{(m,n)}K$ coefficients are frequency-independent material constants characterizing the crystal. The requirement that there be no forces on the internal motions governed by Eq. (2.14) in the natural state of the crystal leads to the relation

$$q^\nu E_i^S = \delta_{iA} {}^{(1,0)}K_A^\nu , \tag{2.22}$$

where $\vec{E}^S$ is the spontaneous electric field.

The total stress tensor[8] of the matter and electromagnetic fields was defined as

$$t_{ij}^L \equiv t_{ij}^y + \mathcal{E}_i P_j + m_{ij} - \rho \dot{x}_i \dot{x}_j , \tag{2.23}$$

where m_{ij} is the vacuum field Maxwell stress tensor given by

$$m_{ij} \equiv \epsilon_0 E_i E_j + B_i B_j / \mu_0 - \tfrac{1}{2}(\epsilon_0 E_k E_k + B_k B_k / \mu_0) \delta_{ij} . \tag{2.24}$$

The total stress tensor satisfies the momentum density conservation equation

$$\frac{\partial}{\partial t} [\rho \dot{x}_i + \epsilon_0 (\vec{E} \times \vec{B})_i] + \frac{\partial}{\partial z_j} (-t_{ij}^L) = 0 , \tag{2.25}$$

and possesses a scalar product with the unit normal to a surface fixed in the spatial coordinate system which is continuous across that surface. It was also shown[8] that a related total stress tensor t_{ij}^B,

$$t_{ij}^B \equiv t_{ij}^y + \mathcal{E}_i P_j + m_{ij} + \epsilon_0 (\vec{E} \times \vec{B})_i \dot{x}_j , \tag{2.26}$$

possesses a continuous scalar product with the unit normal to a surface, such as the body surface, that is moving at a velocity $d\vec{x}/dt$ with respect to the spatial coordinate system.

III. ELIMINATION OF INTERNAL COORDINATES

Elasticity and piezoelectricity are low-frequency phenomena, that is, they are significant only at frequencies low compared to the internal resonances of the solid which are typically in the infrared. At these low frequencies the internal motions of the solid follow the elastic deformations adiabatically. Thus we may ignore the inertia of the internal motions in Eq. (2.14) and use those equations to eliminate the internal coordinates from the other equations. Since we are aiming at a linear theory the expansion of $\rho^0\Sigma$ in Eq. (2.17) is sufficient for use in Eq. (2.14). The latter then becomes

$$2\sum_{\nu}{}' \, {}^{(2,0)}K^{\mu\nu}_{AB}\Lambda^{\nu}_{B} = -\,{}^{(1,1)}K^{\mu}_{ABC}E_{BC} + q^{\mu}F_{A} \,, \tag{3.1}$$

where

$$F_A \equiv \mathcal{E}_i R_{iA} - E^S_i \delta_{iA} \,. \tag{3.2}$$

We define a low-frequency mechanical admittance of the internal coordinates $\Upsilon^{\lambda\mu}_{DA}$ by

$$2\epsilon_0 \sum_{\mu}{}' \, \Upsilon^{\lambda\mu}_{DA}\, {}^{(2,0)}K^{\mu\nu}_{AB} \equiv \delta_{DB}\delta^{\lambda\nu} \quad (\lambda,\ \nu \neq 0) \,. \tag{3.3}$$

It may be used to solve Eq. (3.1) for Λ^{λ}_{D},

$$\Lambda^{\lambda}_{D} = -\epsilon_0 \sum_{\mu}{}' \, \Upsilon^{\lambda\mu}_{DA}\left({}^{(1,1)}K^{\mu}_{ABC}E_{BC} - q^{\mu}F_A\right) \,. \tag{3.4}$$

This can now be used to eliminate Λ^{λ}_{D} from $\rho^0\Sigma$. Combining Eqs. (2.7) and (2.20) and using the orthogonality of the rotation tensor R_{iA},

$$R_{iA}R_{jA} = \delta_{ij} \,, \tag{3.5}$$

yields

$$y^{T\nu}_i = R_{iA}(Y^{\nu}_A + \Lambda^{\nu}_A) \,. \tag{3.6}$$

This can be used with Eq. (3.4) to eliminate $\vec{y}^{\,T\nu}$ from $\vec{P}$ in Eq. (2.5). The nonlinear portions of E_{BC} and F_A in Eq. (3.4) can be dropped at a later stage.

IV. LINEARIZED ELECTROMAGNETIC EQUATIONS

We now linearize the equations of Sec. II, in which the internal coordinates have been adiabatically eliminated, in terms of the displacement $\vec{u}$ and the various electromagnetic fields. The definition of the displacement $\vec{u}$ in Eq. (2.8) specifies the relation of the material and spatial coordinates and the fact that they are measured with respect to a common Cartesian frame. Expansions of quantities such as R_{iA} have been given previously.[9] An alternate approach[2] is to approximate the Lagrangian of the previous paper[1] and obtain the linearized equations directly from it (see the Appendix).

The constitutive expression for the polarization $\vec{P}$ that results is

$$P_i = P^S_i + \epsilon_0 \chi_{ij} E^V_j + (e_{ijk} + 2P^S_{[k}\delta_{i]j} - \epsilon_0 \chi_{i[j}E^S_{k]})u_{j,k} \,, \tag{4.1}$$

where

$$\chi_{ij} \equiv \sum_{\mu\nu}{}' \, q^{\mu}\Upsilon^{\mu\nu}_{ij}q^{\nu} = \chi_{ji} \,, \tag{4.2}$$

$$e_{ijk} \equiv -\delta_{i(j}P^S_{k)} - \epsilon_0 \sum_{\mu\nu}{}' \, q^{\mu}\Upsilon^{\mu\nu}_{il}\, {}^{(1,1)}K^{\nu}_{ljk} = e_{ikj} \tag{4.3}$$

are the linear electric susceptibility and the piezoelectric stress tensor, respectively. The varying electric field present in Eq. (4.1) stands for $\vec{E}^V = \vec{E} - \vec{E}^S$ but will be denoted simply by $\vec{E}$ in the linear equations. Brackets enclosing tensor subscripts denote the antisymmetric part of the expression with respect to interchange of the enclosed subscripts. Parentheses in a similar use denote the symmetric part. We have included some of the explicit dependence of the linear polarization on $\vec{P}^S$ in the definition of e_{ijk} because, as we will see in later sections, it is this combination of terms that has been measured and recorded in the absence of the spontaneous electric field as the piezoelectric stress tensor in the past. The remaining terms in the coefficient of the displacement gradient $u_{j,k}$ that involves $\vec{P}^S$ and $\vec{E}^S$ represent new predictions not present in the traditional Voigt constitutive relation for the polarization.[10] The linear terms involving $\vec{P}^S$ in Eq. (4.3) in combination with those in Eq. (4.1) have the simple interpretation of the effects described in the Introduction, that is, piezoelectric effects arising from the compression and rotation of a volume element which possesses a spontaneous polarization.

To the linear level the dielectric current and charge of Eq. (2.3) and (2.4) are

$$j^D_i = \frac{\partial}{\partial t}(\epsilon_0 \chi_{ij}E_j + e^F_{ijk}u_{j,k}) \,, \tag{4.4}$$

$$q^D = -\epsilon_0 \chi_{ij}E_{j,i} - e^F_{ijk}u_{j,ki} \,, \tag{4.5}$$

where

$$e^F_{ijk} \equiv e_{ijk} - \epsilon_0 \chi_{i[j}E^S_{k]} \,. \tag{4.6}$$

Note that the terms explicitly depending on $\vec{P}^S$ in Eq. (4.1) have disappeared from these two equations. This occurs only because $\vec{P}^S$ is taken as homogeneous. If $\vec{P}^S$ were spatially varying, the terms that cancelled in $\vec{j}^D$ in Eq. (4.4) would instead be

$$\frac{\partial}{\partial t}(2P^S_{[k}\delta_{i]j}u_{j,k}) + \left[\vec{\nabla}\times\left(\vec{P}^S\times\frac{d\vec{u}}{dt}\right)\right]_i = \dot{u}_l P^S_{i,l} - \dot{u}_i P^S_{l,l} \,, \tag{4.7}$$

and the terms that cancelled in q^D in Eq. (4.5) would instead be

$$-(2P^S_{[k}\delta_{i]j}u_{j,k})_{,i} = P^S_{i,i}u_{j,j} - P^S_{k,j}u_{j,k} \,. \tag{4.8}$$

Note also that, when $\vec{E}^S \neq 0$, a coupling to the rotation $u_{[j,k]}$ in contrast to the strain $u_{(j,k)}$ exists.

The expressions for the dielectric displacement $\vec{D}$ and the magnetic intensity $\vec{H}$ of Eqs. (2.9) and (2.10) to the linear level become

$$D_i = \epsilon_0 E_i^S + P_i^S + \epsilon_0 \kappa_{ij} E_j + (e^F_{ijk} + 2P^S_{[k}\delta_{i]j})u_{j,k} , \quad (4.9)$$

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{P}^S \times \frac{d\vec{u}}{dt} . \quad (4.10)$$

The dielectric tensor κ_{ij} is defined by

$$\kappa_{ij} \equiv \chi_{ij} + \delta_{ij} . \quad (4.11)$$

Note that a new term, not considered previously in piezoelectricity, arises in $\vec{H}$ which involves the time derivative of the displacement.

V. LINEARIZED ELASTICITY EQUATION

In order to linearize the center-of-mass equation (2.13) we begin with the local stress tensor t^y_{ij} of Eq. (2.15). Expanding the derivative indicated in that equation yields

$$t^y_{ij} = t^\Lambda_{ij} + \rho x_{j,E} \frac{\partial R_{kA}}{\partial x_{i,E}} \sum_\nu{}' y_k^{T\nu} \frac{\partial \Sigma}{\partial \Lambda^\nu_A}\bigg|_{E_{CD}} , \quad (5.1)$$

where

$$t^\Lambda_{ij} \equiv \rho x_{i,A} x_{j,B} \frac{\partial \Sigma}{\partial E_{AB}}\bigg|_{\Lambda^\nu_c} . \quad (5.2)$$

The derivative $\partial\Sigma/\partial\Lambda^\nu_A$ in Eq. (5.1) can be eliminated with the use of Eq. (2.14) in the adiabatic approximation,

$$\rho^0 \frac{\partial \Sigma}{\partial \Lambda^\nu_A} = q^\nu \mathcal{E}_j R_{jA} , \quad (5.3)$$

that is, we again neglect the inertial effects of the internal motions since frequencies well below the resonances of such motions are being considered. This approximation makes the total stress tensor symmetric.[8] Equation (5.1) then becomes

$$t^y_{ij} = t^\Lambda_{ij} + P_k \mathcal{E}_l x_{j,E} \frac{\partial R_{kA}}{\partial x_{i,E}} R_{lA} . \quad (5.4)$$

Linearization of the second term in the displacement gradient yields

$$t^y_{ij} = t^\Lambda_{ij} - \mathcal{E}_{[i} P_{j]} + \tfrac{1}{4}(\mathcal{E}_l u_{l,(i} P_{j)} - P_k u_{k,(i}\mathcal{E}_{j)} + P_{(i} u_{j),l}\mathcal{E}_l - \mathcal{E}_{(i} u_{j),l} P_l) , \quad (5.5)$$

and linearization of t^Λ_{ij} yields

$$t^\Lambda_{ij} = t^S_{ij} + 2t^S_{k(i} u_{j),k} - t^S_{ij} u_{k,k} + c_{ijkl} u_{k,l} - e_{kij} E_k - e_{lij} E^S_k u_{[k,l]} - E_{(i} P^S_{j)} - \delta_{l(i} P^S_{j)} E^S_k u_{[k,l]} , \quad (5.6)$$

where

$$c_{abcd} \equiv 2\,{}^{(0,2)}K_{abcd} - \epsilon_0 \sum_{\mu\nu}{}' \,{}^{(1,1)}K^\mu_{eab} \Upsilon^{\mu\nu}_{ef}\, {}^{(1,1)}K^\nu_{fcd} , \quad (5.7)$$

$$t^S_{bd} = t^S_{db} \equiv {}^{(0,1)}K_{bd} \quad (5.8)$$

are the elastic stiffness tensor (when $\vec{E}^S = 0$) and the spontaneous stress tensor. Use of Eqs. (5.5) and (5.6) in Eq. (2.13) results in the dynamic elasticity equation for the displacement within a homogeneous crystal,

$$\rho^0 \frac{\partial^2 u_i}{\partial t^2} = c^F_{ijkl} u_{k,lj} - e^F_{kij} E_{k,j} , \quad (5.9)$$

where

$$c^F_{abcd} \equiv c_{abcd} + t^S_{bd}\delta_{ac} + \epsilon_0 E^S_{[a}\chi_{b][c} E^S_{d]} - E^S_{[a} e_{b]cd} - E^S_{[c} e_{d]ab} - \tfrac{1}{2}(E^S_{[a}\delta_{b](c} P^S_{d)} + E^S_{[c}\delta_{d](a} P^S_{b)} - E^S_{(a}\delta_{b)[c} P^S_{d]} - E^S_{(c}\delta_{d)[a} P^S_{b]} + E^S_{[a}\delta_{b][c} P^S_{d]} + E^S_{[c}\delta_{d][a} P^S_{b]}) . \quad (5.10)$$

In the absence of a spontaneous electric field c^F_{abcd} reduces to the usual elastic stiffness tensor c_{abcd} and e^F_{kij} reduces to the usual piezoelectric stress tensor e_{kij}. In the presence of a spontaneous electric field a host of new effects contribute to the elastic stiffness as seen in Eq. (5.10) and an additional term in the definition (4.6) contributes to the piezoelectric interaction.

From the definitions (5.7), (5.8), and (5.10) we find the interchange symmetries,

$$c_{abcd} = c_{(ab)(cd)} = c_{(cd)(ab)} , \quad (5.11)$$

$$c^F_{abcd} = c^F_{cdab} . \quad (5.12)$$

Note the much lower interchange symmetry possessed by c^F_{abcd} compared to c_{abcd}. Based on this interchange symmetry c^F_{abcd} can have 45 different components compared to 21 allowed components for c_{abcd}. Since the $\vec{P}^S$ and $\vec{E}^S$ fields are intrinsic properties of a pyroelectric crystal, c^F_{abcd} can be argued to be a basic intrinsic property of the crystal. On the other hand, the value of $\vec{E}^S$ will depend on the shape of the crystal as well as the surface charge condition of the surfaces and so is not a recordable property applying to every crystal of the same composition.

VI. LINEARIZED TOTAL STRESS TENSOR

In the accompanying paper[8] we showed that there are two important total stress tensors. One, t^L_{ij} given in Eq. (2.23), appears in the spatial or laboratory frame momentum conservation law and has a continuous normal component across a surface fixed in the spatial frame. The other, t^B_{ij} given in Eq. (2.26), has a continuous normal component across a body surface moving at a velocity $d\vec{x}/dt$ with respect to the spatial frame and is particularly important for general considerations of momentum transfer between bodies. These two tensors differ only by nonlinear terms. Thus to the linear level they are identical and so we need consider only t^L_{ij}.

The local stress tensor t^y_{ij} has already been linearized in Eqs. (5.5) and (5.6). The Maxwell stress tensor of Eq. (2.24) to the linear level is

$$m_{ij}=\epsilon_0(2E^S_{(i}E_{j)}-\tfrac{1}{2}E^S_k E^S_k\delta_{ij}-E^S_k E_k\delta_{ij}+E^S_i E^S_j)\ . \tag{6.1}$$

Substitution of Eqs. (5.5), (5.6), and (6.1) into Eq. (2.23) leads to

$$\begin{aligned}t^L_{ij}=&(t^S_{ij}+E^S_{(i}P^S_{j)}+\epsilon_0 E^S_i E^S_j-\tfrac{1}{2}\epsilon_0 E^S_k E^S_k\delta_{ij})\\&+(c_{ijkl}+2t^S_{l(i}\delta_{j)k}-t^S_{ij}\delta_{kl}-E^S_{[k}e_{l]ij}+E^S_{(i}e_{j)kl}\\&-E^S_{(i}P^S_{j)}\delta_{kl}-\epsilon_0 E^S_{(i}\chi_{j)[k}E^S_{l]}+E^S_{(i}\delta_{j)[k}P^S_{l]}\\&-E^S_{[k}\delta_{l](i}P^S_{j)}+\tfrac{1}{2}E^S_{(k}\delta_{l)(i}P^S_{j)}+\tfrac{1}{2}E^S_{(i}\delta_{j)(k}P^S_{l)})u_{k,l}\\&-(e_{kij}-\epsilon_0 E^S_{(i}\chi_{j)k}-2\epsilon_0 E^S_{(i}\delta_{j)k}+\epsilon_0\delta_{ij}E^S_k)E_k\ .\end{aligned} \tag{6.2}$$

It is apparent from Eq. (6.2) that the presence of a spontaneous electric field and a spontaneous elastic stress have greatly complicated the linear stress terms as well as created a constant total stress term.

As already discussed[1] the natural state of a *boundless* pyroelectric can be reasonably taken as a stress free state. This corresponds to setting the constant terms of Eq. (6.2) to zero. Thus the spontaneous elastic stress t^S_{ij} is determined in terms of the spontaneous electric moment and field by

$$t^S_{ij}=\tfrac{1}{2}\epsilon_0 E^S_k E^S_k\delta_{ij}-E^S_{(i}P^S_{j)}-\epsilon_0 E^S_i E^S_j\ . \tag{6.3}$$

Note that, if extrinsic surface charge cancels the spontaneous electric field, the linearized total stress tensor in Eq. (6.2) takes on its conventional form for a nonpyroelectric piezoelectric,

$$t^L_{ij}=c_{ijkl}u_{k,l}-e_{kij}E_k\ . \tag{6.4}$$

A pyroelectric crystal, finite in *all* its dimensions and in possession of its spontaneous electric field, cannot have a homogeneous natural state as proved in the preceding paper.[1] As we wish to avoid here the complications of inhomogeneity, let us consider the form of the linearized total stress tensor for an infinite plate. Consideration of the depolarization field problem[11] for an infinite plate yields the solution inside the plate

$$\vec{E}^S=-\vec{N}(\vec{N}\cdot\vec{P}^S)/\epsilon_0\ , \tag{6.5}$$

where $\vec{N}$ is the unit normal of one of the surfaces, and $\vec{E}^S=0$ outside the plate. In the preceding paper[1] we found the spontaneous stress for this geometry to be

$$t^S_{ij}=(N_{(i}P^S_{j)}-\tfrac{1}{2}N_i N_j P^S_k N_k)P^S_l N_l/\epsilon_0\ . \tag{6.6}$$

Substitution of Eqs. (6.5) and (6.6) into Eq. (6.2) yields

$$\begin{aligned}t^L_{ij}=&(N_kP^S_k)^2(N_iN_j-\delta_{ij})/2\epsilon_0+[c_{ijkl}+(N_mP^S_m/2\epsilon_0)(-2N_{(i}e_{j)kl}-2N_nP^S_nN_{(i}\delta_{j)(k}N_{l)}+N_nP^S_nN_iN_j\delta_{kl}\\&+3N_{(i}\delta_{j)(k}P^S_{l)}+N_{(k}\delta_{l)(i}P^S_{j)})]u_{(k,l)}+(N_mP^S_m/\epsilon_0)(N_{[k}e_{l]ij}-N_nP^S_nN_{(i}\kappa_{j)(k}N_{l)}-N_{[k}\delta_{l](i}P^S_{j)})u_{[k,l]}\\&-[e_{kij}+N_mP^S_m(\chi_{k(i}N_{j)}+2\delta_{k(i}N_{j)}-N_k\delta_{ij})]E_k\ .\end{aligned} \tag{6.7}$$

This equation is the generalization of the conventional stress-strain-electric field relation to the case of an infinite pyroelectric plate in possession of its spontaneous electric field. A number of things are to be noted: (i) A spontaneous stress, which is a combination of spontaneous elastic and electromagnetic stresses, exists. (ii) The stress is coupled to the rotation of the volume element $u_{[k,l]}$ as well as to its strain $u_{(k,l)}$. (iii) The elastic coefficient of the strain $u_{(k,l)}$ contains indirect contributions to the effective stiffness tensor which depend on the spontaneous polarization $\vec{P}^S$ and on the plate geometry through the unit normal $\vec{N}$. (iv) The piezoelectric coefficient of $\vec{E}$ contains indirect contributions to the effective piezoelectric stress tensor which also depend on the spontaneous polarization $\vec{P}^S$ and the unit normal $\vec{N}$. Clearly Eq. (6.7) can be inverted through the use of appropriately defined tensor inverses to yield an equation for the strain in terms of stress, rotation, and electric field. We will not write down such variations of Eq. (6.7), however.

We wish to emphasize that the electric field variable $\vec{E}$ in Eqs. (6.2) and (6.7) includes *both* the applied electric field plus any varying depolarizing field of the crystal. The latter will contribute whenever the boundaries of the crystal are dynamically deforming. Thus the vibration at the surface of such a crystal can effect the vibration of the crystal at distant points through the intermediary of the (long-range) depolarizing electric field.

We conclude this section with a caveat concerning linear stress tensors. The form of Eq. (5.9) might lead one (incorrectly) to believe that the right-hand side of that equation is the divergence with respect to $\partial/\partial z_j$ of a linear stress. Application of Gauss's theorem to the equation within a minute pill box enclosing a body-surface element would lead to the conclusion that the scalar product of that stress with the body-surface normal was continuous at a body surface. This is not true. Only the total stress tensor of Eq. (6.2) possesses such continuity. The error of this reasoning can be seen by observing that the right-hand side of Eq. (5.9) arose from contributions from both a divergence of a stress and from body force terms in Eq. (2.13). In a true divergence of a stress the derivative must be allowed to act on the matter tensors, such as the spontaneous polarization vector, as well as the field variables. This is of utmost importance at a body surface since there the material tensors undergo a rapid (if not abrupt) change. The body force terms of Eq. (2.13) cannot in general be rearranged into such a divergence and only *appear* to have been so rearranged in the linearized form of Eq. (5.9).

VII. QUASIELECTROSTATIC APPROXIMATION

The study of piezoelectricity typically uses crystals whose dimensions are small compared to the electromagnetic wavelength of a free wave at the frequency of use. For this low-frequency regime an approximate or truncated form of the electromagnetic equations is adequate. The approximation used is called the quasielectrostatic approximation. We will use it to obtain a truncated set of equations for piezoelectric studies from the linearized electromagnetic and elastic equations of Secs. IV and V. Our interest is directed particularly at determining the magnetic field contributions to the quasielectrostatic approximation.

We begin by scaling the various independent and dependent variables with respect to characteristic quantities. Let

$$\vec{\zeta} \equiv \vec{z}/L , \quad \tau \equiv \omega t , \quad \vec{\upsilon} \equiv \vec{u}/L , \tag{7.1}$$

$$\vec{\mathcal{B}} \equiv c\vec{B} . \tag{7.2}$$

Equation (7.2) yields a magnetic induction $\vec{\mathcal{B}}$ in the same units as the electric field. Equations (5.9), (2.1), (2.2), (2.11), (2.12), (4.4), and (4.5) then yield

$$c^F_{ijkl}\upsilon_{k,lj} - e^F_{kij}E_{k,j} = \rho^0\omega^2L^2\frac{\partial^2\upsilon_i}{\partial\tau^2} , \tag{7.3}$$

$$\kappa_{ij}E_{j,i} + (e^F_{ijk}/\epsilon_0)\upsilon_{j,ki} = 0 , \tag{7.4}$$

$$\vec{\nabla}\times\vec{E} = -\eta\frac{\partial\vec{\mathcal{B}}}{\partial\tau} , \tag{7.5}$$

$$(\vec{\nabla}\times\vec{\mathcal{B}})_i = \eta\frac{\partial}{\partial\tau}\left(\kappa_{ij}E_j + \frac{e^F_{ijk}}{\epsilon_0}\upsilon_{j,k}\right), \tag{7.6}$$

$$\vec{\nabla}\cdot\vec{\mathcal{B}} = 0 , \tag{7.7}$$

with

$$\eta \equiv \omega L/c . \tag{7.8}$$

The spatial derivatives in Eqs. (7.3)–(7.7) are taken with respect to $\vec{\zeta}$.

We now assume that η is small compared to one, that is, for $L=1$ cm the frequency $\omega/2\pi$ must be less than 1 GHz. We expand the three dependent fields $\vec{E}$, $\vec{\mathcal{B}}$, and $\vec{\upsilon}$ in a series of the form

$$\vec{F} = \sum_{n=0}^{\infty}\eta^n\vec{F}^{(n)} \tag{7.9}$$

with

$$F^{(n)} = 0 , \quad (n<0) . \tag{7.10}$$

After substitution of Eq. (7.9) for each dependent field the sum of coefficients of terms of like powers of η are set to zero. Note that η is not present in either Eq. (7.3) or (7.4) prior to the use of Eq. (7.9).

For $n=0$ the equations with the scaling of Eqs. (7.1) and (7.2) now removed are

$$c^F_{ijkl}u^{(0)}_{k,lj} - e^F_{kij}E^{(0)}_{k,j} = \rho^0\frac{\partial^2u^{(0)}_i}{\partial t^2} , \tag{7.11}$$

$$\kappa_{ij}E^{(0)}_{j,i} + (e^F_{ijk}/\epsilon_0)u^{(0)}_{j,ki} = 0 , \tag{7.12}$$

$$\vec{\nabla}\times\vec{E}^{(0)} = 0 , \tag{7.13}$$

$$\vec{\nabla}\times\vec{B}^{(0)} = 0 , \tag{7.14}$$

$$\vec{\nabla}\cdot\vec{B}^{(0)} = 0 . \tag{7.15}$$

Since $\vec{B}^{(0)}$ is not coupled to the remaining equations, it must represent an applied $\vec{B}$ field. Typically, no such field is used in piezoelectric studies. Equation (7.13) shows the $\vec{E}^{(0)}$ field to be irrotational and hence completely describable as a divergence of the electric potential

$$\vec{E}^{(0)} = -\vec{\nabla}\Phi^{(0)} , \tag{7.16}$$

which may be used to eliminate $\vec{E}^{(0)}$ from Eqs. (7.11) and (7.12). These two equations governing $\vec{u}^{(0)}$ and $\Phi^{(0)}$ thus are the only differential equations needed for the zero-order solution.

For $n=1$ Eqs. (7.3)–(7.7) with the scaling of Eqs. (7.1) and (7.2) removed and with η absorbed into $\vec{u}^{(1)}$, $\vec{E}^{(1)}$, and $\vec{B}^{(1)}$ become

$$c^F_{ijkl}u^{(1)}_{k,lj} - e^F_{kij}E^{(1)}_{k,j} = \rho^0\frac{\partial^2u^{(1)}_i}{\partial t^2} , \tag{7.17}$$

$$\kappa_{ij}E^{(1)}_{j,i} + (e^F_{ijk}/\epsilon_0)u^{(1)}_{j,ki} = 0 , \tag{7.18}$$

$$\vec{\nabla}\times\vec{E}^{(1)} = \frac{-\partial\vec{B}^{(0)}}{\partial t} , \tag{7.19}$$

$$\frac{(\vec{\nabla}\times\vec{B}^{(1)})_i}{\mu_0} = \frac{\partial}{\partial t}\left(\epsilon_0\kappa_{ij}E^{(0)}_j + e^F_{ijk}u^{(0)}_{j,k}\right) , \tag{7.20}$$

$$\vec{\nabla}\cdot\vec{B}^{(1)} = 0 . \tag{7.21}$$

We note that $\vec{u}^{(1)}$ and $\vec{E}^{(1)}$ are uncoupled from other zero- or first-order solutions when $\vec{B}^{(0)}=0$, the usual case. Further we note that $\vec{B}^{(1)}$, whose variation is controlled by Eqs. (7.20) and (7.21), is driven only by the zero order $\vec{u}^{(0)}$ and $\vec{E}^{(0)}$ (or $\Phi^{(0)}$). For this reason the solutions $\vec{u}^{(0)}$, $\Phi^{(0)}$, and $\vec{B}^{(1)}$ are referred to as the quasielectrostatic solutions.

If we examine the differential equations governing the quasielectrostatic solutions, we find that the special properties of a pyroelectric crystal ($\vec{P}^S$ and $\vec{E}^S$) enter only in c^F_{ijkl}, given by Eq. (5.10), and in the piezoelectric coefficient e^F_{ijk}

given by Eq. (4.6). If $\vec{E}^S = 0$, all such special properties vanish. However, the complete solution requires a consideration of boundary conditions and these involve $\overleftrightarrow{t}^L$, $\vec{D}$, and $\vec{H}$ as well as $\vec{u}$, Φ, and $\vec{B}$. Thus we must examine $\overleftrightarrow{t}^L$, $\vec{D}$, and $\vec{H}$ from the quasielectrostatic viewpoint.

An examination of $\overleftrightarrow{t}^L$ in Eq. (6.2) and $\vec{D}$ in Eq. (4.9) shows that only fields of the same order are coupled by these constitutive relations. Hence, we need not write them again. We will consider their effects on quasielectrostatic solutions via boundary conditions in Sec. IX. Equation (4.10) for $\vec{H}$ needs closer examination. If we scale $\vec{H}$ to yield a field $\vec{\mathcal{H}}$ having the dimensions of $\vec{E}$,

$$\vec{\mathcal{H}} \equiv \mu_0 c \vec{H} , \tag{7.22}$$

and apply the above procedure, we find

$$\vec{H}^{(0)} = \vec{B}^{(0)}/\mu_0 , \tag{7.23}$$

$$\vec{H}^{(1)} = \vec{B}^{(1)}/\mu_0 - \vec{P}^S \times \frac{d\vec{u}^{(0)}}{dt} . \tag{7.24}$$

Equation (7.23) is seldom of interest, but Eq. (7.24) states that a first-order $\vec{H}$ field given in terms of $\vec{u}^{(0)}$ and $\vec{B}^{(1)}$, the latter of which depends on $\vec{u}^{(0)}$ and $\Phi^{(0)}$, exists and will possess an interesting dependence on $\vec{P}^S$.

VIII. CANCELLATION OF SPONTANEOUS ELECTRIC FIELD

The spontaneous electric field first entered this theory[1] in the definition of the natural state of the pyroelectric crystal and was left unrelated to the spontaneous polarization in the formulation. The reasons for this were twofold. First, when the spontaneous field exists, its magnitude and orientation depend on the shape of the crystal as well as on $\vec{P}^S$. Hence the relation cannot be specified until the particular geometry of a problem is known. Second, the spontaneous electric field may be cancelled by extrinsic charge attracted to the surfaces from the surrounding atmosphere or by charge flow from the small conductivity (volume and surface) of the crystal itself. Thus the spontaneous electric field exists only for a period of time, sometimes very short, following either a temperature change through the phase transition that creates the spontaneous moment or a reversal of the spontaneous moment in a ferroelectric by an applied electric field. Cancellation of the spontaneous field by extrinsic charge does not affect the spontaneous moment, it merely creates an equal and opposite extrinsic moment.

In order to determine how the free charge will distribute itself to cancel the spontaneous electric field, consider the expression[12] for the potential of a body possessing volume (q) and surface (Σ) charge densities as well as a polarization $\vec{P}$:

$$\Phi(\vec{z}) = \frac{1}{4\pi\epsilon_0} \int \frac{[q(\vec{z}\,') - \vec{\nabla}' \cdot \vec{P}(\vec{z}\,')]\,dv'}{|\vec{z} - \vec{z}\,'|} + \frac{1}{4\pi\epsilon_0} \int \frac{[\Sigma(\vec{z}\,') + \vec{N}\,' \cdot \vec{P}(\vec{z}\,')]\,ds'}{|\vec{z} - \vec{z}\,'|} . \tag{8.1}$$

Here $\vec{N}\,'$ is the unit outward surface normal. The free charge in the volume and on the surface will distribute in a way so as to cancel the electric field everywhere. Since this redistribution is a quasielectrostatic phenomenon, the electric field is simply the negative gradient of the potential. If it is to vanish for a body of *any size and shape*, the *integrands* of the volume and surface integrals in Eq. (8.1) must vanish. If we consider structurally homogeneous crystals as we do throughout this paper for simplicity, the only inhomogeneity in the polarization that can arise is from the effects of the spontaneous electric field back on the finite dimensioned crystals. Thus when the spontaneous electric field is cancelled by extrinsic charge, any polarization inhomogeneity vanishes and no volume distribution of charge is required. Hence

$$q^S = \vec{\nabla} \cdot \vec{P}^S = 0 , \tag{8.2}$$

$$\Sigma^S = -\vec{N} \cdot \vec{P}^S \tag{8.3}$$

when the spontaneous electric field has been cancelled by extrinsic charge.

IX. BOUNDARY CONDITIONS

In order to complete the characterization of linear elasticity and piezoelectricity in pyroelectrics we must obtain the linearized boundary conditions. Since pyroelectrics have spontaneous or constant parts of their electric field and electric displacement field, linear terms may arise in the boundary conditions from first order changes in the unit normal or area element of the boundary surface caused by the deformation of that surface. Thus we begin by linearizing the expressions for the unit normal and the area element.

We begin from Nanson's formula,[13]

$$da_i = J X_{P,i}\, dA_P , \tag{9.1}$$

that relates the oriented area element $d\vec{a}$ in the spatial (deformed) frame to the oriented area element of $d\vec{A}$ representing the same mass points in the material (undeformed) frame. If we introduce unit normals by

$$d\vec{a} = \vec{n}\, da , \quad d\vec{A} = \vec{N}\, dA , \tag{9.2}$$

then Nanson's formula leads to

$$n_i = X_{R,i} N_R (N_P X_{P,j} X_{Q,j} N_Q)^{-1/2} \tag{9.3}$$

and

$$da = J (N_P X_{P,j} X_{Q,j} N_Q)^{1/2}\, dA . \tag{9.4}$$

These may be linearized in terms of the gradient of the displacement vector defined by Eq. (2.8).

The results are

$$n_i \cong (\delta_{ri} - u_{r,i} + N_p u_{p,q} N_q \delta_{ri}) N_r \ , \qquad (9.5)$$

$$da \cong (1 + u_{p,p} - N_p u_{p,q} N_q)\, dA \ . \qquad (9.6)$$

The general electromagnetic boundary conditions were derived in the accompanying paper[14] at a surface that is deforming and moving locally at the velocity $d\vec{x}/dt$. The electric field boundary condition was found to be

$$\left[\vec{E} + \frac{d\vec{x}}{dt} \times \vec{B}\right] \times \vec{n} = 0 \ , \qquad (9.7)$$

where the brackets denote the jump in the enclosed quantity at the boundary. If a spontaneous electric field exists in the natural state, Eq. (9.7) becomes simply

$$[\vec{E}^S] \times \vec{N} = 0 \qquad (9.8)$$

in the natural state. Since the $d\vec{x}/dt \times \vec{B}$ term in the boundary condition is always nonlinear, it can be dropped when considering linear effects as we are doing here. The linear terms from Eq. (9.7) then are

$$(\vec{E}^o - \vec{E}) \times \vec{N} + (\vec{E}^{So} - \vec{E}^S) \times (\vec{n} - \vec{N}) = 0 \ , \qquad (9.9)$$

where o denotes outside fields and $\vec{n}$ is given by Eq. (9.5). We see that linear terms result from the existence of the spontaneous electric field.

The general electric displacement field boundary condition[14] is

$$[\vec{D}] \cdot \vec{n} = \sigma^f = \Sigma^f \frac{dA}{da} \ , \qquad (9.10)$$

where σ^f and Σ^f are the spatial and material frame surface charge densities that include both extrinsic mobile and immobile charge. We have already found in Sec. VIII that, if an extrinsic electric charge is allowed to collect on the surface of a pyroelectric, the spontaneous electric field will be cancelled out with the result

$$\Sigma^S = -\vec{N} \cdot \vec{P}^S \ , \qquad \vec{E}^{So} = \vec{E}^S = 0 \ . \qquad (9.11)$$

If no surface charge is allowed to collect on the surface, then Eq. (9.10) in the natural state is

$$(\epsilon_0 \vec{E}^{So} - \epsilon_0 \vec{E}^S - \vec{P}^S) \cdot \vec{N} = 0 \ . \qquad (9.12)$$

If we let the outside region be a vacuum, use the expression (4.9) for the inside linear $\vec{D}$ field, set $\Sigma^S = 0$, and subtract off from the general condition (9.10) the constant terms of the natural state condition (9.12), the result is

$$(\epsilon_0 E_i^o - \epsilon_0 \kappa_{ij} E_j - e^F_{ijk} u_{j,k}) N_i \, dA + \epsilon_0 (E_i^{So} - E_i^S)(n_i \, da - N_i \, dA) = \Sigma^c \, dA \ , \qquad (9.13)$$

where Σ^c denotes the mobile or conduction part of the surface charge. In practice either Σ^c or the spontaneous fields $\vec{E}^{So}$, $\vec{E}^S$ will be present in Eq. (9.13) but not both.

It is particularly important to note that the form of Eq. (9.13) has resulted because of the exact cancellation,

$$-2P^S_{[k}\delta_{i]j} u_{j,k} N_i \, dA - P_i^S (n_i \, da - N_i \, dA) = 0 \ , \qquad (9.14)$$

between the linear piezoelectriclike term involving $\vec{P}^S$ in the constitutive relation (4.9) for $\vec{D}$ and the constant spontaneous polarization term $\vec{P}^S$ in that relation multiplied by the linear changes in the deformed normal and deformed area element. This exact cancellation eliminates $\vec{P}^S$ from any explicit appearance in the boundary condition. Thus the term $-2P^S_{[k}\delta_{i]j} u_{j,k}$ that is present in the constitutive relation (4.9) for $\vec{D}$ has cancelled out of q^D, Eq. (4.5), $\vec{j}^D$, Eq. (4.4), and hence from the Maxwell differential equations and now has cancelled from the $\vec{D}$ field boundary condition. We are forced to conclude that a term in a constitutive relation is unobservable even though necessary! We say necessary because the effects that it cancels in the boundary condition (9.14)—the spontaneous polarization multiplied by changes in the unit normal and area element resulting from deformation—are real tangible effects. Thus the inclusion in this theory of both this constitutive term and the boundary deformation terms is necessary, correct, and consistent in spite of the final disappearance of linear terms involving $\vec{P}^S$. The Voigt theory included neither of these effects and so presented a correct interpretation only through the good fortune of compensating errors.

The general $\vec{H}$ field boundary condition[14] at a moving deforming surface is

$$\left(\vec{H} - \frac{d\vec{x}}{dt} \times \vec{D}\right) \times \vec{n} = \vec{k}^c \ , \qquad (9.15)$$

where $\vec{k}^c$ is a surface conduction current. In the derivation[14] of this boundary condition it was found that the convective-type surface current that results from the surface moving with an attached charge does not contribute to the boundary condition. Thus if an immobile extrinsic charge, Eq. (8.3), has collected to cancel the spontaneous electric field of a pyroelectric that charge which depends on $\vec{P}^S$ will not enter the boundary condition (9.15). The linear terms of this equation are

$$\left(\vec{H}^o - \vec{H} + \frac{d\vec{u}}{dt} \times \vec{P}^S - \epsilon_0 \frac{d\vec{u}}{dt} \times (\vec{E}^{So} - \vec{E}^S)\right) \times \vec{N} = \vec{k}^c \ . \qquad (9.16)$$

In practice either a surface conduction current $\vec{k}^c$ or the spontaneous electric fields will be present but not both. The explicit dependence of Eq. (9.16) on $\vec{P}^S$ is only apparent. Since $\vec{B}$ is the field found from Eqs. (7.20) and (7.21), the boundary condition (9.16) should be converted to a $\vec{B}$ field condition by substitution of the constitutive relation (4.10) for $\vec{H}$. The boundary condition (9.16) then becomes

$$\left(\frac{1}{\mu_0}(\vec{B}^o - \vec{B}) - \epsilon_0 \frac{d\vec{u}}{dt} \times (\vec{E}^{So} - \vec{E}^S)\right) \times \vec{N} = \vec{k}^c . \tag{9.17}$$

Once again all explicit dependence on $\vec{P}^S$ in linear terms has disappeared. This time a term in the $\vec{H}$ field constitutive relation (4.10) has been cancelled by a moving medium term in the boundary condition (9.15).

The general $\vec{B}$ field boundary condition[14] is

$$[\vec{B}] \cdot n = 0 . \tag{9.18}$$

To the linear level this is simply

$$(\vec{B}^0 - \vec{B}) \cdot \vec{N} = 0 . \tag{9.19}$$

The boundary condition on the total stress has been discussed in an accompanying paper.[8] For a moving deforming body surface it is

$$T_i + [t^B_{ij}] n_j = 0 , \tag{9.20}$$

where t^B_{ij} is defined in Eq. (2.26) and $\vec{T}$ is any traction applied to the surface between the two media. In Sec. VI we showed that to the linear level t^B_{ij} and t^L_{ij} of Eq. (2.23) are identical. The linearized expression is given in Eq. (6.2). The form of the spontaneous stress t^S_{ij} appearing in Eq. (6.2) was discussed in Sec. VI. For all cases except the infinite medium case a constant part of the total stress tensor of Eq. (6.2) results provided $\vec{E}^S \neq 0$ (see the infinite plate example of Sec. VI). This constant part can produce linear contributions in the boundary condition (9.20) by interacting with the linearly varying parts of $\vec{n}$ given in Eq. (9.5). We will not write out the resulting expansion of Eq. (9.20) because of its length.

X. ACOUSTIC PROPAGATION EQUATION

Consider acoustic plane wave propagation in a pyroelectric, piezoelectric crystal of any symmetry using the quasielectrostatic approximation of the questions. Let $\vec{s}$ denote a unit vector in the direction of propagation, the only direction in which there is a spatial variation of the plane wave. Thus

$$\frac{\partial}{\partial z_j} = s_j \frac{\partial}{\partial z} , \tag{10.1}$$

where z on the right-hand side is a scalar coordinate. Note that Eq. (10.1) in conjunction with Eq. (7.16) shows that $\vec{E}$ must be longitudinal, a well-known result. Substitution of this into Eq. (7.12) with the use of Eq. (7.16) yields

$$\frac{\partial^2 \Phi^{(0)}}{\partial z^2} = \frac{s_n e^F_{nkl} s_l}{\epsilon_0 s_p \kappa_{pq} s_q} \frac{\partial^2 u_k^{(0)}}{\partial z^2} . \tag{10.2}$$

This result along with Eq. (10.1) is now substituted into Eq. (7.11) to obtain

$$\rho^0 \frac{\partial^2 u_i^{(0)}}{\partial t^2} = \left(c^F_{ijkl} + \frac{s_m e^F_{mij} s_n e^F_{nkl}}{\epsilon_0 s_p \kappa_{pq} s_q} \right) s_j s_l \frac{\partial^2 u_k^{(0)}}{dz^2} , \tag{10.3}$$

which is the acoustic propagation equation. Since the velocity of propagation is related to components of the tensor enclosed in brackets, we see that acoustic velocity measurements are a way of measuring $\vec{E}^S$ within the volume of the crystal through the altered elastic constants c^F_{ijkl}, given in Eq. (5.10), and through the antisymmetric contribution, $\epsilon_0 \chi_{m[i} E^S_{j]}$, to the effective piezoelectric tensor. Note that if $\vec{E}^S = 0$ the equation takes the form appropriate to a nonpyroelectric, piezoelectric crystal.

XI. SUMMARY AND DISCUSSION

We have produced a complete theory of linear elasticity and piezoelectricity of pyroelectrics beginning from general nonlinear equations derived from a first-principles theory.[1] Our interest has been directed toward exploring the effects that the spontaneous polarization $\vec{P}^S$ and the resulting spontaneous electric field $\vec{E}^S$ may have on *linear* elastic and piezoelectric properties. Let us discuss the $\vec{P}^S$ effects first and the $\vec{E}^S$ effects second.

Our development first yielded piezoelectriclike terms in the polarization (4.1) linear in the displacement gradient that were also proportional to the constant $\vec{P}^S$. These same terms entered the expression (4.9) for the electric displacement vector $\vec{D}$. The origin of these terms was a combination of volume compression and rotation of a medium having a constant polarization, effects noted in the past by others.[15–17] None of these authors, however, showed that a portion of these effects must be included in the definition (4.3) of the normally measured piezoelectric stress tensor nor that the remainder of the terms in the linear polarization and dielectric displacement would not be measurable. We also showed that the constitutive relation (4.10) for $\vec{H}$ would involve a term linear in the velocity $d\vec{u}/dt$ and proportional to $\vec{P}^S$. Next we showed that the linear terms in $\vec{P}$, $\vec{D}$, and $\vec{H}$ involving $\vec{P}^S$ disappeared from the dielectric charge (4.5) and the dielectric current (4.4). This means that such terms disappear from the Maxwell equations *provided* $\vec{P}^S$ is homogeneous. When $\vec{P}^S$ is inhomogeneous, the terms exhibited in Eqs. (4.7) and (4.8) will enter the Maxwell equations. If sufficiently strong spatial derivatives of $\vec{P}^S$ occur in a medium, these equations give expressions for new observable effects involving these derivatives.

Even though the linear terms involving $\vec{P}^S$ disappeared from the differential equations (when $\vec{P}^S$

is homogeneous), it was necessary to consider the boundary conditions carefully since the constitutive expressions for $\vec{D}$ and $\vec{H}$ enter their respective boundary conditions. Initially[2] we believed that the $\vec{H}$ field boundary condition would bring in an observable linear term proportional to $\vec{P}^S$ thus making $\vec{P}^S$ measurable by a new dynamic technique. This resulted from our trust of the $\vec{H}$ field boundary condition derivation in Sommerfeld's textbook on electrodynamics.[18] Our later doubts about this derivation led us to an entirely new derivation of all the electromagnetic boundary conditions at a moving deforming surface by first transforming all the Maxwell equations to the material coordinate system.[14] The $\vec{H}$ field boundary condition we found from this approach, Eq. (9.15), contained a moving medium term which cancelled the constitutive term in $\vec{H}$ involving $\vec{P}^S$ making that term unobservable. The derivation also revealed the error in Sommerfeld's reasoning. It is discussed in the accompanying paper.[14] The $\vec{D}$ field boundary condition we found, Eq. (9.10), also led to a similar cancellation that is exhibited in Eq. (9.14). Here a combination of deformed normal and deformed surface area corrections in combination with the constant spontaneous polarization term of $\vec{D}$ exactly cancel the piezoelectriclike term involving $\vec{P}^S$ in the constitutive expression for $\vec{D}$. The tangibleness of the deformed normal and deformed surface area effects shows the reality and necessity of the constitutive term in $\vec{D}$ in spite of the latter's unobservability! Since none of these effects are included in the Voigt theory of piezoelectricity in pyroelectrics, the agreement of that theory with observations is partly due to the good fortune of having ignored two exactly cancelling phenomena.

It has been a tenet of piezoelectric theory from its earliest days[3] that the direct piezoelectric effect (measurement of a voltage caused by a stress) and the converse piezoelectric effect (measurement of a strain caused by a voltage) measure the same tensor. Our theory supports this equality but not the traditional proof of the equality. Traditionally the proof has been merely to note that the coefficient of the elastic variable in the constitutive expression for the linear polarization was the same tensor (apart from a sign convention) as the coefficient of the electric field in the constitutive expression for the linear stress tensor. In our theory (even when $\vec{E}^S = 0$) these coefficients are different. Nevertheless, our theory is consistent with the direct effect—converse effect equality since only a single piezoelectric tensor e_{ijk} enters all the differential equations and boundary conditions.

Recently Baumhauer and Tiersten[7] have considered a related problem to the one of this paper. They have considered the electroelastic equations for small fields superposed on a biasing field which creates a permanent polarization in a dielectric medium. They apply their results to polarized ferroelectric ceramics and conclude that the linearized equations (differential equations and boundary conditions) for such a material are identical with the equations of linear piezoelectricity. Our results are in agreement with theirs on this conclusion. Their work begins from the zeroth-order electrostatic approximation and so does not consider the $\vec{H}$ field. They also assume that extrinsic surface charge has cancelled the spontaneous electric field and so obtain no results for $\vec{E}^S \neq 0$. They perform most of their calculations in the material coordinate system and do not write any constitutive relations in the spatial or laboratory coordinate system. Thus there are no equations to compare to our spatial frame constitutive relations for $\vec{P}$, $\vec{D}$, $\vec{H}$, and $\overleftrightarrow{t}^L$.

Our theory makes new predictions for the linear elastic and piezoelectric tensors of a pyroelectric crystal when its spontaneous electric field is present. The elastic stiffness tensor c^F_{abcd} in the presence of $\vec{E}^S$ is given in Eq. (5.10). Its lower interchange symmetry compared to the stiffness tensor c_{abcd} that applies in the absence of $\vec{E}^S$ allows c^F_{abcd} to have 45 different components compared to 21 for c_{abcd}. In contrast to c_{abcd}, c^F_{abcd} can couple to rotation. The many new contributions to c^F_{abcd} depend on $\vec{E}^S$ and so will depend on the shape of the crystal which determines the depolarizing field. These contributions will disappear in a few dielectric relaxation times of the crystal plus ambience. The new terms depending on $\vec{E}^S$, however, are large and easily measurable. In materials like $LiNbO_3$, in fact, they can be larger than the normal terms in c_{abcd} which indicates that under such conditions nonlinear effects would also be present at the same time.

We also found that a new effective piezoelectric stress tensor e^F_{ijk}, given in Eq. (4.6), is present when $\vec{E}^S$ exists. The new term in it is antisymmetric with respect to interchange of the indices that couple to the displacement gradient. Thus, this term couples only to rotation while the normal term e_{ijk} couples only to strain. Again we find that the new term is measurably large but will depend on the shape of the crystal and the surface charge condition of the surfaces.

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APPENDIX

An alternate procedure to linearizing the equations of motion as done in this paper is to truncate the Lagrangian to linear, bilinear, and quadratic terms. This approach was used in Ref. 2.

Consider first the interaction Lagrangian in the material frame in the electric dipole approximation as given by Eq. (3.12) of Ref. 1:

$$\mathcal{L}_I^M = \sum_\nu{}' q^\nu \vec{y}^{T\nu} \cdot \vec{\mathcal{E}} = \sum_\nu{}' q^\nu R_{iA}(Y_A^\nu + \Lambda_A^\nu)\mathcal{E}_i \ . \quad \text{(A1)}$$

Adiabatic elimination of the internal coordinates via Eq. (3.4) yields

$$\mathcal{L}_I^M = [P_A^S + (e_{ACD} + \delta_{A(C} P_{D)}^S)E_{CD} + \epsilon_0 \chi_{AB} F_B](F_A + \delta_{iA} E_i^S) \ , \quad \text{(A2)}$$

with the use of Eqs. (2.6), (2.16), (3.2), (4.2), and (4.3). In Ref. 2 the notation

$$e'_{ACD} \equiv e_{ACD} + \delta_{A(C} P_{D)}^S \quad \text{(A3)}$$

was used. The constant term in Eq. (A2) may be dropped since it cannot affect the equations of motion. The matter Lagrangian in the material frame after adiabatic elimination of the internal coordinates is

$$\mathcal{L}_M^M = \tfrac{1}{2}\rho^0 \left(\frac{d\vec{x}}{dt}\right)^2 - \rho^0 \Sigma \quad \text{(A4)}$$

where

$$\rho^0\Sigma = t_{AB}^S E_{AB} + (e_{CAB} + \delta_{C(A} P_{B)}^S)E_{AB} + \tfrac{1}{2}c_{ABCD} E_{AB} E_{CD} + \epsilon_0 \chi_{AB} F_A \delta_{iB} E_i^S + \tfrac{1}{2}\epsilon_0 \chi_{AB} F_A F_B \ . \quad \text{(A5)}$$

The field Lagrangian in the spatial frame is

$$\mathcal{L}_F^S = \tfrac{1}{2}\epsilon_0(\vec{E}^2 - c^2\vec{B}^2) \ , \quad \text{(A6)}$$

where the fields $\vec{E}$ and $\vec{B}$ are regarded as functions of the scalar and vector potentials in the usual manner.

By combining Eqs. (A2)–(A6) the total Lagrangian is

$$L = \int \tfrac{1}{2}\epsilon_0(\vec{E}^2 - c^2\vec{B}^2)\, dv + \int \left[\frac{1}{2}\rho^0\left(\frac{d\vec{x}}{dt}\right)^2 - \tfrac{1}{2}c_{ABCD} E_{AB} E_{CD} - t_{AB}^S E_{AB} + (e_{ACD} + \delta_{A(C} P_{D)}^S)E_{CD} F_A + P_A^S F_A + \tfrac{1}{2}\epsilon_0 \chi_{AB} F_A F_B\right] dV \ . \quad \text{(A7)}$$

This was the starting point of the presentation in Ref. 2. There, since we considered the $\vec{E}^S = 0$ case only, we set $t_{AB}^S = 0$.

If E_{AB} and R_{iA} are expanded in terms of $u_{A,B}$ and F_A is eliminated via Eq. (3.2), then the total Lagrangian can be put into an alternative form most useful for obtaining the equations of motion:

$$L = \int \tfrac{1}{2}\epsilon_0(\vec{E}^2 - c^2\vec{B}^2)\, dv + \int \left[\frac{1}{2}\rho^0\left(\frac{d\vec{u}}{dt}\right)^2 - \tfrac{1}{2}c_{ABCD}^F u_{A,B} u_{C,D} + (E_{[A}^S P_{B]}^S - t_{AB}^S)u_{A,B} + (e_{ACD}\, \delta_{AC} P_D^S + \delta_{AD} P_C^S + \epsilon_0 E_{[A}^S \chi_{D]C})u_{C,D}\, \mathcal{E}_A + P_A^S \mathcal{E}_A + \tfrac{1}{2}\epsilon_0 \chi_{AB} \mathcal{E}_A \mathcal{E}_B\right] dV \ . \quad \text{(A8)}$$

Here c_{ABCD}^F is given by Eq. (5.10) and $\vec{\mathcal{E}}$ contains no spontaneous electric field part.

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