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Piezoelectric and pyroelectric coefficients for ferroelectric crystals with polarizable molecules

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Expressions for piezoelectric and pyroelectric coefficients for a crystal of polarizable point dipoles are derived. The effect of crystal structure on the local electric field acting to polarize the molecules is included via the Lorentz-factor formalism. The derived expressions for the piezo- and pyroelectric coefficients are found to contain terms dependent on derivatives of the Lorentz factors. These terms reflect the changing of molecular dipole moments in response to the changing local electric field in the strained crystal. Inclusion of this effect results in predictions of coefficients substantially different from those obtained using the Lorentz field approximation.

I. INTRODUCTION

The internal electric field acting on a molecule in a crystal of dipoles depends on the crystal structure[1–3] and changes when the crystal is strained.[1,2] If the molecular dipoles are polarizable, the polarization of the crystal will depend on the internal field and therefore on the crystal structure. Furthermore, changes of the internal field due to small deformations of the crystal such as those expected in piezoelectric and pyroelectric response measurements will contribute to the measured changes in sample polarization.

In this paper expressions for device-measured[4] piezoelectric and pyroelectric coefficients are developed for a model system which is a single crystal composed of polarizable point dipoles with permanent electric dipole moments. The effect of crystal structure on the electric fields acting to polarize the dipoles is included by revising the Clausius-Mossotti relation according to the Lorentz tensor formalism.[1,2] The revised relation is then employed to obtain an expression relating sample polarization to the permanent dipole moments and the crystal geometry. This, in effect, revises the "enhancement" factor of $(\kappa+2)/3$ familiar from classical theory. Appropriate derivatives of sample polarization are taken to obtain expressions for piezoelectric and pyroelectric coefficients.

II. MODEL SYSTEM

The system to be considered is a uniformly polarized single crystal of dielectric constant κ with an orthorhombic lattice and in the shape of a thin slab. The faces of the slab are presumed oriented along the lattice directions, as illustrated in Fig. 1. The molecules at the lattice sites are treated as point dipoles with permanent moments p_0 in the $\hat{z}$ direction, and with polarizability α. Sample dimensions are X,Y,Z in the three coordinate directions. Lattice constants are taken to be c,a,b in $\hat{x},\hat{y},\hat{z}$, respectively. The sample is presumed to have electrodes applied to its large-area faces so that the applied field is in $\hat{z}$.

The electric field acting on a molecule in the lattice can be written[1–3]

$$\vec{E}_{\rm loc}=\vec{E}_{\rm med}+\tilde{L}\cdot\vec{P}\ , \tag{1}$$

where $\vec{E}_{\rm med}$ is the macroscopic electric field in the medium, $\vec{P}$ is the polarization, and $\tilde{L}$ is the Lorentz tensor which depends on the lattice geometry. For the case of general orthorhombic lattices (including body- and base-centered), $\tilde{L}$ is diagonal. With the geometry specified in Fig. 1, the vector notation may be suppressed, because $\vec{P}$ and $\vec{E}_{\rm med}$ are in the $\hat{z}$

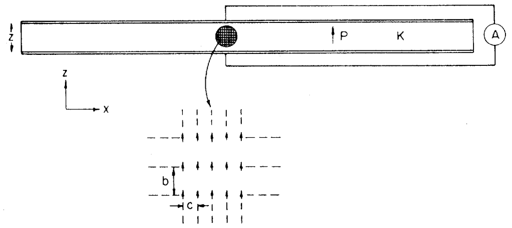

FIG. 1. Model system geometry: macroscopic and microscopic views.

direction. If the lattice is cubic, each of the three diagonal elements of $\tilde{L}$ is equal to $\frac{1}{3}$, and Eq. (1) gives the well-known Lorentz field.

Now, the dipole moment p of a molecule in the lattice is given by

$$p=p_0+\alpha E_{\text{loc}} , \tag{2}$$

and if n is the number of dipoles per unit volume, the polarization of the sample is

$$P=P_0+n\alpha E_{\text{loc}}=P_0+n\alpha\left[E_{\text{med}}+\frac{LP}{\epsilon_0}\right] , \tag{3}$$

where $P=np$ and $P_0=np_0$. In previous work,[1,2] a relationship between α and the dielectric constant κ was found for the case in which $p_0=0$. This relation,

$$n\alpha=\frac{\epsilon_0(\kappa-1)}{[1+L(\kappa-1)]} , \tag{4}$$

was then inserted into the equivalent of Eq. (3) to relate P and P_0 for zero macroscopic field ($E_{\text{med}}=0$). It is useful to rederive Eq. (4) for the present case because it serves to clarify the assumptions and to identify κ as the high-frequency (electronic) dielectric constant, which is often referred to as the clamped dielectric constant in discussions of piezoelectricity.[5]

To do this, consider the way in which the dielectric constant is determined experimentally, by placing a sample between electrodes and measuring the capacitance as the voltage V on the plates varies near $E_{\text{med}}=0$. That is, one measures

$$C=\left.\frac{dQ}{dV}\right|_{E_{\text{med}}=0} , \tag{5a}$$

$$E_{\text{med}}=\frac{V}{Z} , \tag{5b}$$

with Q the charge on the electrodes and Z the thickness of the sample. For the configuration of Fig. 1, the capacitance is just

$$C=\frac{\epsilon_0\kappa A}{Z} , \tag{6}$$

with $A=XY$ the sample area. The electric displacement is given by

$$\frac{Q}{A}=\epsilon_0 E_{\text{med}}+P ,$$

so

$$Q=\epsilon_0 A E_{\text{med}}+AP . \tag{7}$$

A relation among P, E_{med}, and κ can be obtained by differentiation of Eq. (7) and substitution into Eq. (5a), using Eqs. (5b) and (6). However, the simple expression required to give Eq. (4) can only be obtained if this is done with A and Z held fixed. Thus, the dielectric constant appearing in the relation must be the high-frequency (electronic or clamped) one. With A and Z fixed, one finds

$$\left[\frac{\partial P}{\partial E_{\text{med}}}\right]_{A,Z}=\epsilon_0(\kappa-1) . \tag{8}$$

A second expression for $\partial P/\partial E_{\text{med}}$ may be found by differentiating Eq. (3). If A and Z are fixed, so are L and n, whence

$$\left[\frac{\partial P}{\partial E_{\text{med}}}\right]_{L,n}=\frac{n\alpha}{(1-n\alpha L/\epsilon_0)} . \tag{9}$$

Equating the expressions for $\partial P/\partial E_{\text{med}}$ in (8) and (9) returns Eq. (4), i.e.,

$$n\alpha=\frac{\epsilon_0(\kappa-1)}{[1+L(\kappa-1)]} .$$

Substitution of this into Eq. (3), and setting $E_{\text{med}}=0$ (for example, by shorting the electrodes) returns

$$P=[1+L(\kappa-1)]np_0=[1+L(\kappa-1)]Np_0\Omega^{-1} , \tag{10}$$

where N is the number of dipoles in the sample and Ω is its volume ($\Omega=XYZ$). The total dipole moment $\mathscr{P}$ of the sample is then

$$\mathscr{P}=\Omega P=[1+L(\kappa-1)]Np_0 . \tag{11}$$

III. PIEZOELECTRIC COEFFICIENTS

The device-measured piezoelectric coefficients d_{3i} of the system in Fig. 1 are given by[4]

$$d_{3i}=\frac{1}{R_i}\left[\left[\frac{\partial\mathscr{P}}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}-\mathscr{P}\left[\frac{\partial \ln Z}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}\right] , \tag{12}$$

where $R_i=X,Y,Z$ for $i=1,2,3$, respectively, and g_i are the device-measured forces in the $\hat{x},\hat{y},\hat{z}$ (1,2,3, respectively) directions. The g_i can be related to effective stresses σ_i by defining cross-sectional areas A_i from $A_i=\Omega(R_i)^{-1}$. In this case $\sigma_i=g_i(A_i)^{-1}$.

The subscripts on the derivatives in Eq. (12) indicate that temperature (T) and voltage (V) are held constant, and force is applied in only one direction.

The sample dipole moment $\mathscr{P}$ is given by Eq. (11). If we assume that N and p_0 are fixed, the derivative of $\mathscr{P}$ in Eq. (12) becomes

$$\left[\frac{\partial \mathscr{P}}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}=(\kappa-1)Np_0\left[\frac{\partial L}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}+LNp_0\left[\frac{\partial \kappa}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}. \tag{13}$$

Equation (4) provides a relation between κ and L which may be written

$$\Omega\epsilon_0(\kappa-1)=N\alpha[1+L(\kappa-1)]\ .$$

Differentiation with respect to g_i, with N and α fixed and rearrangement, yields

$$\left[\frac{\partial \kappa}{\partial g_i}\right]=(\kappa-1)^2\left[\frac{\partial L}{\partial g_i}\right]-(\kappa-1)[1+L(\kappa-1)]\times\left[\frac{\partial \ln\Omega}{\partial g_i}\right]. \tag{14}$$

Evaluation of the derivative of L proceeds by observing that L depends only on the lattice geometry so that, with temperature and voltage fixed, and $g_{j(\neq i)}=0$, then L can depend on g_i only through changes in the lattice geometry resulting from g_i. Thus

$$\left[\frac{\partial L}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}=\left[\left[\frac{\partial L}{\partial \ln a}\right]_{b,c,\vec{f}}\left[\frac{\partial \ln a}{\partial g_i}\right]_{b,c,\vec{f}}+\left[\frac{\partial L}{\partial \ln b}\right]_{a,c,\vec{f}}\left[\frac{\partial \ln b}{\partial g_i}\right]_{a,c,\vec{f}}+\left[\frac{\partial L}{\partial \ln c}\right]_{a,b,\vec{f}}\left[\frac{\partial \ln c}{\partial g_i}\right]_{a,b,\vec{f}}\right]_{T,V,g_{j(\neq i)}=0}, \tag{15}$$

where $\vec{f}=(x/c,y/a,z/b)$, the position in the unit cell normalized to cell dimensions,[1,2] and where use has been made of the fact that the number of unit cells remains constant, i.e., the change in sample volume is due to changes in unit-cell dimensions. Thus

$$\left[\frac{\partial \ln X}{\partial g_i}\right]_{Y,Z}=\left[\frac{\partial \ln c}{\partial g_i}\right]_{a,b,\vec{f}},$$

$$\left[\frac{\partial \ln Y}{\partial g_i}\right]_{X,Z}=\left[\frac{\partial \ln a}{\partial g_i}\right]_{c,b,\vec{f}},$$

$$\left[\frac{\partial \ln Z}{\partial g_i}\right]_{X,Y}=\left[\frac{\partial \ln b}{\partial g_i}\right]_{a,c,\vec{f}}.$$

These logarithmic derivatives of the sample or lattice dimensions with respect to the force components can be related to elastic compliances s_{ij}. The latter are defined from

$$\left[\frac{\partial \ln R_j}{\partial \sigma_i}\right]_{T,V,\sigma_{j(\neq i)}=0}=s_{ji}\ ,$$

with σ_i the stress components, which are related to the g_i by $\sigma_i=g_i(A_i)^{-1}$. Near $g_i=0$,

$$\left[\frac{\partial \sigma_i}{\partial g_i}\right]_{T,V,\vec{g}=0}=A_i^{-1}=\frac{R_i}{\Omega}\ ,$$

so that

$$\left[\frac{\partial \ln R_j}{\partial g_i}\right]_{T,V,\vec{g}=0}=\frac{R_i}{\Omega}s_{ji}\ .$$

Thus, Eq. (15) can be written as follows:

$$\left[\frac{\partial L}{\partial g_i}\right]_{T,V,\vec{g}_{j(\neq i)}=0}=\frac{R_i}{\Omega}\left[\left[\frac{\partial L}{\partial \ln a}\right]_{b,c,\vec{f}} s_{yi}+\left[\frac{\partial L}{\partial \ln b}\right]_{a,c,\vec{f}} s_{zi}+\left[\frac{\partial L}{\partial \ln c}\right]_{a,b,\vec{f}} s_{xi}\right]_{T,V,g_{j(\neq i)}=0} . \tag{16}$$

The remaining differentials to be evaluated are simply various elastic compliances,

$$\left[\frac{\partial \ln \Omega}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}=\frac{R_i}{\Omega}(s_{xi}+s_{yi}+s_{zi}) , \tag{17a}$$

$$\left[\frac{\partial \ln Z}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}=\frac{R_i}{\Omega}s_{zi} . \tag{17b}$$

Equations (14), (16), and (17a) may now be substituted into Eq. (13) to obtain for the derivative of the sample dipole moment,

$$\left[\frac{\partial \mathscr{P}}{\partial g_i}\right]_{T,V,g_{j(\neq i)}=0}=\frac{R_i\mathscr{P}}{\Omega}\left\{(\kappa-1)\left[\left[\frac{\partial L}{\partial \ln a}\right]_{b,c,\vec{f}} s_{yi}+\left[\frac{\partial L}{\partial \ln b}\right]_{a,c,\vec{f}} s_{zi}+\left[\frac{\partial L}{\partial \ln c}\right]_{a,b,\vec{f}} s_{xi}\right]_{T,V,g_{j(\neq i)}=0} - L(\kappa-1)(s_{xi}+s_{yi}+s_{zi})\right\} . \tag{18}$$

Then, with Eq. (17b), the expressions for the piezoelectric coefficients [Eq. (12)] become

$$d_{3i}=P\left\{(\kappa-1)\left[\left[\frac{\partial L}{\partial \ln a}-L\right]s_{yi}+\left[\frac{\partial L}{\partial \ln b}-L\right]s_{zi}+\left[\frac{\partial L}{\partial \ln c}-L\right]s_{xi}\right]-s_{zi}\right\} , \tag{19}$$

where P is the sample polarization, and the subscripts on the derivatives have been suppressed for notational simplicity.

A similar expression for the hydrostatic piezoelectric coefficient of the model system can be obtained by either of two approaches. One is to observe that

$$d_h=\sum_i d_{3i} ,$$

and to add the three coefficients. The other is to write

$$d_h=-\Omega^{-1}\left[\left[\frac{\partial \mathscr{P}}{\partial \mathscr{p}}\right]_{T,V}-\mathscr{P}\left[\frac{d\ln Z}{\partial \mathscr{p}}\right]_{T,V}\right] , \tag{20}$$

with $\mathscr{p}$ the hydrostatic pressure, which is the negative of the stress in each direction, i.e., $\sigma_x=\sigma_y=\sigma_z=-\mathscr{p}$ for the hydrostatic case. Evaluation of Eq. (20) leads to

$$d_h=P\left\{(\kappa-1)\left[\left[\frac{\partial L}{\partial \ln a}-L\right]\beta_y+\left[\frac{\partial L}{\partial \ln b}-L\right]\beta_z+\left[\frac{\partial L}{\partial \ln c}-L\right]\beta_x\right]-\beta_z\right\} , \tag{21}$$

where the β_i are coefficients of linear compressibility for zero applied field, defined by

$$\left[\frac{\partial \ln R_i}{\partial \mathscr{p}}\right]_{R_{j(\neq i)},T,V}=-\beta_i ,$$

and the fact that $[(\partial \ln a)/(\partial \mathscr{p})]_{b,c,\vec{f}}=[(\partial \ln Y)/(\partial \mathscr{p})]_{X,Z}$, etc. has been used. Evidently $\beta_x+\beta_y+\beta_z=\beta$, the volume compressibility of the crystal. The β_i are related to the elastic compliances by

$$\beta_i=\sum_j s_{ij} .$$

IV. PYROELECTRIC COEFFICIENT

The device-measured pyroelectric coefficient Π is defined from[4]

$$\Pi=\Omega^{-1}\left[\left[\frac{\partial\mathscr{P}}{\partial T}\right]_{\vec{g},V=0}-\mathscr{P}\left[\frac{\partial\ln Z}{\partial T}\right]_{\vec{g},V=0}\right]. \tag{22}$$

The temperature derivative of $\mathscr{P}$ can be evaluated in the same manner as were the force and pressure derivatives to obtain

$$\left[\frac{\partial\mathscr{P}}{\partial T}\right]_{\vec{g},V=0}=\mathscr{P}\left\{(\kappa-1)\left[\left[\frac{\partial L}{\partial\ln a}\right]_{b,c,\vec{f}}\alpha_y+\left[\frac{\partial L}{\partial\ln b}\right]_{b,c,\vec{f}}\alpha_z+\left[\frac{\partial L}{\partial\ln c}\right]_{a,b,\vec{f}}\alpha_x\right]\right.$$
$$\left.-L(\kappa-1)(\alpha_x+\alpha_y+\alpha_z)\right\}, \tag{23}$$

where α_i are coefficients of linear thermal expansion at zero field, defined by

$$\left[\frac{\partial\ln R_i}{\partial T}\right]_{R_{j(\neq i)},V=0}=\alpha_i .$$

This yields for Π,

$$\Pi=P\left\{(\kappa-1)\left[\left[\frac{\partial L}{\partial\ln a}-L\right]\alpha_y+\left[\frac{\partial L}{\partial\ln b}-L\right]\alpha_z+\left[\frac{\partial L}{\partial\ln c}-L\right]\alpha_x\right]-\alpha_z\right\}. \tag{24}$$

V. DISCUSSION

The essentially new terms in the expressions in Eqs. (19), (21), and (24) for the piezoelectric and pyroelectric coefficients are those involving the derivatives of the Lorentz factor. Physically, these terms arise because, when the lattice is strained, the internal electric field changes. This change in field causes a change in the molecular dipole moments which results in a change in the polarization, because the molecules are polarizable. These terms should contribute to changes in P even for cubic lattices, because the derivatives of the Lorentz factors are nonzero for such lattices.

If the material is highly isotropic the terms containing the derivatives of the Lorentz factors will sum to zero in consequence of a sum rule for the derivatives.[1,2] This will occur in the case of the pyroelectric coefficient Π if thermal expansion is isotropic, i.e., if $\alpha_x=\alpha_y=\alpha_z$, and in the case of the hydrostatic piezoelectric coefficient d_h if $\beta_x=\beta_y=\beta_z$. It will not occur for the piezoelectric coefficients for uniaxial stress, d_{3i}, unless $s_{xi}=s_{yi}=s_{zi}$, which seems most unlikely, as this implies a material which expands uniformly under uniaxial stress. Normally, one expects materials to expand in the stress direction and contract in the two perpendicular directions. Only in rare circumstances will the Poisson ratios be negative,[6] and even then are unlikely to be such as to cause complete cancellation.

The influence of the new terms on predicted piezoelectric reponse can be examined by comparing the coefficients computed using (19) and (21) with those which would have been obtained using the Lorentz field approximation, i.e., with $L=\frac{1}{3}$ and $dL=0$, for specific assumptions on the s_{ij}. Consider the case of a crystal for which s_{xx}, s_{yy}, and s_{zz} are positive and $s_{ij}=0$ for $i\neq j$. If the crystal is mechanicaly isotropic, i.e., if $s_{xx}=s_{yy}=s_{zz}$, and cubic, Eq. (21) for d_h will give the same result as the Lorentz field calculation because the derivative terms will sum to zero.

For the general crystal having $s_{ij}=0$ for $i\neq j$, Eq. (19) yields

$$d_{31}=P(\kappa-1)s_{xx}\left[\frac{\partial L}{\partial\ln c}-L\right],$$

$$d_{32}=P(\kappa-1)s_{yy}\left[\frac{\partial L}{\partial\ln a}-L\right], \tag{25a}$$

$$d_{33}=Ps_{zz}\left[(\kappa-1)\left[\frac{\partial L}{\partial\ln b}-L\right]-1\right],$$

where, in the subscripts on d, the indices 1,2,3 are associated with x,y,z, respectively, which is the usual way of describing the piezoelectric coefficients.

Throughout this section the vector quantities have been assumed to have nonzero components only in the $\hat{z}$ (or 3) direction, which is associated with lattice spacing b. Therefore the L appearing in all the equations is L_b. Then, if the lattice structure is simple orthorhombic, it can be shown that[1,2]

$$\frac{\partial L_b}{\partial \ln c} - L_b > 0 \, ,$$

$$\frac{\partial L_b}{\partial \ln a} - L_b > 0 \, ,$$

$$\frac{\partial L_b}{\partial \ln b} - L_b < 0 \, ,$$

so that Eq. (25a) implies d_{31} and d_{32} are positive and d_{33} is negative for such lattices for any choice of a,b,c. This will not necessarily be true for more complex lattices, e.g., body- or base-centered orthorhombic. If the lattice is simple cubic, we have[1,2]

$$\frac{\partial L_b}{\partial \ln c} = \frac{\partial L_b}{\partial \ln a} = 0.505$$

and $\partial L_b / \partial \ln b = -1.01$, so Eq. (25a) becomes, for this case,

$$\begin{aligned} d_{31}^{C} &= P^{C}(\kappa - 1) s_{xx} (0.505 - 0.333) > 0 \, , \\ d_{32}^{C} &= P^{C}(\kappa - 1) s_{yy} (0.505 - 0.333) > 0 \, , \\ d_{33}^{C} &= -P^{C} s_{zz} [(\kappa - 1)(1.01 + 0.333) + 1] < 0 \, . \end{aligned} \tag{25b}$$

The predicted values of the coefficients which would have been obtained using $L = \frac{1}{3}$, $dL = 0$ are

$$\begin{aligned} d_{31}^{\mathrm{LF}} &= -P^{C} \frac{(\kappa - 1)}{3} s_{xx} < 0 \, , \\ d_{32}^{\mathrm{LF}} &= -P^{C} \frac{(\kappa - 1)}{3} s_{yy} < 0 \, , \\ d_{33}^{\mathrm{LF}} &= -P^{C} \frac{(\kappa + 2)}{3} s_{yy} < 0 \, , \end{aligned} \tag{25c}$$

where the superscript C on P in Eqs. (25b) and (25c) indicates that $L = \frac{1}{3}$ is used in relating P to P_0. Note that all three coefficients are negative in the Lorentz field (LF) case, whereas only d_{33} is negative in Eq. (25b). Thus, even if $s_{xx} = s_{yy} = s_{zz}$, the predictions for the two theories would be different.

For the case under consideration, (i.e., $s_{ij} = 0$, $i \neq j$), $\beta_i = s_{ii}$ and Eq. (21) yields for the hydrostatic piezoelectric coefficient,

$$\begin{aligned} d_h = P \Bigg\{ (\kappa - 1) \Bigg[& \left[\frac{\partial L}{\partial \ln c} - L \right] \beta_x \\ & + \left[\frac{\partial L}{\partial \ln a} - L \right] \beta_y \\ & + \left[\frac{\partial L}{\partial \ln b} - L \right] \beta_z \Bigg] - \beta_z \Bigg\} \, , \end{aligned} \tag{26a}$$

which becomes, for the simple cubic lattice,

$$\begin{aligned} d_h^{C} = P^{C} \{ & (\kappa - 1) [(0.505 - 0.333)(\beta_x + \beta_y) \\ & - (1.01 + 0.333) \beta_z] - \beta_z \} \, , \end{aligned} \tag{26b}$$

which may be either positive or negative depending on the relative magnitudes of the β_i and the value of κ. In the special case of isotropic compression, i.e., for $\beta_x = \beta_y = \beta_z = \beta_0$, one finds

$$d_h^{I} = -P\beta_0 [3L(\kappa - 1) + 1] \, ,$$

from which $d_h^{\mathrm{CI}} = -P^{C} \kappa \beta_0$ for the isotropic cubic case. The Lorentz field calculation would have given

$$d_h^{\mathrm{LF}} = -P^{C} \left[\left[\frac{\kappa - 1}{3} \right] (\beta_x + \beta_y + \beta_z) + \beta_z \right] \, , \tag{26c}$$

which is always negative. For the isotropic case this gives $d_h^{\mathrm{LFI}} = -P^{C} \kappa \beta$, so that in this very special case the predictions of the two theories coincide.

In a similar fashion the pyroelectric coefficient calculated by the present method reduces to that found using the Lorentz field approximation only in the special case of a thermally isotropic cubic crystal. This is not surprising, given the assumption inherent in the Lorentz field approximation, but is notable because it points out the implications of these assumptions.

VI. CONCLUSION

Inclusion of the dependence of the internal electric field on crystal structure in computing piezoelectric and pyroelectric coefficients for the model crystal system has resulted in the appearance of new terms in the expressions for the coefficients. These reflect the changing of molecular dipole moments in response to the changing internal field in the strained crystal. They appear because the point dipoles representing the molecules are polarizable as well as having permanent moments. Comparison of present results to those obtained using the Lorentz field approximation indicates that the predictions of the two models will be very different in general, even for cubic crystals.

While the accuracy of modeling real molecules as point dipoles may be questioned, the importance of including the influence of the fields due to neighboring molecules on each other is brought out clearly in the calculation. Evidently it is an important effect to include in modeling piezoelectric and pyroelectric response.

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