Theory of piezoelectricity, electrostriction, and pyroelectricity in molecular crystals

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A microscopic theory is presented for piezoelectricity, electrostriction, and pyroelectricity in molecular crystals. The required coefficients are derived by combining a theoretical treatment of the dependence of molecular dipole moments on molecular displacement and a generalized elastic theory for internal strain. © 2010 American Institute of Physics. [doi:10.1063/1.3340405]

I. INTRODUCTION

Piezoelectricity concerns the dependence of the dimensions of a material on electric field or of the electric polarization in the material on stress. Because electric polarization and applied electric field are related through the electric susceptibility while strain and applied stress are related through the elastic constants, there are various cognate and inverse piezoelectric effects, all of which also depend on the mechanical, electrical, and thermal boundary conditions. Ordinary linear piezoelectricity is restricted to 20 of the 32 crystal classes, including all those that lack a center of symmetry except for the class 432 where the other symmetry elements preclude piezoelectricity, but the corresponding quadratic effect electrostriction is nonzero under any symmetry. Piezoelectric materials that belong to the ten polar crystal classes also show pyroelectricity, i.e. a dependence of the electric polarization on temperature or of the entropy on electric field.

Piezoelectricity is of importance in its own right for various practical applications such as transducers and actuators. It is also a phenomenon that must be taken into account in electrical or elastic measurements on piezoelectric materials. This is particularly clear in quadratic nonlinear optical response, which is restricted to materials with a symmetry that must also admit piezoelectricity. As a result, for some molecular crystals the quadratic nonlinear optical response and the piezoelectric properties have both been reported. One example is 3-nitroaniline (mNA), a simple prototypical molecule for nonlinear optical response. Another example is the well-studied crystal of 3-methyl-4-nitroaniline (MNA) where the dearth of microscopic treatments of piezoelectricity at the time was noted. A third example is 2-furyl methacrylic anhydride, where it was noted that the piezoelectric coefficients were large enough to make a significant contribution to the phase retardation in measuring the linear electro-optic coefficients. There is a particular interest in the nonlinear optics of molecular materials because the response can be rather strong and can in principle be enhanced by tailoring the molecules in suitable ways. This possibility arises because the material response arises from a combination of the molecular response, the molecular arrangement, and the molecular interactions.

There are also several measurements of the pyroelectric properties of molecular crystals (mostly substituted benzenes), some concentrating on associated luminescence phenomena. Among other molecular materials, there is considerable interest in pyroelectric response in ferroelectric polymers such as poly(vinylidene fluoride) and host-guest systems. Theories of pyroelectricity in molecular materials typically consider the changes in the molecular dipole moment and its orientation that arise from the anharmonicity of the crystal vibrations. The theories typically take into account of the displacement produced by thermal excitation of internal molecular modes and lattice librational and translational modes and then fit parameters to reproduce the observed results. Even so, it has been remarked that the theory of pyroelectricity is far from complete. There are also rather general treatments for insulating crystals that start from the crystal energy as a function of electric field and strain, but these do not use models constructed specifically for molecular crystals.

Theories of nonlinear optics in molecular materials have often concentrated on the contribution from the electronic response of the molecules, which can be tailored directly. However, the preceding paper has treated the additional contributions to the nonlinear optics of molecular crystals that arise when, in addition to the electrons being displaced relative to the nuclear framework of each molecule, the molecules themselves can be displaced by the applied electric field. This work cases the task of calculating the coefficients that describe piezoelectricity and electrostriction because it yields the displacement of the molecules by the applied electric field. In Sec. II of the present paper this quantity is combined with a suitable treatment of the crystal elasticity, leading directly to the linear piezoelectric coefficients.

The previous work also yields the change in dipole moment on displacement of the molecules so that a similar treatment also readily leads to the pyroelectric coefficient, as shown in Sec. III. The work presented here complements work on surface pyroelectricity in otherwise nonpolar molecular crystals and extends it by showing in more algebraic detail how to calculate the strain dependence of the
polarization, previously done numerically for surfaces.\textsuperscript{20} The present work also extends previous results on linear piezoelectricity and pyroelectricity for a simple orthorhombic lattice of point polarizable dipoles.\textsuperscript{21}


\section{II. MICROSCOPIC THEORY OF PIEZOELECTRICITY AND ELECTROSTRICTION}

Among the various piezoelectric coefficients, the isothermal linear piezoelectric strain coefficient is defined as

\begin{equation}
q_{\lambda\alpha} = \frac{\partial \eta_k}{\partial E_a},
\end{equation}

where \(\eta_k\) is a component of the external macroscopic strain (a Lagrangian finite strain parameter in the abbreviated Voigt notation with \(\lambda = 1, \ldots, 6\)) and \(E_a\) is a Cartesian component of the macroscopic electric field. The subscripts \(T\) and \(t\) denote that temperature and external stress are held constant during differentiation. The isothermal electrostriction coefficient is defined similarly as the next derivative, i.e. the quadratic piezoelectric strain coefficient

\begin{equation}
q_{\lambda\alpha\beta} = \frac{1}{2} \frac{\partial^2 \eta_k}{\partial E_a \partial E_{\beta^*} T},
\end{equation}

For present purposes, it is more convenient to use this electrostriction coefficient defined in terms of the electric field dependence rather than the alternative coefficient defined in terms of the polarization dependence, even though the latter can remain independent of electric field even at electric fields high enough for the polarization itself to become nonlinear.\textsuperscript{22} Finally, the cubic piezoelectric strain coefficient, required to relate the free and clamped cubic susceptibilities, is defined similarly as

\begin{equation}
q_{\lambda\alpha\beta\gamma} = \frac{1}{6} \frac{\partial^3 \eta_k}{\partial E_a \partial E_{\beta^*} \partial E_{\gamma^*} T},
\end{equation}

Piezoelectricity and electrostriction occur when the energy of the crystal changes in the electric field because of the interaction between the field and the molecules via their permanent electric moments, polarizabilities, and hyperpolarizabilities. The molecules move so as to minimize the crystal energy in the field at the given temperature and stress, and the size and shape of the unit-cell change accordingly. Hence evaluation of Eqs. (1)–(3) requires the dependence of the molecular displacements on electric field and the dependence of the unit-cell dimensions on the molecular displacements.

The molecules are identified by the label \(k\) denoting one of the \(Z\) molecules within the unit cell. Forces between molecules are typically much weaker than those within them, and so the molecules are treated as rigid bodies that may rotate and translate. The molecules are treated as polar and polarizable, with “effective” properties that incorporate the effect of the crystal environment. To keep the formalism as simple as possible, the treatment deals with molecules as whole entities, but for numerical calculations the molecules are treated as a set of submolecules (atoms or functional groups) that combine to yield the molecular contribution. The submolecule treatment partly incorporates higher-order multipole moments through the distribution of dipole moment over the molecules, but induced higher-order multipole moments are otherwise ignored. The treatment assumes local response throughout, but could be extended to take into account of nonlocal response as already done for the electronic contributions to the susceptibilities.\textsuperscript{23}

In a uniform electric field the displacements are the same in every unit cell, and the displacement of molecule \(k\) is written as the six-component vector \(x_k = (u_k, \theta_k)\), with \(u_k\) the translational displacement and \(\theta_k\) the rotational displacement. At equilibrium, the electric force on the molecules arising from their dipole moments is balanced by the elastic restoring force, which serves to determine the equilibrium displacements as a function of the electric field. Then the derivatives of the molecular displacements with respect to electric field, given in the accompanying paper,\textsuperscript{18} are

\begin{equation}
y_{k\alpha} = \frac{\partial x_k}{\partial E_a},
\end{equation}

\begin{equation}
= \epsilon_0 \nu \sum_{k',k''} (A^{-1})_{kk''} \left[ \tilde{m}_{k'}, \frac{\partial L_{k'k''}}{\partial x_k} \chi^{(1)}_{k''} + \tilde{m}_{k''} \cdot L_{k'k''} \chi^{(1)}_{k'\prime} \chi^{(1)}_{k''} \chi^{(1)}_{k''} \right],
\end{equation}

\begin{equation}
y_{k\alpha\beta} = \frac{\partial^2 x_k}{\partial E_a \partial E_{\beta^*}},
\end{equation}

\begin{equation}
= \epsilon_0 \nu \sum_{k',k''} (A^{-1})_{kk''} \left[ \tilde{m}_{k'}, \frac{\partial L_{k'k''}}{\partial x_k} \chi^{(2)}_{k''} + \tilde{m}_{k''} \cdot L_{k'k''} \chi^{(1)}_{k'\prime} \chi^{(2)}_{k''} \chi^{(2)}_{k''} \right],
\end{equation}

and

\begin{equation}
y_{k\alpha\beta\gamma} = \frac{\partial^3 x_k}{\partial E_a \partial E_{\beta^*} \partial E_{\gamma^*}},
\end{equation}

\begin{equation}
= \epsilon_0 \nu \sum_{k',k''} (A^{-1})_{kk''} \left[ \tilde{m}_{k'}, \frac{\partial L_{k'k''}}{\partial x_k} \chi^{(3)}_{k''} + \tilde{m}_{k''} \cdot L_{k'k''} \chi^{(1)}_{k'\prime} \chi^{(3)}_{k''} \chi^{(3)}_{k''} \right],
\end{equation}

where \(v\) is the unit-cell volume, \(A_{kk''}\) is the elastic force constant matrix that determines the lattice dynamics, the open circle denotes a \(6 \times 6\) matrix product over the components of molecular displacement (internal strain), and the tilde denotes the transpose.

In these equations, \(\tilde{m}_k\) is an effective source dipole moment at zero applied electric field, either the permanent electric dipole moments of molecule \(k\) or, for nonpolar molecules, the dipole moment induced in molecule \(k\) by the electric field of higher multipole moments. The local-field
tensor \( \mathbf{d}_k \) relates the local electric field to the macroscopic electric field, while the \( L_{ikr} \) are the Lorentz-factor tensors, dimensionless lattice dipole sums. Finally, \( \chi_k^{(1)}, \chi_k^{(2)}, \) and \( \chi_k^{(3)} \) are sublattice contributions to the linear, quadratic, and cubic susceptibility, respectively, which they yield when summed over all \( k \). The linear expression has an extra term compared with the nonlinear expressions because it has a contribution from the permanent moment \( \mathbf{m}_k \) as well as from the induced moments described by \( \chi_k^{(1)} \), whereas the quadratic and cubic expressions have only the induced moments described by \( \chi_k^{(2)} \) and \( \chi_k^{(3)} \). The sum over \( k'' \) of the last term on the right-hand side (RHS) of Eq. (4) in parentheses also yields the local-field tensor \( \mathbf{d}_k \).

The dependence of the unit-cell dimensions on the molecular displacements can be obtained from work on the thermodynamics of internal strain in crystals,24–26 where changes in internal coordinates that specify the crystal structure for given unit-cell dimensions are treated as distinct variables in addition to the external strains that specify changes in the unit-cell dimensions. This approach has practical advantages in working out the consequences of theoretical models that are naturally formulated in terms of such an extended set of variables. Nevertheless, the internal strains must minimize the generalized Helmholtz energy for given external strains at a given temperature and hence are completely determined by the external strains.

This description of strain requires the molecular displacement variables described above to be specified more clearly. For molecules treated as rigid, the set of translational and rotational displacements of all the molecules from equilibrium relative to a space-fixed set of axes completely defines the configuration of the strained crystal. However, if these displacements are used as the internal strain variables together with the external strain variables, the strained configuration of the crystal is overdetermined. Moreover, internal strain variables must be translationally and rotationally invariant so that the energy of the crystal does not change under pure translation or rotation. Hence the molecular displacements are defined relative to the primitive unit cell of the crystal after the external strain, with the center of mass of one molecule fixed at the origin so that only relative displacements are included.24 This yields a complete set of strain variables \( \{ \mathcal{E}_A \} = \{ \eta_k, \mathbf{x}_k \} \) in what is known as the general regime.

The external strain is expanded in terms of the internal strains

\[
\eta_k = \sum_{k'} Q_{kk'} \circ \mathbf{x}_{k'} + \frac{1}{6} \sum_{kk'r'} Q_{kk'r'} \circ \circ \mathbf{x}_k \mathbf{x}_{k'} \mathbf{x}_{r'} + \frac{1}{6} \sum_{kk'rr'} Q_{kk'rr'} \circ \circ \circ \mathbf{x}_k \mathbf{x}_{k'} \mathbf{x}_{r'} \mathbf{x}_{r'}. \tag{7}
\]

where the coefficients \( Q_{kk...} \) that relate the macroscopic strain to the internal strain are independent of the electric field. The generalized elastic stiffness \( C_{AB} \) is obtained from the second derivative of the generalized Helmholtz energy with respect to the generalized strains \( \mathcal{E}_A \) and \( \mathcal{E}_B \).24 Then the leading coefficient in Eq. (7) can be recognized as the bridging matrix given by

\[
Q_{kk'} = -\mathcal{S}_{km} C_{mk'}. \tag{8}
\]

Here \( \mathcal{S}_{km} \) is an elastic compliance in the external regime which is the inverse of the diagonal sub-block \( C_{km} \) of the generalized elastic stiffness matrix \( C_{AB} \) between external strains \( \eta_k \) and stresses \( \tau_{k'k} \), while \( C_{mk'} \) is the off-diagonal sub-block of the generalized elastic stiffness matrix between external strains \( \eta_k \) and internal strains \( x_{k'} \). Here all quantities are understood to refer to constant temperature and electric field. The higher-order coefficients \( Q_{kk'k'}, Q_{kmm'} \) are evaluated by generalizations of Eq. (8) involving the third and fourth-order elastic stiffnesses \( C_{pkk'k'} \) and \( C_{pmm'p'}. \)

The linear piezoelectric coefficient then follows as:

\[
q_{ka} = \sum_k Q_{kk} \circ \mathbf{y}_{k\alpha}. \tag{9}
\]

the quadratic piezoelectric coefficient or electrostriction coefficient as

\[
q_{ka\beta} = \sum_k Q_{kk} \circ \mathbf{y}_{k\alpha} + \sum_k Q_{kk'} \circ \circ \mathbf{y}_{k\alpha} \mathbf{y}_{k'\beta}. \tag{10}
\]

and the cubic piezoelectric coefficient as

\[
q_{ka\beta\gamma} = \sum_k Q_{kk} \circ \mathbf{y}_{k\alpha} \mathbf{y}_{k'\beta} + \sum_k Q_{kk'} \circ \circ \mathbf{y}_{k\alpha} \mathbf{y}_{k'\beta} \mathbf{y}_{k'\gamma} + \mathbf{y}_{k\alpha} \mathbf{y}_{k'\beta} \mathbf{y}_{k'\gamma} + \sum_k Q_{kk''} \circ \circ \circ \mathbf{y}_{k\alpha} \mathbf{y}_{k'\beta} \mathbf{y}_{k''\gamma}. \tag{11}
\]

From these expressions and the expressions for the \( \mathbf{y} \) tensors given earlier, it can be seen that the piezoelectric strain coefficients and electrostriction coefficients depend on how readily the external strains respond to the internal strains and on how readily the lattice responds to the macroscopic electric field. It can also be seen that since \( \mathbf{y}_{k\alpha}, \mathbf{y}_{k'\beta} \) and \( \mathbf{y}_{k''\gamma} \) are odd, even, and odd under inversion, respectively, then in a centrosymmetric structure \( q_{ka\beta} \) and \( q_{ka\beta\gamma} \) are zero, while the electrostriction coefficient \( q_{ka\beta\gamma} \) is non-zero, as required. However, if the molecules in a centrosymmetric structure also lie on centrosymmetric sites, they have zero first hyperpolarizability \( \beta \), which makes \( \chi_k^{(2)} \) and hence \( y_{k\alpha} \) zero, so that \( q_{ka\beta} \) is then determined solely by the last term in Eq. (10). The linear result (9) has an algebraic form consistent with the general result for the contribution to the piezoelectric coefficient of an insulator from ion relaxation.17

III. MICROSCOPIC THEORY OF PYROELECTRICITY

The primary pyroelectricity is the rate of change of polarization with temperature in a clamped crystal, i.e. at constant external strain \( \eta \) (indicated by the superscript on the coefficient)

\[
Y_{\alpha\beta} = (\partial P_{\alpha}/\partial T)_{\eta,E}. \tag{12}
\]

This is convenient for theoretical calculation, but because clamping a crystal is not always easy or convenient in practice, more usually one would measure the pyroelectric coefficient at constant stress.
The total molecular dipole moment in a molecular crystal with \( Z \) molecules in the unit cell is given by

\[
\mathbf{a}_k = \left( \partial \mathbf{x}_k / \partial T \right)_{\eta, E.}
\]  

(16)

Combining Eq. (15) with Eq. (16) then yields the primary pyroelectric coefficient of Eq. (12) as

\[
Y^\eta_a = (1/v) \sum_k \mathbf{C}_{ak} \cdot \mathbf{a}_k.
\]  

(17)

The internal thermal expansion can be calculated from the heat capacity at constant external and internal strain in the generalized regime; the internal elastic compliance \( \mathbf{S}_{kk'} \), which is the inverse of the diagonal sub-block \( C_{kk} \) of the generalized elastic stiffness matrix \( C_{AB} \) between internal strains \( \mathbf{x}_k \) and \( \mathbf{x}_{k'} \); and the internal Grüneisen function \( \Gamma_k \) which follows from the second derivative of the generalized Helmholtz energy with respect to temperature and internal strain, and gives the entropic driving force for thermal expansion, dependent on the lattice anharmonicity. Hence the pyroelectric strain coefficient depends on how strongly the effective source dipole moment and the local electric field vary with the molecular displacements, and how readily the internal strains respond to the temperature.

Interpreting measured pyroelectric coefficients requires separation of the primary and secondary contributions, which in turn requires the thermal expansion, elastic stiffnesses, and piezoelectric coefficients. Particular attention has been given to crystals in which the measured pyroelectric coefficient changes sign in the absence of a detectable phase transition (although the absolute sign of the coefficient is not always measured). In mNA, where the coefficient changes sign below about 130 K, all the contributions to the secondary piezoelectricity measured around room temperature are positive (although two piezoelectric coefficients for shear strain were not measured), suggesting that the primary pyroelectricity may be negative at low temperatures. In 1,3-dinitrobenzene, where the pyroelectric coefficient changes sign above about 175 K, the two smallest thermal expansion coefficients turn negative at low temperatures, and one of the piezoelectric coefficients is negative, but except at the lowest temperatures the secondary pyroelectricity is positive and hence the primary pyroelectricity is negative. The present treatment shows that negative primary pyroelectricity requires some displacements that reduce the unit-cell dipole moment (negative \( \mathbf{C}_k \)) or that themselves reduce with increasing temperature (negative \( \mathbf{a}_k \)), for example, so that the molecular dipole moment rotates away from the crystal polar axis.
\[ p_k = \sum_{k'} (1 - \mathbf{a} \cdot \mathbf{L})_{kk'}^{-1} \cdot \mu_{k'}, \quad \sum_{k'} \mathbf{D}_{kk'} \cdot \mu_{k'}, \quad (18) \]

where \( \mathbf{L} \) is the \( 3Z \times 3Z \) unit matrix, \( \mathbf{a} \) is the \( 3Z \times 3Z \) matrix having submatrices \( a_{kk'} \), where \( a_{kk'} = a_{kk} / \epsilon_k \), is the dimensionless reduced polarizability, and \( \mathbf{L} \) is the \( 3Z \times 3Z \) matrix having the Lorentz-factor tensors \( L_{kk'} \), as submatrices; the local-field tensor \( \mathbf{d} \) is given by \( \Sigma_{kk'} \mathbf{D}_{kk'} \). In terms of these quantities, the sublattice contribution to the linear susceptibility which is of similar form to the first term in square brackets

\[ d_{kk'} \]

which converts the unit-cell dipole moment \( \mathbf{G} = \Sigma_{k'} \mu_{k'} \) with respect to a unit-cell parameter \( z \) then yields

\[ \frac{\partial G}{\partial z} = \sum_{kk'} \left( a^{-1} - \mathbf{L} \right)_{kk'}^{-1} \cdot \left( \frac{\partial L_{kk'}}{\partial z} \right) \cdot \mu_{k'}, \]

\[ = \sum_{kk'} \chi_{kk'}^{(1)} \cdot \left( \frac{\partial L_{kk'}}{\partial z} \right) \cdot \mu_{k'}, \quad (19) \]

which is of similar form to the first term in square brackets on the RHS of Eq. (4). For \( Z=1 \) all dependences on \( k \) disappear and the result [Eq. (19)] is consistent with that in Eq. (18) of Purvis and Taylor (who used \( \kappa -1 \), where \( \kappa \) is the dielectric constant, rather than the linear susceptibility \( \chi \)). The strain dependence given by Eq. (19) is converted to a stress dependence through an elastic compliance, and their results include a contribution from the stress dependence of the unit-cell volume (which converts the unit-cell dipole moment \( \mathbf{G} \) to the polarization \( \mathbf{P} \)), also determined by the elastic compliances.

Because the model with \( Z=1 \) precludes internal strain and hence also precludes primary piezoelectricity, it has only the secondary pyroelectricity given by Eq. (14). Then the elastic stiffening in this term cancels out its inverse, the compliance required to obtain the piezoelectric stress coefficient from the strain dependence of the unit-cell dipole moment. As a result, the pyroelectric coefficient depends on the same strain dependence of the unit-cell dipole moment as the piezoelectric coefficient and on the macroscopic thermal expansion coefficient, consistent with Eq. (23) of Purvis and Taylor.

These derivations indicate that the approach adopted in the present treatment is consistent with the earlier work. However, the model in the previous treatment was explicitly ferroelectric with a bulk polarization, and its results depend on the molecular dipole moment. In general defining the polarization in an external electric field and under strain is an issue, although this is not a practical problem in systems like those here that have strongly localized dipoles. In practice a crystal with a bulk polarization usually attracts surface charges that serve to annul the bulk moment, as pointed out elsewhere. Hence how far a crystal actually exhibits the bulk polarization that its crystal structure implies will depend on the electrical boundary conditions imposed by the experimental conditions (which were carefully specified by Purvis and Taylor); the conditions then lead to measurement of an effective or apparent pyroelectric coefficient. Nevertheless, the change in polarization can be calculated without assuming a nonzero bulk polarization.

The present results also show the value of the general thermodynamic theory of internal strain in providing a direct connection between different properties as well as a prescription for calculating them efficiently from a suitable model. Numerical calculations for a model of any specific crystal are beyond the scope of this paper, which does however provide the necessary groundwork.

The various piezoelectric coefficients determine the difference between the clamped and free electric susceptibilities which refer to constant external strain and stress, respectively. The preceding paper gave a microscopic treatment of the clamped linear, quadratic, and cubic electrical susceptibilities and presented the macroscopic expressions that relate them to the free electric susceptibilities. The present results therefore complete a microscopic treatment of the free susceptibilities.