

Very-low-temperature pyroelectric response of a triglycine sulfate single crystal

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Triglycine sulfate gives a low-temperature pyroelectric response which has been studied down to 0.4 K. This pyroelectricity exhibits two principal features: (i) The pyroelectric responsivity (i.e., ratio of pyroelectric coefficient to specific heat) shows a broad maximum at about 16 K, which can be explained by the influence of a low-lying mode at $\sim 46 \text{ cm}^{-1}$, in agreement with specific-heat and spontaneous-polarization measurements, and within the framework of previously developed models; (ii) for $T < 1.9 \text{ K}$, the pyroelectric responsivity, measured with a specially designed pumped liquid- ^3He cryostat, is significantly constant down to 0.4 K. It could thus be the first experimental verification of the statement of Born and of Szigeti about the pyroelectric behavior near $T=0$.

I. INTRODUCTION

The recent interest in the low-temperature behavior of pyroelectric materials continues from several points of solid-state basic physics which are not clearly established.

(i) From Debye's theory,¹ the low-temperature heat capacity of common crystals is proportional to T^3 ; this behavior is supposed to occur when the temperature is lowered to the (10–15)-K region. In fact, since 1935, Blackmann² showed that such behavior occurs at much lower temperatures, i.e., at just a few degrees above 0 K. Furthermore, for several ferroelectric materials (and in analogy with the ferromagnetic case), Lawless^{3–5} has found experimentally a $T^{3/2}$ contribution in addition to the Debye background, leading to the very low-temperature approximation $C \simeq AT^3 + BT^{3/2}$. In the case of triglycine sulfate (TGS), the term $BT^{3/2}$ is preponderant for $T < 4 \text{ K}$, while no experimental data exist in the (0–2)-K range.

(ii) For higher temperatures (i.e., 10–20 K), the value of the pyroelectric coefficient Π seems closely related to the lattice vibrations. The first attempt to fit pyroelectric data was made by Boguslawski in 1914,⁶ who explained Ackerman's measurements on tourmaline.⁷ This was developed by Glass and Lines^{8,9} to describe the low-temperature pyroelectricity of LiTaO_3 and LiNbO_3 after a successful application of the self-consistent phonon theory,¹⁰ which included low-frequency optic modes (soft modes).

In the last ten years, after work of Lang on lithium sulfate monohydrate,¹¹ several authors have suggested the particular importance of low-lying Einstein modes, while the role played by acoustic modes was never clearly established. Theoretically, it was

proposed by Born and Huang¹² and Szigeti,^{13,14} in a slightly different way, that at a sufficiently low temperature, the primary pyroelectric coefficient is proportional to T^3 . This result is obtained for pyroelectric but nonferroelectric crystals, which do not exhibit low-frequency modes, giving just the acoustic contribution, and taking into account a T^4 temperature dependence of the internal energy U . [More precisely, $C_v = (\partial U / \partial T)$ is proportional to $\pi_1 = (\partial \Delta P_S / \partial T)$.] This is also the conclusion of Radebaugh,¹⁵ beginning with thermodynamic considerations: If $C \propto T^3$ near $T=0$, we also have $\Pi_l \propto T^3$ in the same temperature region.

In the case of TGS, recent measurements of $\Delta P_S = f(T)$ performed by Vieira *et al.*¹⁶ with the charge integration technique have shown that $\Delta P_S \propto e^{-\Theta/T}$ from 8 to 20 K with $\dot{\nu} = 45.7 \text{ cm}^{-1}$, (where $\dot{\nu} \equiv \nu/c$) in good accordance with our own determination. For the lower temperature range (2.2–4 K) they have also proposed $\Delta P_S \propto T^{3/2}$.

Our study is tentatively made to give additional experimental data on the very-low-temperature pyroelectricity of TGS, which uses for the first time a specially designed liquid- ^3He -pumped cryostat, in a temperature region sufficiently low to freeze out an eventual low-lying Einstein-mode contribution. For higher temperatures (i.e., from about 4 to 25 K), we have used a liquid- ^4He cryostat, and the influence of such a mode should be analyzed through pyroelectric response measurements in the framework of previously developed models.^{8,17}

II. EXPERIMENTAL

The best way to get highly accurate pyroelectric data is the well-known Chynoweth's method¹⁸ where

the sample is heated by a sinusoidally modulated thermal flux. This dynamic technique gives the response Π/C vs T , with Π being the total pyroelectric coefficient and C the heat capacity.¹⁹ The frequency modulation of the 1-mw He-Ne laser heating source, given by an acousto-optic modulator, is of 800 Hz, which is well below piezoelectric resonances of the TGS crystals. In these conditions, the waveform of the pyroelectric response is always the same in the (0.4–5)-K region. This was checked by observation of its shape through a PAR model TDH-9 waveform eductor, as described elsewhere.¹⁷ The samples, cut perpendicular to the polar b axis were Ag electroded; if desired, they are forced into a monodomain state by poling them under a field of 1 MV/m from over their transition ($T_c = 322$ K) down to liquid-helium temperature, the field then being removed.

The charge integration method was also used from 4 to 20 K, with the help of an operational amplifier. The change of total spontaneous polarization ΔP_S can be recorded versus T , with the electric field E across the crystal being essentially zero at all times.²⁰ The electrode area was approximately 1 cm², and an accuracy measurement of 10^{-13} C was largely sufficient in this temperature region.

A. Measurements from 25 to 4 K

The samples are mounted in a liquid-⁴He cryostat, where gaseous ⁴He at a pressure of 1 mm Hg is used

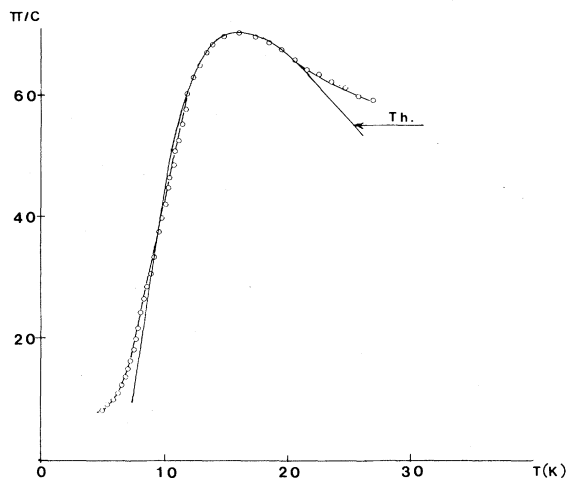


FIG. 1. Pyroelectric responsivity Π/C vs T ; the full curve represents the fitting of experimental values (circled points) using formula (4). As pointed out elsewhere,⁸ only relative measurements are accurate and an evaluation of the ordinate scale can be made from Fig. 3 (leading to Π by derivation vs T) and the use of the low-temperature specific-heat data of Lawless.

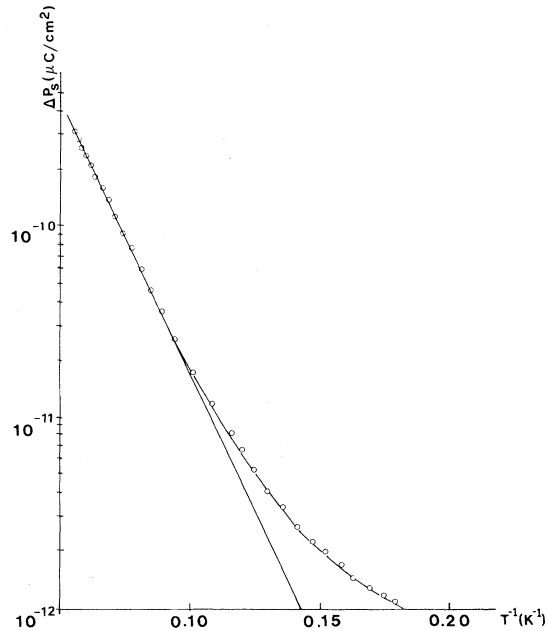


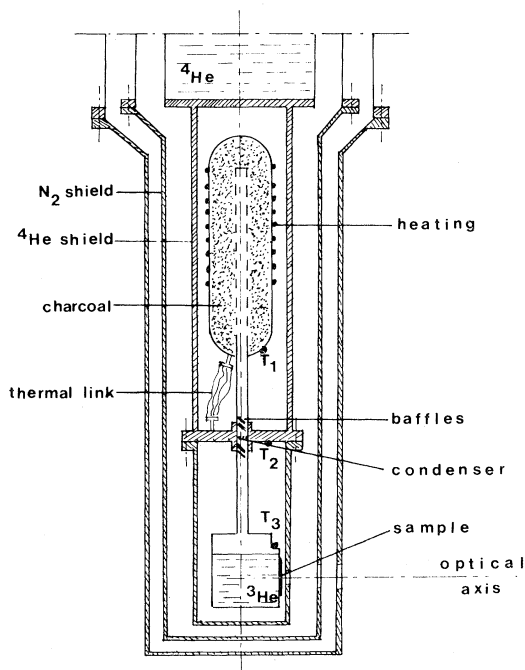
FIG. 2. Semilogarithmic plot of the change of spontaneous polarization ΔP_S vs $1/T$; the straight line corresponds to $\Delta P_S \propto e^{-\Theta/T}$, leading to formula (1) with $\Theta = 66$ K.

for thermal exchanges. A temperature regulation of ± 0.1 K, controlled with a GaAs diode (Lake Shore Cryotronics) located on the top of the sample holder, can be achieved in the (4–50)-K temperature range. To avoid a misalignment of the sample during a cooling or heating process, the laser beam is directed along the cryostat axis. The samples can be held in either a nearly unclamped or in a surface clamped manner.

The curve drawn in Fig. 1 gives the pyroelectric response Π/C of TGS from 4 to 25 K; the uncertainty is indicated by circled experimental points. It was also verified that the dielectric constant ϵ is quasiconstant ($\epsilon \approx 9.5$) in this region, using a Wayne-Kerr bridgeline Universal B221.

We note a broad maximum around 16 K, with the better responsivity being obtained with a sample of thickness $e = 0.1$ mm and electrode area $A = 7.2$ mm². The unpoled sample gives a lower responsivity (from about 15%), but the general feature of the Π/C vs T curve is not affected, representing thus the same physical phenomenon.

Figure 2 presents the semilog plots of ΔP_S vs $1/T$. For the following analysis, we determine an Einstein frequency of 45.8 cm⁻¹ obtained with a poled sample of area 1 cm² and thickness $e = 0.7$ mm. We note that the validity of an Einstein representation of ΔP_S vs T is limited to the (8–20)-K temperature range.

FIG. 3. Detail of the ^3He cryostat.

B. Measurements from 6 to 0.4 K

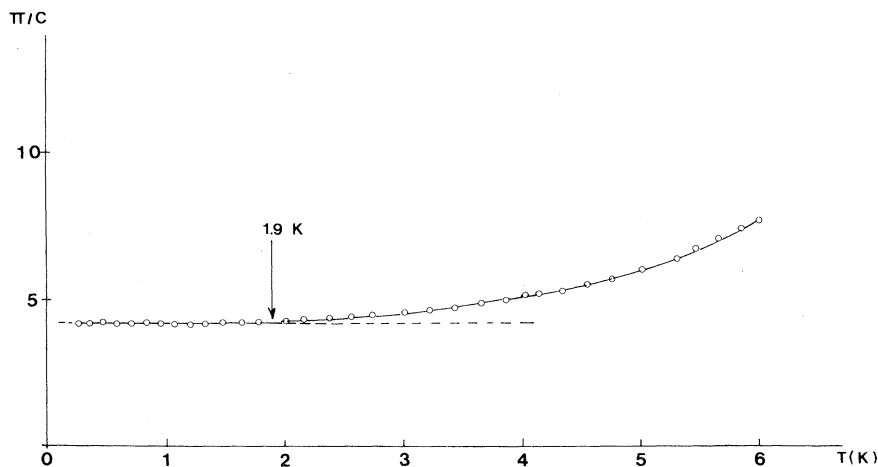
Figure 3 shows the pumped liquid- ^3He cryostat specially designed for very-low-temperature measurements.²¹ It is important to realize an adsorption pump at low temperature by setting charcoal in a sealed volume, which contains ^3He at high pressure at room temperature (≈ 90 atm). This volume is divided into two parts, soldered to a central flange through thin stainless-steel tubes. The upper part (pump) contains active charcoal, inserted in a copper grid; the lower part is the liquid- ^3He tank (10 cm³).

The central flange is fixed between two copper shields, and thermal exchanges uniquely occur from the ^4He tank to the ^3He tank by conduction through the flange via the upper shield.

The first step is to pump in liquid ^4He ; when the flange reaches a temperature of about 1.5 K, ^3He begins to be liquefied; a copper grid condenser realizes the cold point necessary to the liquefaction. Liquid ^3He begins to cool down the ^3He tank and a condensation-evaporation cycle occurs, up to a sufficiently low temperature of the ^3He tank, which is then progressively filled with liquid ^3He .²²

The lowest temperatures are obtained when the adsorption effect of charcoal occurs, i.e., for a pump temperature of about 30 K. A copper wire thermal link between the flange and the pump improves the cooling. The lowest obtained temperature is 0.3 K after a (6–7)-h working procedure.

The sample is fixed with a thin layer of a silver thermal glue on a copper plate, soldered to the liquid ^3He tank (partially clamped sample). Calibrated carbon resistances T_1 , T_2 , and T_3 give different temperature controls. The sample temperature is given by T_3 ; this was verified by exchanging the TGS single crystal against a calibrated germanium resistance (Lake Shore Cryotronics) and in the case of the dynamic method, an incident power of 50 μW gives rise to a temperature difference of 0.02 K between the resistance and T_3 . We thus consider, for very thin plates, that the sample temperature is equal to that given by T_3 , through a model VS-3 resistance bridge (Instruments for Technology) specially designed for ultralow-temperature measurements (nominal dissipated power of 10^{-12} W). Figure 4 shows from 0.4 to 6 K the response of a 25- μm -thick TGS sample. The signal is constant from 0.4 to about 1.9 K and then increases.

FIG. 4. Pyroelectric responsivity Π/C vs T in the very-low-temperature region.

III. ANALYSIS

The dynamic method used gives the response Π/C vs T , C being the heat capacity of the crystal, and Π , the total pyroelectric coefficient¹⁷

$$\Pi = \Pi_1 + \Pi_2 + \Pi_3,$$

where Π_1 is the primary pyroelectric coefficient (at constant strain); Π_2 is the secondary one, due to thermal expansion via the piezoelectric effect; and Π_3 is a term due to pure thermal expansion in directions perpendicular to the polar axis, which can be neglected in a first approximation.

A. Evaluation of the piezoelectric contribution at low temperature

Π_2 can be expressed as²³ $\Pi_2 = d_{2i} C_{ij} \alpha_j$ where $i, j = 1, 2, 3$ label coordinate directions (with direction 2 parallel to the polar axis), d_{2i} are piezoelectric compliances, C_{ij} the elastic moduli, and α_j the thermal expansion coefficients. This Einstein notation implies a summation over 12 terms in the case of TGS, which belongs to the $mm2$ class of the monoclinic crystallographic system.

An evaluation of the piezoelectric contribution at low temperature can be obtained in the following way:

(i) We suppose a linear decrease of piezoelectric compliances and elastic moduli, starting from the data given elsewhere,^{24,25}

(ii) The low-temperature values of the α_j coefficients were derived from the thermodynamic relations²⁶

$$\alpha_v = \gamma \frac{C_v \chi}{V}, \quad C_P - C_v = \frac{\alpha_v^2 VT}{\chi},$$

where α_v , γ , χ , and V are the volumetric thermal expansion, Grüneisen parameter, compressibility, and molar volume, respectively.

From the values of C_P and α_j at room temperature, we determine a Grüneisen parameter value of 1.35. Supposing γ equals const varying T and a temperature variation of each α_j proportional to α_v , we find that the piezoelectric contribution Π_2 to the total piezoelectric coefficient Π of TGS at 10 K does not exceed 15% of its value. It is thus straightforward to expect a good representation of the Π temperature dependence by only the Π_1 variations in the (8–20)-K region.

B. Low-temperature behavior of the primary effect

Following previously developed models,^{8,17} the influence of a low-lying mode on Π_1 at low temperature can be described by

$$\Pi_1 = K \left[\frac{\Theta}{T} \right]^2 e^{-\Theta/T}, \quad (1)$$

where K is a constant and Θ the Einstein temperature of this mode, and in the case of a nondispersion of the wave vector. Admitting a quadratic dispersion, Eq. (1) becomes⁸

$$\Pi_1 = K \left[\frac{\Theta}{T} \right]^{1/2} e^{-\Theta/T}. \quad (2)$$

A suitable analytical representation of the C temperature dependence of TGS in the low-temperature region is given by³

$$C = C_D \left[\frac{\Theta_D}{T} \right] + 3Rrx^2(e^x - 1)^{-2}, \quad (3)$$

where C_D is the Debye function: $x = \Theta/T$ represents the reduced frequency of one Einstein oscillator with $\Theta_D = 104$ K, $\Theta = 67.5$ K, and $r = 0.786$.³ Hence

$$\frac{\Pi_1}{C} = K \frac{x^2 e^{-x}}{C_D \left[\frac{\Theta_D}{T} \right] + 3Rrx^2(e^x - 1)^{-2}}. \quad (4)$$

From the charge integration technique (Fig. 2), we get $\Theta \approx 66$ K, for the (8–20)-K temperature range.

The computed curve, labeled as “theoretical” and drawn in Fig. 1, represents Π_1/C vs T given by formula (4); we note a maximum at $T \approx 16$ K which is very close to that observed on the Π/C experimental curve. The fitting was done by the adjustment of the K parameter in (4). We have to insist on the fact that this fitting is done taking into account the influence of one low-lying Einstein mode, regardless of the acoustic background which probably leads to the very-low-temperature discrepancy. For $T > 20$ K, the experimental deviation from the one-phonon theoretical curve is probably due to the many Einstein polar modes²⁷ which become excited and bring either a positive or negative contribution to the spontaneous polarization, added to an increasing secondary contribution.

In the case of a quadratic wave-vector dispersion, formulas (2) and (3) would lead to a theoretical maximum of the Π_1/C curve at 27.4 K which is far from the observed value. Such a dispersion of the low-lying mode at approximately 46 cm^{-1} seems thus improbable.

C. Very-low-temperature behavior

Between 0.4 and ~ 1.9 K, where the responsivity Π/C is significantly constant (signal to noise ratio is greater than 30), the low-lying mode is no longer ex-

cited. Indeed, in the harmonic-oscillator approximation, we have $N_0/N=1-e^{-\Theta/T}$ (at about 10^{-16}) at $T=1.5$ K for $\dot{\nu}=46$ cm^{-1} (where $\dot{\nu}=\nu/c$).

The unique contribution to Π_1 could thus be expected as due to acoustic phonons. Starting from a T^4 dependence law of the energy U near $T=0$, Born and Huang,¹² Szigeti,^{13,14} and Radebaugh¹⁵ have demonstrated that $\Pi_1 \propto T^3$ which is similar to the Debye specific-heat term.

Moreover, in the case of TGS, Lawless has experimentally found the influence of a $T^{3/2}$ term added to the Debye background in the value of C due to a domain-wall contribution (within the framework of a Bloch wave treatment²⁸) or a surface layer excitation.²⁹ In these conditions and according to the observed constant value of Π/C from 0.4 to ~ 1.9 K, our measurements tend to show the following:

(i) A disagreement with the spontaneous polarization data from Vieira *et al.*: If $\Delta P_S \propto T^{3/2}$, as they did claim in the (2.2–4)-K region, we should have $\Pi/C \propto 1/T$ which is not the case; Fig. 4 does not show any divergence of the responsivity.

(ii) An experimental verification of the previous theoretical developments^{12,13,15} which predicts the same temperature dependence of Π_1 and C near $T=0$, even in the case where C should be proportional to $T^{3/2}$. In our experiment, this was observed for $T < T_0$, with $T_0 \approx 1.9$ K, but this temperature may depend on the nature of the sample.²⁹

IV. CONCLUSION

The high accurate pyroelectric responsivity measurements performed on TGS single crystal from 0.4

to 25 K have shown:

(i) The predominance of a low-lying Einstein mode at $\dot{\nu} \approx 46$ cm^{-1} in the value of Π/C from 8 to 25 K. This behavior seems a general feature of pyroelectric materials.^{30,31} We also note that the frequency observed through pyroelectric and specific-heat measurements is not very far from the lower (and very strong) mode at 38 cm^{-1} given by the infrared spectrum of TGS for an electric field \vec{E} parallel to the polar axis.²⁷ The difference in frequency may occur from the dispersion of the TO branch where all allowed frequencies give their contribution to the spontaneous polarization.

(ii) For $T < T_0$, with $T_0 \approx 1.9$ K, we have found a constant value of Π/C .

(iii) These observations should allow us to propose the relation $\Delta P_S = aT^{5/2} + bT^4 + Ke^{-\Theta/T}$ for the general behavior of ΔP_S from 0.4 to 25 K in the assumption of a predominant $T^{3/2}$ contribution to the specific heat.

To rule out the uncertainty concerning the first term, measurements of ΔP_S with the charge integration technique from 0.4 to 4 K should be a good solution. However, such an experiment involves the use of very large samples (because of the very low value of ΔP_S), which was not possible in our ³He cryostat.

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