Temperature Dependence of Pyroelectricity

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An expression is derived for the "primary" pyroelectric coefficient. In contrast to currently accepted theory, it is proportional to T^3 near absolute zero, and it depends on the anharmonic potential in the same way as on the second-order dipole moment.

The pyroelectric effect is usually divided into two parts, namely into the effect occurring when the crystal is heated "clamped," i.e., at constant volume and shape, and the effect due to the small changes of size and shape which occur when a free crystal is heated. For purely historical reasons, the first is usually called the *true* or *primary* and the second the *apparent* or *secondary* pyroelectric effect. We shall denote the primary pyroelectric coefficient by Π_1 and the secondary by Π_2.

The currently accepted theory for the primary pyroelectricity is due to Born.[1] This theory indicates that at very low temperature Π_1 is proportional to the temperature T and thus dominates the total effect, since Π_2 is only proportional to T^3. Born also concluded that Π_1 is due essentially to the second-order dipole moment. In contrast, I shall show that in the low-temperature limit Π_1 is in fact proportional to T^3 and not to T, and also that Π_1 depends on the cubic potential in the same way and in the same order as on the second-order dipole moment. This latter conclusion was to be expected from the author's earlier work on the anharmonic contributions to the static dielectric constant[2] and its temperature derivative.[3]

The pyroelectric coefficient represents the change produced in the macroscopic dipole moment by heating. I shall exclude cases where heating produces phase transitions; with this restriction, and in the absence of external forces, pyroelectricity can only occur in crystal structures exhibiting permanent polarization. I shall also exclude ferroelectricity, i.e., the case where a weak external electric field can change the direction of polarization.

If M is the macroscopic dipole moment of the crystal and N_m the number of moles, we introduce p defined by $p = M/N_m$. I normalize to a mole rather than to unit volume, because in changes of density one should compare the dipole moment produced by the same amount of material. Heating of a noncubic crystal produces small changes in shape as well as in volume, both of which can be specified by the macroscopic strain tensor s, with components s_i. If σ is the macroscopic stress tensor, we can thus write

$$\left(\frac{\partial p}{\partial T}\right)_\sigma = \left(\frac{\partial p}{\partial T}\right)_s + \sum_i \left(\frac{\partial p}{\partial s_i}\right)_T \left(\frac{\partial s_i}{\partial T}\right)_\sigma . \tag{1}$$

It will be understood that in all the differentiations throughout this paper the macroscopic electric field is also kept constant, and that this constant value is zero or near zero. If on the left-hand side of Eq. (1) σ is also zero, then the left-hand side is the total pyroelectric coefficient Π of the free crystal. The first term on the right-hand side is Π_1 and the second is Π_2.

In some crystal structures the direction of p may change with heating. I shall exclude this effect as it does not affect the nature of the results but it complicates the equations.

We now consider Π_1 for an infinitely periodic crystal. Following Born and Huang's procedure[4] [cf. their Eq. (39.19)], for a given macroscopic strain the equilibrium configuration is chosen to be the one of minimum potential energy compatible with the strain, and the normal coordinates Q_j measure the displacements from this configuration. The periodic boundary condition assures that the displacements do not change the macroscopic strain. In a displacement the molar dipole moment, up to second order, is equal to $p_0 + \sum \alpha_a Q_a + \sum \beta_{jj'} Q_j Q_{j'}$, where p_0 is the moment in the undisplaced configuration and the α and β are expansion coefficients. The Q_a are the *active* normal coordinates, i.e., those which produce uniform polarization in the direction of p. For a diatomic crystal there is of course only one active mode. The macroscopic value p is therefore given by

$$p = p_0 + \sum_a \alpha_a \langle Q_a \rangle + \sum_{jj'} \beta_{jj'} \langle Q_j Q_{j'} \rangle . \tag{2}$$

Since we imposed the condition that the electric field is zero and since this condition is also valid for the free transverse-optical waves, it follows that each α_a and ω_a is equal, respectively, to the effective charge and the frequency of the corresponding long-wave transverse-optical mode. In this connection it may be noted that by symmetry p is always parallel to one of the principal axes of the dielectric tensor.

Similarly to p, all other quantities are also normalized to one mole of substance. For W, the potential energy of the displacement, we write, to third order,

$$W=\tfrac{1}{2}\sum \omega_j^2 Q_j^2+\sum b_{jj'j''}Q_jQ_{j'}Q_{j''}\,. \tag{3}$$

Let n_j, $n_{j'}$, $n_{j''}$ etc., denote the quantum numbers of the various lattice modes in a particular vibrational state and n_j', $n_{j'}'$, $n_{j''}'$ etc., the same quantities in another state. Further, $\tilde{n}$ will be an abbreviation for all the quantum numbers in the first state and $\tilde{n}'$ for the quantum numbers in the second state. Thus $\tilde{n}$ and $\tilde{n}'$ each specify a vibrational state. In the state $\tilde{n}$, $\Psi_{\tilde{n}}$ will denote the vibrational wave function in the harmonic approximation. Treating the cubic terms in W as a perturbation, for the perturbed wave function $\Phi_{\tilde{n}}$ we write

$$\Phi_{\tilde{n}}=\Psi_{\tilde{n}}+\sum_{\tilde{n}'\neq\tilde{n}}\Delta_{\tilde{n}\tilde{n}'}\,,$$

$$\Delta_{\tilde{n}\tilde{n}'}=-\sum_{jj'j''}b_{jj'j''}\langle\tilde{n}'|Q_jQ_{j'}Q_{j''}|\tilde{n}\rangle/(W_{\tilde{n}'}-W_{\tilde{n}})\,,$$

where the Dirac brackets of course represent matrix elements between unperturbed states. We first consider the case when there is only one Q_a. For the expectation value of Q_a in the perturbed $\tilde{n}$ state we have

$$(\langle Q_a\rangle)_{\tilde{n}}=2\sum_{\tilde{n}'\neq\tilde{n}}\langle\tilde{n}'|Q_a|\tilde{n}\rangle\Delta_{\tilde{n}'\tilde{n}}\,.$$

$\langle\tilde{n}'|Q_a|\tilde{n}\rangle$ is nonzero only for those two states $\tilde{n}'$ for which $n_a'=n_a+1$ or $n_a'=n_a-1$, and $n_j'=n_j$ for all j except $j=a$. For these two states $\Delta_{\tilde{n}'n}$ is nonzero only for terms of the type $Q_aQ_j^2$. Inserting the appropriate values and neglecting the fact that the contribution is somewhat different from the one term where $j=a$, we obtain

$$(\langle Q_a\rangle)_{\tilde{n}}=-\sum_j\alpha_a b_{ajj}(n_j+\tfrac{1}{2})\hbar/\omega_a^2\omega_j\,.$$

For several active modes, we sum over a. In Eq. (2), in the lowest order $\sum\beta_{jj'}\langle Q_jQ_{j'}\rangle=\sum\beta_{jj}\times\langle Q_j^2\rangle=\sum\beta_{jj}(n_j+\frac{1}{2})\hbar\omega_j$. Taking the thermal average over the quantum numbers we thus get

$$p=p_0+\sum_j\left(\beta_{jj}-\sum_a\frac{\alpha_a b_{ajj}}{\omega_a^2}\right)\frac{\bar{n}_j+\frac{1}{2}}{\omega_j}\hbar\,. \tag{4}$$

As the potential and the dipole moment are given as a power series in the Q, the expectation value p is obtained as a power series in the matrix elements of the Q (cf. for instance Ref. 3, pages 275 and 276). Equation (4) contains, apart from p_0, the terms which are of lowest order in the matrix elements. It can be easily verified that the neglected terms are of higher order in the matrix elements, i.e., they contain higher powers of $\hbar$.

It is thus seen that in Eq. (4) the cubic potential terms and the second-order dipole terms, represented by the $\alpha_a b_{ajj}$ and the β_{jj}, respectively, appear in the same order. The terms in $\alpha_a b_{ajj}$ represent the fact that, in the direction of p, positive and negative displacements are not equally probable and hence the $\langle Q_a\rangle$ change with vibrational amplitude even at constant strain. I also point out that while the b_{ajj} and β_{jj} would vanish in crystals with symmetry centers, in pyroelectric crystals they do not.

We note that C_j, the contribution of the jth vibration to the specific heat, is given by $C_j=\hbar\omega_j(\partial\bar{n}_j/\partial T)$. Since the primary pyroelectric coefficient Π_1 is $(\partial p/\partial T)_s$, and since the various parameters in Eqs. (2) and (3) depend only on the macroscopic strain s, from Eq. (4) we get

$$\Pi_1=\left(\frac{\partial p}{\partial T}\right)_s=\sum_j\left(\beta_{jj}-\sum_a\frac{\alpha_a b_{ajj}}{\omega_a^2}\right)\frac{C_j}{\omega_j^2}\,. \tag{5}$$

Born's expression is written for $p-p_0$; apart from the different normalization, at this stage his β_{jj} terms are identical with ours in Eq. (4), but the anharmonic-potential terms are missing from his expression. Born then considered very low temperatures where only the very long acoustic waves are excited and the Debye approximations should be valid. He replaced the β_{jj} by a constant, independent of j, so that $p-p_0$ became proportional to $\sum(\bar{n}_j+\frac{1}{2})/\omega_j$. He showed that this sum is proportional to T^2 and therefore concluded that at low temperature $p-p_0\propto T^2$ and $\Pi_1\propto T$. As it is generally accepted that Π_2 varies with temperature as the specific heat and hence $\Pi_2\propto T^3$ for small T, it followed that the pyroelectric effect was dominated by Π_1, at least at low temperature.

In fact, however, at low temperature it is unjustified to replace the β_{jj} by a constant which is independent of j, because for long acoustic waves β_{jj} varies strongly with wave number k_j. As $k_j=0$ represents uniform translation, which cannot affect either potential or dipole moment, and as β_{jj}, b_{ajj}, and ω_j^2 must be even functions of k_j, it follows that β_{jj}, b_{ajj}, and ω_j^2 vanish for $k_j = 0$, and for small k_j all three must be proportional to k_j^2 and hence to each other. Thus we may put $b_{ajj} = b_{aj}'\omega_j^2$ and $\beta_{jj} = \beta_j'\omega_j^2$, where b_{aj}' and β_j' are independent of the magnitude of k_j but depend on its direction and on whether the jth wave is longitudinal or transverse. Considering first the β for longitudinal waves, we have

$$\sum \beta_{jj} C_j/\omega_j^2 = \sum \beta_j'(\theta_j, \varphi_j) C_j(\omega_j), \tag{6}$$

where the sum goes over the longitudinal modes; θ_j and φ_j represent the direction of k_j in a spherical coordinate system where the polar axis is in the direction of the permanent moment p. The β_j' depend on direction because they represent the dipole moment in the p direction, and because it is as a result of the asymmetry in the p direction that the sum in Eq. (6) does not vanish when summed over direction. But this asymmetry cannot affect appreciably the frequency distribution. Assuming, therefore, that the directional distribution of the modes for a given frequency is the same as for any other frequency, which is certainly true for the Debye distribution, we can replace the β_j' by their directional average β_l'. The right-hand side of Eq. (6) thus becomes $\beta_l' C_l$, where C_l denotes the contribution of all the longitudinal modes to the specific heat. We proceed for the transverse waves similarly, and also for the b_{ajj}, and denote the directional averages by β_t', b_{al}', and b_{at}', respectively, and the total specific heat of the transverse modes by C_t. For low temperatures Eq. (5) thus becomes

$$\Pi_1 = \left(\beta_l' - \sum_a \frac{\alpha_a b_{al}'}{\omega_a^2}\right) C_l + \left(\beta_t' - \sum_a \frac{\alpha_a b_{at}'}{\omega_a^2}\right) C_t . \tag{7}$$

As both C_l and C_t are proportional to T^3, Eq. (7) shows that Π_1 is proportional to T^3 at low temperature. Moreover, as also $\Pi_2 \propto T^3$, it follows that $\Pi \propto T^3$ and there is no reason to think that $\Pi_2 \ll \Pi_1$.

Born's theory was connected with earlier experimental measurements by Ackermann,[5] which were believed to imply proportionality between Π and T at small T. This interpretation of the measurements was never really justified as below 100°K Ackermann only measured Π at 23 and 88°K. Moreover, more recent measurements[6,7] seriously disagree with Ackermann's low-temperature data.

Heiland and Ibach[8] measured the pyroelectric coefficient of ZnO down to 9°K and at low temperature definitely found proportionality to T^3. For other materials there seems to be no clear experimental information on the temperature dependence of Π near $T = 0$. Measurements by Lang[7] on $LiSO_4 \cdot H_2O$ extend down to 4.2°K, but while above 30°K the coefficient is clearly not proportional either to T^3 or to T, it is not clear from the published data whether or not there is proportionality to T^3 at the lowest temperatures. This material, in common with most strongly pyroelectric materials, has many atoms in its unit cell; this may result in some of the optical branches having very low frequencies, in which case one would expect the T^3 behavior only at very low temperatures.

In order to predict from Eq. (5) the temperature dependence of Π_1 above the T^3 region, one needs information on the various constants. We note, however, that Eq. (7) is valid for long acoustic waves and therefore for the Debye model it should be valid at all temperatures. Hence, when the Debye approximation is valid, Π_1 is approximately proportional to the specific heat C_v. The same is true for Π_2, as the T dependence of Π_2 is determined by the thermal expansion which for the Debye model is also proportional to C_v. Indeed, Heiland and Ibach[8] have found that Π for ZnO was proportional to C_v over the entire range of their measurements, which extended from 9°K to well above room temperature.

But we cannot expect the Debye approximation to hold generally, in particular for polyatomic materials. Equation (5) shows that deviations from the Debye model can affect Π_1 much more drastically than they affect C_v. The β_{jj} and b_{ajj} may *a priori* have either sign, and they may have very different types of vibration, in particular for materials with many atoms in the unit cell. If this happens then the temperature dependence can be rather complicated.

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