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Primary Pyroelectric Effect in $LiTaO_3$

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By a careful analysis of the pyroelectric effect in $LiTaO_3$ between 10 and 200°K, we have demonstrated for the first time the dominance of the lowest-order (polar-mode) contributions to the primary pyroelectric effect over a wide temperature range in a strongly pyroelectric material. In doing so we confirm, as an excellent approximation for the effect, a simple analytic form the theoretical origins of which go back to a paper by Boguslawski in 1914.

The first calculation of the pyroelectric effect based on nonclassical physics was presented by Boguslawski[1] more than sixty years ago using an Einstein-oscillator formalism. The theory predicted an expression for the temperature dependence of the pyroelectric coefficient $\Pi = |dP_s/dT|$ (where P_s is the spontaneous polarization) proportional to the Einstein specific-heat function. Since the lowest-order contributions to the pyroelectric coefficient for a crystal at constant *strain* (the so-called primary pyroelectric coefficient $\Pi_{\rm prim}$) are now recognized as coming from the polar optic lattice-vibrational modes, for which an Einstein approximation per mode is presumably quite realistic, Boguslawski's finding remains essentially valid in the slightly embellished form,

$$\Pi^{(1)}_{\rm prim} = \sum_i C_i E(\hbar\Omega_i/2kT), \tag{1}$$

in which C_i are coefficients describing the relative amplitudes of the contributions from each pertinent Einstein mode i (of frequency Ω_i), superscript (1) denotes the lowest-order contribution, and the Einstein function is given by

$$E(x) = x^2/\sinh^2 x. \tag{2}$$

In spite of the striking simplicity of this finding, no convincing experimental verification that Einstein terms of the form (1) do indeed dominate the primary pyroelectric coefficient $\Pi_{\rm prim}$ for *any* pyroelectric has ever been forthcoming. Indeed, controversy continues concerning the possibility that higher-order terms may dominate the primary coefficient in real pyroelectrics[2-5] and even as to what form these higher-order terms should take.[6-8] This Letter provides a verification of Eq. (1) over a wide temperature range for $LiTaO_3$. Lithium tantalate is actually a high-temperature ferroelectric with Curie temperature $T_C \approx 890$°K. However, below room temperature it is a conventional pyroelectric (i.e., with essentially temperature-independent phonon modes) and with a moderately strong pyroelectric coefficient at 300°K of 0.018 ± 0.001 μC cm^{-2} K^{-1}.

In general, a convincing experimental verification of the form (1) is difficult for two reasons. Firstly, conventional measurements of Π are performed either statically or at frequencies well below the fundamental crystal resonances. They therefore measure the pyroelectric response $\Pi = \Pi_{\rm prim} + \Pi_{\rm sec}$ at constant *stress* which includes, in addition to the constant-strain term $\Pi_{\rm prim}$, a secondary contribution

$$\Pi_{\rm sec} = d_{ij} c_{jk} \alpha_k, \tag{3}$$

where i, j, and k label coordinate directions (with direction i parallel to the spontaneous polarization), repeated indices imply summation, d_{ij} are piezoelectric compliances, c_{jk} are elastic moduli, and α_k are linear thermal expansion coefficients. This contribution is normally a significant fraction of the total and actually dominates in many systems (indeed there was a period of time not long back where the very existence of the primary term Π_{prim} was difficult to establish experimentally). As seen from Eq. (3), Π_{sec} cannot be quantitatively subtracted from the total pyroelectric response Π unless the complete temperature dependences of the thermal expansion and relevant piezoelectric and elastic moduli are known. This complete information exists for very few, if any, pyroelectric materials which might be good candidates for testing (1). Secondly, most pyroelectrics possess many optically active vibrational modes i with comparable mode strengths and frequencies. These must all be expected to contribute significant amounts to Π_{prim} but with relative amplitudes C_i which are unknown *a priori* since they involve lattice-mode anharmonicities, the accurate calculation of which is beyond the capability of existing shell-model theories. The existence of a large number of free parameters C_i then diminishes dramatically both the uniqueness and reliability of any fit of Eq. (1) to experiment, even if the relevant frequencies Ω_i are known from infrared or Raman spectroscopy. The full impact of all these difficulties was felt by Lang,[9] who to date has made the only previous attempt to fit a form (1) to experimental pyroelectric data over a wide temperature range.

The fortuitous circumstances which make $LiTaO_3$ an ideal candidate for testing (1) are threefold. Firstly, the infrared reflectivity measurements[10] establish that of those (A_1 symmetry) optic modes which can contribute to $\Pi_{\text{prim}}^{(1)}$, one ($i=1$, say) with frequency $\Omega_1 = 218\ \text{cm}^{-1}$ at $T = 0°\text{K}$[11] ($201\ \text{cm}^{-1}$ at room temperature) has an optic-mode strength $S_1 = 30$, a full order of magnitude larger than all the others put together, and is therefore likely to dominate in (1). Secondly, the secondary contribution Π_{sec} is negligibly small in $LiTaO_3$ (as a fraction of Π) at all temperatures above $T \sim 10°\text{K}$, a fact which has been verified by performing dynamic pyroelectric measurements[12] both well below and well above the mechanical resonances and observing no detectable difference above 10°K. The smallness of Π_{sec} results from a fortuitous partial cancellation of the terms summed in (3). Using room-temperature values of the relevant compliances as given by Smith and Welsh,[13] we find $\Pi_{\text{sec}}/\Pi \approx 0.04$ at this temperature. Finally, and perhaps most importantly, the dominant pyroelectric mode ($i=1$) at room temperature is just that mode which becomes ferroelectrically soft as $T \to T_C$. Since a very thorough analysis of the ferroelectric properties of $LiTaO_3$ in the "one-dominant-mode" approximation has been carried out[14,15] with encouraging self-consistency using a mean-field statistical approximation, the detailed anharmonicity of the mode $i=1$ has, in fact, already been determined (to the degree of accuracy of the statistical theory). It follows that for $LiTaO_3$ an independent theoretical estimate of C_1 can be made. Indeed, to our knowledge, $LiTaO_3$ and the isomorphic $LiNbO_3$ are the only pyroelectric or ferroelectric materials for which any quantitative knowledge concerning the anharmonic form of the soft-mode potential functions has been given.

Following Ref. 12, if we describe the motion of ions in the $i=1$ mode by a unit-cell displacement operator ξ_l, with conjugate momentum operator π_l, and express the corresponding ion-displacement Hamiltonian in the form

$$\mathcal{H} = \frac{1}{2}\sum_l \pi_l^2 + \sum_l V(\xi_l) - \frac{1}{2}\sum_l \sum_{l'} v_{ll'}\xi_l \xi_{l'}, \tag{4}$$

then the low-temperature development of the thermally averaged displacement operator $\langle \xi \rangle$ follows in the Einstein-oscillator approximation as[12]

$$\frac{d\langle \xi \rangle}{dT} = -\frac{1}{2}\left(\frac{\partial^3 V}{\partial \xi_l^3}\right)_0 \frac{k\,\text{csch}^2(1/2t)}{4\Omega_1^4 t^2}, \tag{5}$$

in which $t = kT/\hbar\Omega_1$ and the calculation is carried out to only the first order in $\delta\langle \xi \rangle / \langle \xi \rangle$. The subscript zero on the derivative indicates that it is to be taken at the $T=0$ equilibrium value of displacement, $\langle \xi \rangle_{t=0}$. Writing $1/\eta'$ as that fraction of P_s arising from ionic displacements, we have $P_s = \eta' P_s(\text{ionic}) = (\eta' S/v)\langle \xi \rangle$, following Ref. 14, where S is an effective-charge parameter and v is the unit-cell volume; the contribution to the lowest-order primary pyroelectric coefficient from mode 1 follows directly as

$$\Pi_{\text{prim}}^{(1)}(\Omega_1) = -\frac{1}{2}\frac{\eta' S}{v}\frac{k}{\Omega_1^4}\left(\frac{\partial^3 V}{\partial \xi_l^3}\right)_0 E\left(\frac{1}{2t}\right). \tag{6}$$

For $LiTaO_3$ the anharmonic contribution to V can be expressed[14] as $A\xi_l^4 + B\xi_l^6$ to give

$$C_1 = \frac{\eta' S}{v}\frac{k}{\Omega_1^4}\left(12A\langle \xi \rangle_{t=0} + 60B\langle \xi \rangle_{t=0}^3\right). \tag{7}$$

The $t=0$ displacement can be deduced from the room-temperature x-ray structure[16] and the known form $P_s(T=0)=1.044P_s(T=300)$, which can be deduced from Fig. 1 of this paper. It is $\langle\xi\rangle_{t=0}=2.48\ (\mathrm{amu})^{1/2}$ Å. The other parameters in (7) can be taken from the statistical analysis of Ref. 14 and are $\eta'S=500\ \mathrm{cm}^{3/2}\ \mathrm{sec}^{-1}$, $v=106$ (Å)^3, $A=-71k\ (\mathrm{amu})^{-2}$ (Å)$^{-4}$, and $B=4.5k\ (\mathrm{amu})^{-3}$ (Å)$^{-6}$. Putting $\Omega_1=218\ \mathrm{cm}^{-1}$, we find from theory the value

$$C_1^{\mathrm{theor}}=0.010\ \mu\mathrm{C\ cm}^{-2}\ \mathrm{K}^{-1}. \tag{8}$$

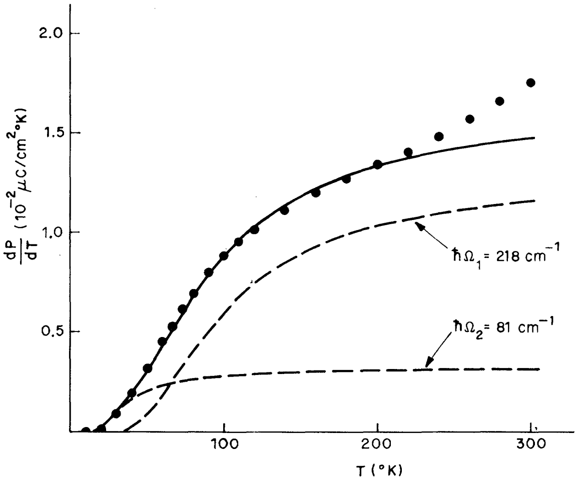

FIG. 1. The filled circles show the experimentally measured pyroelectric data for LiTaO$_3$. The two dashed curves are Einstein functions for modes at 81 and 218 cm^{-1} as marked, while the full curve is the sum of the two dashed ones.

The experimental data[12] for $\Pi\approx\Pi_{\mathrm{prim}}$ for LiTaO$_3$ as measured by the dynamic pyroelectric method are shown in Fig. 1. A very-low-temperature analysis of this data has been carried out before,[4,12] and it was observed that between 10°K and 30°K the pyroelectric coefficient followed a single-mode Einstein form if $\Omega_i\approx85\ \mathrm{cm}^{-1}$ (some evidence of mode dispersion with an energy minimum at 63 cm^{-1} was also suggested). However, at that time no such mode was known to exist, Ω_1 being the lowest of the four A_1 modes allowed for the C_{3v} symmetry of the lattice. Recent Raman measurements[17] suggest that the correct point group for LiTaO$_3$ at room temperature is C_3. The small C_3 distortion from C_{3v} enables the silent $A_2(C_{3v})$ modes to become A_1 active and Penna *et al.*[17] have now reported the lowest A_1 mode to be at 81 cm^{-1} (with the next highest at 186 cm^{-1} and then Ω_1). Although the mode strength $\mathcal{S}$ of this perturbed silent mode must be very small, its low frequency relative to the other A_1 modes, coupled with the Ω^{-4} frequency dependence of the pyroelectric coefficient, make its contribution to $\Pi_{\mathrm{prim}}^{(1)}$ significant. Indeed, since $\mathcal{S}\propto S^2/\Omega^2$ we have $C_i\propto\mathcal{S}_1^{1/2}/\Omega_i^3$ so that, other things being equal, a mode at 81 cm^{-1} can have a mode strength up to three orders of magnitude smaller than that of the dominant 218-cm^{-1} mode and still compete in terms of its contribution to $\Pi_{\mathrm{prim}}^{(1)}$.

Fitting the (10–30)°K response to an $E(\hbar\Omega_2/2kT)$ function, where $\hbar\Omega_2=81\ \mathrm{cm}^{-1}$, we now find that the experimental LiTaO$_3$ response to 200°K can be *quantitatively* fitted by just two terms:

$$\Pi(\mu\mathrm{C\ cm}^{-2}\ \mathrm{K}^{-1})\approx\Pi_{\mathrm{prim}}^{(1)}=0.013E(\hbar\Omega_1/2kT)+0.003E(\hbar\Omega_2/2kT), \tag{9}$$

as shown in Fig. 1. The independent estimate of C_1 in (8) is therefore in error (too small) by only some 25% which is well within the limits of accuracy expected.

The quality of the fit in Fig. 1 coupled with the independent estimate of the amplitude of the dominant term we find to be convincing evidence of the dominance of the lowest-order polar-mode contributions to the primary pyroelectric effect in LiTaO$_3$. It is also, therefore, strong evidence (at least for LiTaO$_3$) against the contention[2,3] that higher-order terms, and in particular those of acoustic-mode origin, normally dominate Π_{prim} in strong pyroelectrics. As pointed out in Ref. 4, this does *not* require the validity of a rigid-ion-lattice model but does suggest that only the shell-core motion which is *linearly* proportional to the ionic displacement in any polar mode is important. The deviations which develop between the form (9) and experiment above 200°K are caused dominantly by the softening of the mode Ω_1 (which is known[11] to begin at about 200°K) and represents the start of the ferroelectric behavior which, as $T\to T_C$, eventually brings about the divergence of Π in LiTaO$_3$.[14]

The present work does not answer the question[6,7] concerning the form of the higher-order acoustic-mode contributions to Π_{prim} (below 10°K there is some evidence[4] in LiTaO$_3$ that a linear T dependence may take over although the findings are not conclusive). It does, however, suggest that the point in contention may be somewhat academic in the sense that, as a relative contribution to a (moderate to) strong pyroelectric coefficient ($\Pi_{\mathrm{prim}} \gtrsim 10^{-2}$ C cm^{-2} K^{-1}) such terms are probably insignificantly small.

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Onset of an Inhomogeneous State in a Nonequilibrium Superconducting Film

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We discuss a phenomenological theory of the onset of an inhomogeneous state in a nonequilibrium superconducting film. The length scale of the initial instability is given by the geometric mean of the coherence length and an effective quasiparticle diffusion length.

Recent experiments[1-5] suggest that a superconducting film, driven sufficiently far out of equilibrium, may go into some type of mixed state. Various forms for this have been proposed: a stationary inhomogeneous state consisting of separate superconducting and normal regions,[6] or regions with different gaps[4,7]; a temporally varying state which oscillates between the superconducting and normal phases.[1] Here we discuss a phenomenological model for a nonequilibrium film which exhibits an instability towards a stationary inhomogeneous state with spatial variations in the excess quasiparticle density and the order parameter.

The presence of quasiparticles in a superconducting film reduces the gap Δ and hence lowers the superconducting condensation energy. In the absence of a magnetic field, if the quasiparticle distribution is thermal, the film undergoes a second-order transition from the superconducting to normal phase as the quasiparticle density is increased. However, if the quasiparticle distribution is nonthermal, the system may become unstable with respect to a phase separation in which some regions go normal (or have a smaller gap) and drain off quasiparticles from other regions which can then become more strongly superconducting. Chang and Scalapino[6] have shown that the μ^* model[8] for a nonequilibrium superconductor exhibits this type of instability. In order to explore the nature of this instability and to determine its characteristic spatial scale, we consider a phenomenological model similar to one which has been used to describe striations in chemical reactions.[9] Another closely related problem is that of the inhomogeneous state of ferroelectric photoconductors.[10]

Inhomogeneities can naturally arise if the thin films, their thermal contact to the substrate, or the drive are nonuniform so that different portions are driven normal at different drive intensities. Film inhomogeneities were discussed in connection with the laser-irradiation experiments of Ref. 2. Here we are interested in exploring