# Theory for the thermopolarization effect in dielectrics having a center of inversion

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A phonon mechanism for the thermopolarization effect in crystals exhibiting a center of inversion is analyzed. The thermopolarization coefficient is calculated for an ordinary dielectric and for a ferroelectric.

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The thermopolarization effect is the appearance of a dielectric polarization $P$ in a dielectric in which there is a temperature gradient $\partial T/\partial x_i$. In the linear approximation, the polarization is related to the gradient by

$$P_i = b_{ij} \frac{\partial T}{\partial x_j} ,$$

where $b$ is the so-called thermopolarization coefficient tensor.[1)] One of the present authors has recently published a paper on the thermopolarization effect in crystals which do not possess a center of inversion.[1] The recent discovery of this effect in a ferroelectric having a center of inversion,[2] $PbMg_{1/3}Nb_{2/3}O_3$, makes it worthwhile to derive a theory for the effect in crystals which possess a center of inversion. We might note that crystals having a center of inversion are particularly convenient for observing this effect, because it would not be masked by the "third-order" pyroelectric effect.[3]

The thermopolarization effect has two components: a thermodynamic component and a kinetic one. We will not study the thermodynamic component in the present paper. We will simply write an order-of-magnitude estimate of this component, which is the same as that derived in Ref. 1:

$$b_{ij}^{(T)} \cong \gamma_{ijmn} \alpha_{mn} , \qquad (1)$$

where $\alpha$ is the tensor of thermal expansion coefficients, and the tensor $\gamma$ relates the polarization to the strain gradient $\partial U_{mn}/\partial x_j$:

$$P_i = \gamma_{ijmn} \frac{\partial U_{mn}}{\partial x_j} .$$

To describe the mechanism responsible for the kinetic component, we consider the simplest example of a polar dielectric. The contribution of branch $j$ to the crystal polarization $P$ is proportional to the average value of the normal coordinate, $\langle \xi_k^j \rangle$, at the wave vector $k \approx 0$. This average value is found from the average equation of motion

  

$$\langle \xi_0^j \rangle = -\frac{1}{\Omega_{0j}} \sum_{\mathbf{k}} \sum_{j'} V_{0\,\mathbf{k}-\mathbf{k}}^{jj'j''} \langle \xi_{\mathbf{k}}^{j'} \xi_{\mathbf{k}}^{j''*} \rangle ,$$

where $V_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{jj'j''}$ is the triple anharmonic matrix element, and $\Omega_{0j}$ is the frequency of branch $j$ at $\mathbf{k}=0$. Since $V_{0\,\mathbf{k}-\mathbf{k}}^{jj'j''}$ is nonzero only if $j' \neq j''$, $\langle \xi_0^j \rangle$ and thus $P$ appear only to the extent that there is a correlation between the phonon states of different branches at a given value of $\mathbf{k}$. The correlation in which we are interested here arises only in first order in the phonon scattering. In this order we find the following expression to relate $P$ to the nonequilibrium increment in the phonon distribution function, $\Delta N_{\mathbf{k}j}$:

$$P_i = -2i \sum_{\mathbf{k}, j \neq j', p} \sqrt{\frac{\hbar}{2\rho v \Omega_{0j}^3}} \frac{Q_p e_p^i(0,j)}{a^3} V_{0\,\mathbf{k}-\mathbf{k}}^{jj'j''} \times \frac{2\Omega_{\mathbf{k}j'}}{\Omega_{\mathbf{k}j''}^2 - \Omega_{\mathbf{k}j'}^2} (\hat{I}\Delta N)_{jj'} \tag{2}$$

where $e_p^i(\mathbf{k}, j)$ and $Q_p$ are the polarization vector of the oscillation of the $p$th atom of the unit cell and the charge of this atom, respectively; and $\rho$, $a$, and $v$ are the density, lattice constant, and volume of the crystal, respectively. The quantity $(\hat{I}\Delta N)_{jj'}$ may be termed the off-diagonal collision integral; in the case $j=j'$ it becomes the ordinary linearized collision integral (see Ref. 4, for example). For $j \neq j'$ [and only such components contribute to (2)] this quantity differs from $(\hat{I}\Delta N)_{j'j'}$ in that the square modulus of the matrix element is replaced by the product of the corresponding different matrix elements. The nonequilibrium increment in the distribution, function, $\Delta N_{\mathbf{k}j}$, is to be found from the kinetic equation

$$N_{\mathbf{k}j}(N_{\mathbf{k}j}+1) \frac{\hbar \Omega_{\mathbf{k}j}}{T^2} \frac{\partial \Omega_{\mathbf{k}j}}{\partial k_i} \frac{\partial T}{\partial x_i} = -(\hat{I}\Delta N)_{jj} , \tag{3}$$

where $N_{\mathbf{k}j}$ is the equilibrium phonon distribution function.

Expression (2) along with (3) constitutes the solution of our problem. Using the standard estimate[4] for $\mathbf{V}_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{jj'j''}$, we easily find from (2) and (3) an estimate of the kinetic component of the thermopolarization coefficient:

$$b^{(k)} \cong b \equiv \frac{\epsilon}{4\pi} \frac{k_B}{a^2 \rho^{1/2} w} \quad \text{for} \quad T \gtrsim \Theta , \tag{4}$$

where $k_B$ is the Boltzmann constant, $w$ is the average sound velocity, $\epsilon$ is the dielectric constant, $\Theta$ is the Debye temperature, and

$$b^{(k)} \cong b_0 \left(\frac{T}{\Theta}\right)^3 \quad \text{for} \quad T \ll \Theta . \tag{5}$$

These results agree with (1) for the thermodynamic component $b^{(T)}$. It is important to note, however, that these components can in principle be distinguished ex-

perimentally; one possibility is to independently measure the thermal expansion coefficient and the coefficient in the linear relation between the polarization and the strain gradient.

For displacement-type ferroelectrics at $T \gtrsim \Theta$, the estimate in (4) remains valid; at $T \ll T_0$, expression (5) holds [$T_0$ is the temperature at which the soft mode "freezes out," determined from the equation $k_B T_0 = \hbar\Omega_0(T_0)$, where $\Omega_0$ is the frequency of the soft mode]; and for $T_0 \lesssim T \ll \Theta$ we have

$$b^{(k)} \cong b_0 \frac{T}{\Theta} \quad .$$

In summary, an anomalously large effect should be expected in ferroelectrics. The thermopolarization coefficient found experimentally[2] for $PbMg_{1/3}Nb_{2/3}O_3$ is in reasonable agreement with the rough estimate in (4).

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[1)]The term "electrothermic" effect was used in Ref. 1, but the term "thermopolarization" effect now seems more appropriate.

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