New Pyroelectric Contributions to Piezoelectricity

D. F. Nelson
Bell Laboratories, Murray Hill, New Jersey 07974

and

M. Lax
City College of the City University of New York, New York, New York 10031, and Bell Laboratories, Murray Hill, New Jersey 07974*

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We show that the Voigt constitutive equations, the traditional algebraic proof of the equality of the direct and converse piezoelectric effects, and the usual neglect of the magnetic field are incorrect in pyroelectrics. A measurement of $\vec{H}$ will yield a *new* piezoelectric tensor.

We present a summary of an *ab initio* linear theory of acoustic and piezoelectric effects in pyroelectrics, materials including ferroelectrics that possess a spontaneous electric moment. We find that there are several sizable indirect piezoelectric effects depending upon the spontaneous electric moment. These effects invalidate the Voigt constitutive relations[1] of linear piezoelectricity as applied to pyroelectrics and thus invalidate the usual algebraic proof[1] of the equality of direct and converse piezoelectric effects in these materials. A measurement of the usually ignored magnetic field $\vec{H}$ should *yield a new piezoelectric tensor* and so test our theory.

The effect of a spontaneous polarization on the constitutive relations of linear piezoelectricity has been considered many times. The conclusion that there is no effect has been reached often.[2] In another study[3] no dependence on the spontaneous polarization of the elastic stress, the dielectric current, or the electric displacement boundary condition was found, although a spontaneous polarization contribution to the linear polarization in agreement with ours was obtained.

Our procedure, which will be published in full elsewhere, resembles that previously applied to dielectrics.[4] In brief, we construct a microscopic, discrete particle Lagrangian consisting of parts arising from the vacuum electromagnetic field, the field-particle interaction, the particle kinetic energy, and the particle stored energy, the latter being required to satisfy invariance under displacements, rotations, and crystal group operations. Passage to the continuum limit is then made. The positions of the particles are expressed in terms of the c.m. position and a set of internal coordinates. The latter in certain combinations represent the ionic and electronic resonances in the infrared and ultraviolet regions. At microwave or lower frequencies of interest here they follow essentially without inertia. Thus the Lagrange equations for the internal coordinates with the inertial terms neglected can be used to eliminate the internal coordinates from the Lagrangian. Here, we discard terms which will contribute only nonlinear terms to the field or particle equations of motion. We also discard multipole terms higher than electric dipole. For simplicity here, we present results only for the case in which the spontaneous electric field is canceled out by collected surface charge. This elimination yields an effective Lagrangian

$$L=\tfrac{1}{2}\epsilon_0\int(\vec{E}^2-c^2\vec{B}^2)\,d^3z+\int(\tfrac{1}{2}\rho_0\dot{\vec{X}}^2-\tfrac{1}{2}c_{ABCD}E_{AB}E_{CD}+e_{ABC}{}'F_AE_{BC}+P_A{}^sF_A+\tfrac{1}{2}\epsilon_0\chi_{AB}F_AF_B)\,d^3X. \quad (1)$$

Here $\vec{x}$ ($\vec{X}$) is the c.m. position (designation) in the spatial (material) Cartesian coordinate system where components are designated in lower- (upper-) case subscripts. $\vec{z}$ spans the spatial or lab frame. Transformation[4] between the frames is done to obtain a Lagrangian density in a single system for the purposes of obtaining the equations of motion. The first two terms are the Lagrangian of the vacuum electromagnetic field. The electric field $\vec{E}$ and the magnetic induction field $\vec{B}$ are functions of the vector and scalar potentials, $\vec{A}$ and Φ, in the usual way: $\vec{E}\equiv-\nabla\Phi-\partial\vec{A}/\partial t$, $\vec{B}\equiv\nabla\times\vec{A}$. $\vec{A}$ and Φ are the Lagrangian variables for obtaining the electromagnetic field equations. The third term is the kinetic energy

of the center of mass, ρ_0 being the density of the undeformed crystal. The fourth term is the usual elasticity term, c_{ABCD} being the elastic stiffness tensor and E_{AB} being the Green measure of finite strain.[4] The fifth term is the direct piezoelectric term in that it will give the entire piezoelectric effect when the spontaneous polarization P^s vanishes. Here e_{ABC}' is the piezoelectric tensor and $F_A \equiv [E_i + (\dot{\vec{x}} \times \vec{B})_i] R_{iA}$, where R_{iA} is the finite rotation tensor.[4] The sixth term represents the contribution caused by the presence of a spontaneous polarization. The seventh term arises from the electrical polarizability of the crystal, χ_{AB} being the linear electric susceptibility. We employ mks units.

The electromagnetic field equations that result from the above effective Lagrangian are

$$\mu_0^{-1} \nabla \times \vec{B} - \epsilon_0 \partial \vec{E}/\partial t = \partial \vec{P}/\partial t + \nabla \times (\vec{P} \times \dot{\vec{x}}) \equiv \vec{j}, \quad (2)$$

$$\epsilon_0 \nabla \cdot \vec{E} = - \nabla \cdot \vec{P}, \quad (3)$$

where to the linear level

$$P_i = P_i^s + \epsilon_0 \chi_{ij} E_j + e_{ijk}^{(P)} u_{j,k},$$
$$e_{ijk}^{(P)} \equiv e_{ijk}' - P_i^s \delta_{jk} + \tfrac{1}{2}(\delta_{ij} P_k^s - \delta_{ik} P_j^s). \quad (4)$$

The indirect piezoelectric terms depending on $\vec{P}^s$ will be sizable in materials, e.g., $LiNbO_3$, in which P_i^s and e_{ijk}' are of comparable size. Here $\vec{u} \equiv \vec{x} - \vec{X}$ is the displacement vector, $u_{j,k} \equiv \partial u_j/\partial x_k$; $\vec{j}$, defined in (2), was referred to as the dielectric current previously. The other two electromagnetic field equations follow directly from the definitions of $\vec{E}$ and $\vec{B}$. Equations (2)–(4) reduce to the customary Maxwell equations if the electric displacement field $\vec{D}$ and the magnetic field $\vec{H}$ at the linear level are defined to be

$$D_i = P_i^s + \epsilon_0 \kappa_{ij} E_j + e_{ijk}^{(P)} u_{j,k}, \quad (5)$$

$$H_i = \mu_0^{-1} B_i - (\vec{P}^s \times \dot{\vec{u}})_i, \quad (6)$$

where κ_{ij} is the dielectric tensor. The c.m. (elasticity) equation that results from the Lagrangian is

$$\rho_0 \ddot{u}_i = c_{iljk} u_{j,kl} - e_{jil} E_{j,l} \equiv T_{il,l}, \quad (7)$$

$$e_{jil} \equiv e_{jil}' - \tfrac{1}{2}(\delta_{ji} P_l^s + \delta_{jl} P_i^s). \quad (8)$$

For acoustic wave propagation the electric field in (7) that is created by and carried along with the acoustic wave in a piezoelectric medium should be determined from the driven electric-field wave equation formed from (2) and the Maxwell equation $\nabla \times \vec{E} + \partial \vec{B}/\partial t = 0$:

$$c^2 \nabla \times (\nabla \times \vec{E}) + \partial^2 \vec{E}/\partial t^2 = - \epsilon_0^{-1} \partial \vec{j}/\partial t. \quad (9)$$

For plane waves this electric field is given to a high degree of accuracy as a longitudinal field of the form

$$E_j = - s_j s_k e_{kmn} u_{m,n} / \epsilon_0 \vec{s} \cdot \overleftrightarrow{\kappa} \cdot \vec{s}, \quad (10)$$

where $\vec{s}$ is a unit vector in the direction of the wave vector. Thus, from (7) and (10) we obtain

$$\rho_0 \ddot{u}_i = \left[c_{iljk} + \frac{e_{mil} s_m s_n e_{njk}}{\epsilon_0 s_a \kappa_{ab} s_b} \right] u_{j,kl}. \quad (11)$$

Thus, the piezoelectric stiffening of the elastic constants for plane-wave sound propagation involves e_{jil} of (8).

Consider next a static problem where $\vec{P}^s \times \dot{\vec{u}}$, which was important in (9), will be absent. A rectangular plate of arbitrary crystallographic orientation is subjected to static, uniform surface tractions on the two opposite large faces. Two opposite side surfaces are electroded; the two others are not; all four are traction free. For each surface our boundary conditions are of the form

$$T_{ij} n_j = F_i / \mathcal{A}, \quad (12)$$

$$(D_i^{\text{in}} - D_i^{\text{out}}) n_i = Q^T / \mathcal{A}, \quad (13)$$

$$[(\vec{E}^{\text{in}} - \vec{E}^{\text{out}}) \times \vec{n}]_i = 0, \quad (14)$$

where F_i is the applied surface traction (zero on the four side surfaces), $\mathcal{A}$ the *deformed* area of the side, and Q^T the total surface charge including both the deformation-induced charge and a constant collected charge, possibly on all surfaces depending on crystallographic orientation, to make null the spontaneous electric field. A geometric (not crystallographic) coordinate system is used with axes normal to the faces. The unit normal $\vec{n}$ to the *deformed* surface is related to the unit normal $\vec{N}$ of the undeformed surface to linear accuracy in the displacement gradient by

$$n_i = N_i - N_j u_{j,i} + N_i N_j u_{j,k} N_k. \quad (15)$$

The deformed area $\mathcal{A}$ is related to the undeformed area A to the linear level by

$$\mathcal{A} = A(1 + u_{j,j} - N_j u_{j,k} N_k). \quad (16)$$

Note that the linear terms in (15) and (16), which can include both strain and rotation, will produce via (13) further indirect contributions to the piezoelectric effect involving P^s. By combining (12)–(16) for each of the three pairs of faces we obtain the equation

$$Q = CV + dF, \quad (17)$$

where Q is the deformation induced charge on an electroded face. The voltage to first order is $V = w\vec{E}\cdot\vec{N}^e$, w is the separation of the electroded faces, $\vec{N}^e$ is the unit normal to the undeformed electroded face, and $F \equiv |\vec{F}|$ is the magnitude of the applied traction. The capacitance and effective piezoelectric coefficient are

$$C \equiv (\epsilon_0 A_e/w) N_i^e (\kappa_{in} + e_{ijk} s_{jklm} e_{nlm}/\epsilon_0) N_n^e, \quad (18)$$

$$d \equiv N_i^e e_{ijk} s_{jkmn} f_a N_b^f, \quad (19)$$

where $a \equiv \frac{1}{2}(m+n-|m-n|)$, $b \equiv \frac{1}{2}(m+n+|m-n|)$, and s_{jklm} is the compliance tensor. Here the unit vector in the direction of applied traction is $\vec{f} \equiv \vec{F}/F$; $\vec{N}^f$ is a unit normal to the undeformed surface to which the traction is then applied. Thus, static measurements of d or the low-frequency dielectric tensor in brackets in (18) will also yield e_{ijk} even though $\vec{P}^s \times \dot{\vec{u}}$ is not present in this static problem. The combination of the deformed surface normal and area (which do not enter time-of-flight or resonant-frequency measurements) have changed $e_{ijk}^{(P)}$ of (5), used in (13), into e_{ijk}.

Next consider a thickness-mode piezoelectric plate.[5] The component of $\vec{H}$ generated in the crystal parallel to the major plate surfaces is coupled outside the plate for thin electrodes because of continuity of tangential $\vec{H}$. This field can then be detected with a pickup coil. If $\vec{n}$ is a unit vector normal to the major plate surfaces, w the coordinate measured in this direction, and single frequency (ω) excitation is assumed, then (2) with (4) and (6) yields

$$H_i^{\text{tang}} = (-iv_A^2/\omega)\epsilon_{ijk} n_j (\partial/\partial\omega) \times [\epsilon_0 \kappa_{kl} E_l + e_{klm}^{(P)} n_m \partial u_l/\partial w], \quad (20)$$

where v_A is the velocity of the acoustic eigenmode excited. The solutions[5] for $\vec{E}$ and $\vec{u}$ must be substituted into (20). This is not needed for the point we wish to emphasize. Consider the simplest case: a principal direction of $\overleftrightarrow{\kappa}$ aligned with $\vec{n}$. Then $\overleftrightarrow{\kappa}\cdot\vec{E} \| \vec{n}$ and the $\overleftrightarrow{\kappa}\cdot\vec{E}$ term drops from (20). We then see that $\vec{H}^{\text{tang}}$ *measures a new piezoelectric tensor* $e_{klm}^{(P)}$*—different in symmetry and magnitude from* e_{ijk} *measured in conventional piezoelectric experiments.* Such would not be true under the old theory. $\vec{H}^{\text{tang}}$ is readily observable *at piezoelectric resonance:* In $LiNbO_3$, at a 2-MHz resonance with a Q of 10^3, a 2×2-cm^2 100-turn pickup coil oriented normal to the plate surface will detect about 0.1 V for 10 V applied to the plate. A comparison of the piezoelectric tensor measured via $\vec{H}^{\text{tang}}$ and e_{ijk} of (8) will *yield a bulk, dynamic measurement of* $\vec{P}^s$ for crystals in which extrinsic surface charge nulls out $\vec{E}^s$.

Equations (4)–(7) for $\vec{P}$, $\vec{D}$, $\vec{H}$, and $\overleftrightarrow{T}$ disagree with the traditional Voigt constitutive relations because of the presence of terms involving the spontaneous polarization $\vec{P}^s$. Such terms also enter the boundary condition on $\vec{D}$ through the deformed surface area and normal. The ratios of polarization to strain (4) and of stress to electric field in (7), the traditional definitions[1] of the direct and converse piezoelectric coefficients, are clearly unequal. Nevertheless, since the direct effect really measures the surface charge (20) or the dielectric current $\dot{\vec{j}}$ (2), and not just the polarization, both direct and converse effects will measure the same tensor (8). Also, we have shown that static and dynamic electrical measurements yield the same tensor even though a velocity dependent term (6) will contribute only to dynamic experiments.

In three of the indirect piezoelectric effects—those appearing in the polarization, the magnetic field $\vec{H}$, and the deformed normal—the displacement gradient can possess an antisymmetric part, that is, a rotation part as well as a strain part. In spite of the presence of these rotational effects we find, as expected, that they do not affect measurement of piezoelectric constants from acoustic wave velocity measurements, see (11), or from static measurements when the electrodes are attached to the crystal, see (22). However, the rotation part appears detectable by measuring $\vec{H}$.

Measurement of $\vec{H}$ in (20) will test our theory compared to the old theory. It should measure a new piezoelectric tensor of different symmetry and lead to a bulk dynamic measurement of $\vec{P}^s$.

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Interaction Barrier in Charged-Particle Nuclear Reactions*

C. Y. Wong

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Simple expressions are obtained for the total reaction cross section in terms of the interaction barrier for the s wave. These expressions allow the interaction barrier to be determined experimentally. Analysis of experimental data for heavy ions on ^{238}U shows that the effective radius parameter decreases as projectile charges increase.

In charged-particle nuclear reactions, it is of interest to measure the height of the barrier between the interacting nuclei. Such a measurement provides information on the fusion process,[1] which is an important intermediate step in the production of superheavy nuclei by heavy-ion reactions. It may also facilitate the study of distortion effects[2-6] and of the dependence of the barrier height on the charges and shapes of the interacting nuclei.[7]

It is known that the probability of penetration is one-half at the top of an inverted harmonic-oscillator potential. It is therefore convenient to define the interaction barrier for the lth partial wave as the energy E_l at which the absorption probability $P(E_l, l)$ is one-half. While such a definition is model independent, it assumes a simple physical meaning in the ingoing-wave strong-absorption model[8] with parabolic barriers.

With such a definition, the barriers can be readily obtained by analyzing the elastic scattering or reaction cross-section data with an optical model or by parametrizing the phase shifts. For a given incident energy E, one finds the value of l_b for which the absorption probability is given by $1-|\eta_{l_b}|^2=\frac{1}{2}$. It can then be said that the interaction barrier for the l_bth partial wave is the incident energy E. If data are available for different energies, the interaction barrier for various values of l can be obtained.

Of particular interest is the interaction barrier for the s wave which is traditionally called the "Coulomb barrier." We wish to present in this article another way to measure this barrier by employing a simple analytic expression for the total reaction cross section obtained in the ingoing-wave strong-absorption model.

We shall consider first two spherical nuclei and the case of no dynamical distortion. Following Thomas,[9] Huizenga and Igo,[10] and Rasmussen and Sugawara-Tanabe,[11] we approximate the various barriers for different partial waves by inverted harmonic-oscillator potentials of height E_l and frequency ω_l. For an energy E, the probability $P(l, E)$ for the absorption of the lth partial wave is then given by the Hill-Wheeler formula[12]

$$P(l,E)=\{1+\exp[2\pi(E_l-E)/\hbar\omega_l]\}^{-1}. \tag{1}$$

In consequence, the total reaction cross section is

$$\sigma_r(E)=\frac{\pi}{k^2}\sum_l\frac{2l+1}{1+\exp[2\pi(E_l-E)/\hbar\omega]}. \tag{2}$$

Instead of parametrizing the nuclear interaction in the form of a diffused potential well, as is done in Refs. 9–11, we wish to write E_l and $\hbar\omega_l$ as a function of l directly so that the interaction barrier E_0 enters explicitly. This can be done using a diffuse potential as a guide. The effective potential for the reaction is

$$V(r)=-V_0/\{1+\exp[(r-\mathcal{R}_1-\mathcal{R}_2)/a]\}$$
$$+Z_1Z_2e^2/r+\hbar^2l(l+1)/2\mu r^2, \tag{3}$$

where $\mathcal{R}_1$ and $\mathcal{R}_2$ are the potential radii and μ is the reduced mass. The interaction barrier for the lth partial wave is just

$$E_l=V(R_l), \tag{4}$$

where the radial separation R_l is obtained from the condition

$$[dV(r)/dr]_{R_l}=0. \tag{5}$$