

Behavior of the Pyroelectric Coefficient at Low Temperatures

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The third law of thermodynamics is used to show that the primary pyroelectric coefficient as $T \rightarrow 0$ K cannot have a linear temperature dependence when the coefficient is negative and when the specific heat is proportional to T^3 . The argument is consistent with previous microscopic theories that predict a cubic temperature dependence for the pyroelectric coefficient but not with those that predict a linear temperature dependence. Electrocaloric cooling effects in lithium sulfate monohydrate below 1 K must then be smaller than predicted earlier.

The behavior of the primary pyroelectric coefficient Π_1 at low temperatures has been of considerable interest recently. Published papers on a fundamental understanding of pyroelectricity disagree in regard to the temperature dependence of Π_1 near absolute zero. The often-quoted work of Born¹ predicts a linear temperature dependence, but later work of his² predicts a T^3 dependence. Recent work of Grout and March³ predicts a linear T dependence from molecular-field theory whereas the work of Szigeti⁴ predicts a T^3 dependence. Lang⁵ has extended Born's original work to analyze his data for the pyroelectric coefficient of lithium sulfate monohydrate at low temperatures. Lang⁶ also uses the linear- T -dependent theory of Born to predict large cooling effects in lithium sulfate monohydrate below 1 K. Because Lang did not measure the pyroelectric coefficient below 4.2 K, his prediction^{6,7} of a large cooling effect relies strongly on the assumption of a linear T dependence of Π_1 . Lines and Glass⁸ recently show how Einstein functions explain the behavior of Π_1 in LiTaO_3 from 10 to 200 K. However, they point out that the temperature dependence below 10 K is still an open question. The purpose of this work is to show that the third law of thermodynamics can be used to rule out a linear T dependence for Π_1 in the limit of $T \rightarrow 0$, and to show a consistency with a T^3 dependence in most cases. The argument is limited to the case of negative Π_1 , and in practice it is sometimes difficult to determine the sign of Π_1 .

The total pyroelectric coefficient Π is related to the spontaneous polarization P_s by the equation

$$\Pi = (\partial P_s / \partial T)_{E, \sigma}, \quad (1)$$

where T , E , and σ represent the temperature, applied electric field, and elastic stress, respectively. The total pyroelectric coefficient is usually divided into two parts, $\Pi = \Pi_1 + \Pi_2$, which are called the primary and secondary pyroelectric

coefficients, respectively. The primary coefficient is the part measured at constant volume and shape and the secondary coefficient is that due to thermal expansion. At low temperatures Π_2 is proportional to T^3 because of the T^3 dependence of the thermal expansion. In this paper we are concerned only with the primary pyroelectric coefficient, given by

$$\Pi_1 = (\partial P_s / \partial T)_{E, \epsilon}, \quad (1a)$$

where the subscript ϵ refers to constant elastic strain.

The change in entropy of the material at constant strain during a field and temperature change is given by

$$dS = \Pi_1 dE + (C_E / T) dT, \quad (2)$$

where C_E is the specific heat at constant applied electric field and constant strain. The entropy at the point (E', T') is evaluated by integrating Eq. (2) from $(0, 0)$ to $(0, T')$ and then from $(0, T')$ to (E', T') . For $T = 0$ the entropy is taken as 0. Then

$$S(E', T') = \int_0^{E'} \Pi(E, T') dE + \int_0^{T'} (C_0 / T) dT. \quad (3)$$

Present theories of pyroelectrics⁹ suggest that only the acoustic phonon modes are excited at very low temperatures. In that case $C_0 = \beta T^3$, where β is a constant. However, little experimental work exists at low enough temperatures to confirm this behavior in the limit of $T \rightarrow 0$. Data down to 2 K by Lawless¹⁰ show a $T^{3/2}$ contribution for ferroelectrics, but a T^3 behavior for antiferroelectrics and paraelectrics. The $T^{3/2}$ contribution in ferroelectrics is ascribed¹⁰ to domain-wall effects rather than an intrinsic behavior. Previous calculations¹⁻⁷ on the pyroelectric coefficient have all assumed that C_0 for a pyroelectric material is of the form $C_0 = \beta T^3$. Since we are dealing with those previous calculations, I also assume a T^3 temperature dependence for

C_0 .

The first term on the right-hand side of Eq. (3) can be evaluated easily for small E' , provided the function $\Pi_1(E, T')$ is analytic in E and T' for $0 \leq E \leq E'$ and $0 \leq T' \ll \Theta$, where Θ is the Debye temperature. In that case Π_1 can be expanded in a Taylor series about $E=0$,

$$\Pi_1(E, T') = \Pi_1(0, T') + E(\partial\Pi_1/\partial E)_{E=0} + (\text{higher-order terms}). \quad (4)$$

When Eq. (4) is substituted into Eq. (3) and the higher-order terms neglected, we have

$$S(E, T) = E\Pi_1(0, T) + \frac{1}{2}E^2(\partial\Pi_1/\partial E)_{E=0} + \frac{1}{3}\beta T^3. \quad (5)$$

For $\Pi_1(E, T)$ analytic about $T=0$, the temperature dependence of $(\partial\Pi_1/\partial E)_{E=0}$ must be the same order as, or greater than, that of $\Pi_1(0, T)$. Thus, for sufficiently small values of E the second term on the right-hand side of Eq. (5) can be neglected compared with the first at any temperature as $T \rightarrow 0$. As mentioned in the introduction, we consider only the case of a negative Π_1 in the limit of $T \rightarrow 0$. If Π_1 is proportional to T , as argued by some,^{1,3,5-7} the entropy from Eq. (5) is then

$$S(E, T) = -\gamma TE + \frac{1}{3}\beta T^3, \quad (6)$$

where γ is a positive constant. For any given value of E that is small the entropy $S(E, T)$ in Eq. (5) must become negative at some low temperature as $T \rightarrow 0$. The third law of thermodynamics would then be violated since the entropy was chosen to be zero at $T=0$. If, however, Π_1 is proportional to T^3 , then the entropy becomes

$$S(E, T) = -\delta T^3 E + \frac{1}{3}\beta T^3, \quad (7)$$

where δ is a positive constant. As $T \rightarrow 0$ the entropy will always be positive provided $\delta < \beta/3E$. We then conclude that when $\Pi_1(E, T)$ is a negative analytic function in the region near and including $T=0$, the function $\Pi_1(0, T)$ must be proportional to T^3 or to some higher power of T .

The important point to consider here is whether the function $\Pi_1(E, T)$ for pyroelectrics is analytic about $E=0$ and $T=0$. From the definition of Π_1 in Eq. (1a), we note that the term $\partial\Pi_1/\partial E$ can be changed to $\partial^2 P/\partial T \partial E$, which is just $\partial\epsilon/\partial T$. The term ϵ is the dielectric constant and defined by $\epsilon = \partial P/\partial E$. If $\Pi_1(E, T)$ is analytic, the temperature dependence of $(\partial\epsilon/\partial T)_{E=0}$ must be of the same order as or greater than that of $\Pi_1(0, T)$ in order for the expansion in Eq. (4) to be valid about $E=0$ and $T=0$. Unfortunately the only mea-

surements¹¹ of $\epsilon(T)$ down to very low temperatures on some pyroelectrics were done at frequencies too high to be free of relaxation effects.¹² At 1 kHz it was found that $\partial\epsilon/\partial T = \text{const}$ over a wide temperature range. Siegwath and Morrow¹² have shown that at helium temperatures the low-frequency behavior of $\epsilon(T)$ is entirely different from the 1-kHz behavior.

The arguments^{1,3,5-7} which lead to a linear T dependence for Π_1 are based on the fact that the polarization is proportional to the mean square of the amplitude of oscillation for the acoustic phonons. For that case Lang⁵ shows that $\Pi_1 \propto B(\Theta/T)$, where B is the Born function. At low temperatures $B \propto T/\Theta$. Then $\partial\Pi_1/\partial E \propto (d\Theta/dE)T/\Theta^2$. Because $d\Theta/dE$ remains finite at $T=0$, the term Π_1 is analytic at $T=0$. Lang⁶ also considers Π_1 to be analytic in his calculation of cooling effects. Therefore in these cases where only the acoustic phonons contribute to the polarization, the primary pyroelectric coefficient cannot have a linear T dependence but rather at least a T^3 dependence.

Though the third-law argument of Eq. (5) is independent of any model, it does require that $\Pi_1(E, T)$ be analytic about $E=0$, $T=0$. Analyticity of Π_1 does depend in a very general way on a model for the polarization. We have seen that a model based on excitation of only the acoustic phonon modes does lead to an analytic $\Pi_1(E, T)$. Any other excitation responsible for polarization must also have a linear dispersion curve to give a T^3 specific heat. If an applied electric field were to lift the dispersion curve by an amount proportional to E , then Π_1 would no longer be analytic about $T=0$. Such behavior is similar to the spin-wave dispersion curve for ferromagnets, except that the frequency varies quadratically with the wave vector. In the magnetic case we have¹³

$$M_s/M_0 = 1 - AT^{3/2}e^{-\mu H/kT}, \quad (8)$$

$$C_0 = BT^{3/2}, \quad (9)$$

where μ is the Bohr magneton and H is the applied field. By analogy, the polarization and specific heat in a material with a dispersion curve for excitations of the form

$$\hbar\omega = \alpha q + \beta E \quad (10)$$

will be

$$P_s/P_0 = 1 - A_1 T^3 e^{-\beta E/kT}, \quad (11)$$

$$C_0 = B_1 T^3. \quad (12)$$

Equation (11) can be differentiated with respect to T to obtain $\Pi_1(E, T)$. We then find $\Pi_1(0, T) \propto T^2$ for $T \rightarrow 0$. Even though this $\Pi_1(E, T)$ is not analytic at $T = 0$ it may be substituted into Eq. (3) to yield

$$S(E, T)_{T \rightarrow 0} = (4kA_1/p)T^3 + \frac{1}{3}\beta T^3, \quad (13)$$

which is positive for $A_1 < p\beta/12k$. Certainly it is possible to have a nonanalytical form for $\Pi_1(E, T)$ which would have $\Pi_1(0, T) \propto T$ and still satisfy Eq. (3). However, excitation dispersion curves which are physically significant appear to rule out such a behavior. Because a negative Π_1 cannot be linear in T at low temperatures, electrocaloric cooling effects in lithium sulfate monohydrate below 1 K will be much smaller than predicted by Lang.⁶

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Work-Function Dependence of Negative-Ion Production during Sputtering

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A systematic study was made of negative-ion formation by sputtering from a Mo(100) surface with and without adsorbate layers. Correlation with the work-function change when the surface electronic state was modified by a Cs overlayer reveals a possible tunneling mechanism. Tunnel barrier widths and heights were estimated for Mo^- , O^- , H^- , and D^- from the experimental data.

The formation of secondary ions during sputtering is the basis of secondary-ion mass spectrometry (SIMS). SIMS has rapidly become an important analytic technique especially for surface and metallurgical studies. Extremely high detection sensitivity for both elements and compounds has been achieved.¹ Quantitative application of SIMS, however, is unfortunately hindered by our lack of understanding of the secondary-ion formation process. In particular, there is still no microscopic description of negative SIMS. In this Letter, I report a systematic experimental study of the negative-ion formation process through its dependence on the work function of the specimen surface. An electron tunneling model has evolved from this work which can possibly form the basis for a microscopic theory of sec-

ondary ion formation.

The energy threshold of negative-ion formation is the difference between the surface work function and the electron affinity of the ion. A lower work function enhances the electron capture process as observed during sputtering with Cs^+ ions.^{2,3} I have looked into Mo^- formation⁴ from clean Mo(100) surfaces and the formation of H^- , D^- , $^{16}\text{O}^-$, and $^{18}\text{O}^-$ from adsorbed layers on Mo(100). In this experiment I deposited a submonolayer of Cs onto the sample surface to modify the surface work function. The secondary ion yields during low-energy Ne^+ bombardment were monitored as the work function changed with the Cs coverage. Some results with K overlayers are also presented.

The experiment was performed inside an ion-