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Spontaneous Polarization of Ferroelectric Triglycine Sulfate between 2.2 and 20 K

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The temperature dependence of the spontaneous polarization of ferroelectric triglycine sulfate has been determined in the range 2.2–20 K by measuring the charge released by a large crystalline sample with a Keithley electrometer. Above ~8 K this temperature dependence is $\Delta P_s = Ce^{-\Delta/kT}$, corresponding to a two-level system with energy splitting $\Delta = h\nu_E = 9.08\times10^{-15}$ erg, while between 2.2 and 4 K it is $\Delta P_s = AT^{3/2}$. Both temperature dependences are consistent with recent specific-heat measurements by Lawless.

Low-temperature specific-heat measurements[1,2] on a number of hydrogen-bonded and displacive ferroelectrics have consistently shown a contribution proportional to $T^{3/2}$. This contribution will eventually become dominant over the Debye T^3 contribution as $T \rightarrow 0$. On the other hand, it has been suggested,[3] on thermodynamic grounds, that in zero field the specific heat and the spontaneous polarization (as $T \rightarrow 0$) should both be proportional to the same power of T; in particular $C_0(T) = B'T^3$ would require $\Delta P_s(T) = A'T^3$ (i.e., $\pi_1 = \partial P_s/\partial P_s/\partial T \propto T^2$), and in analogy with the ferromagnetic case, $C_0(T) = BT^{3/2}$ would require $\Delta P_s(T) = AT^{3/2}$. These considerations imply that accurate measurements of possible slight changes in the spontaneous polarization as $T \rightarrow 0$ would lend further support to the specific-heat findings of Lawless[1,2] if the same T dependence is observed. To our knowledge, no measurements of P_s down to 2.2 K have been reported in the literature. Thus, we think that the observations presented here are the first of their kind in any ferroelectric material. They appear to be consistent with the specific-heat observations.

The samples were single-crystal plates, ranging in size from 5 cm^2×0.5 cm to 1 cm^2×0.2 cm, made available to us by B. Jimenez from the Consejo Superior de Investigaciones Cientisicas, Madrid. Gold electrodes were attached to the main surfaces (perpendicular to the ferroelectric b axis) by evaporation in a vacuum.

The samples were placed within the can of a liquid-He cryostat in which He gas at a pressure of 1 Torr was kept, to insure good thermal equilibrium. The larger sample, with which most measurements below 4 K were performed, was sandwiched between two stainless-steel plates (which provided for the electrical contacts) and freely suspended within the can to avoid inhomogeneous stresses.

This can was temperature controlled by means of an electronic controller. The sample temperature was measured by a calibrated Cryocal germanium resistor (using the standard four-terminal potentiometric method) attached to the ground electrode of the sample. Another thermometer was placed in the external surface of the inner can, and was used to check that the temperature was the same as that at the sample. The inner can was surrounded by an outer can, which was immersed in the liquid-He bath pumped to 2.2 K. Exchange gas between the cans was used to effect heating and cooling of the sample and then removed (10^{-7} Torr) at the desired temperature. The accuracy of the temperature readings was 5×10^{-3} K. The stability of the temperature at the sample was better than 10^{-3} K.

The electrical connections to the sample were well insulated and connected by short coaxial cables to a Keithley 610 electrometer, in which the charge released after each heating step was measured and registered in a Hewlett-Packard chart recorder, with an error (due to the graphical analysis) of $\sim10^{-14}$ C. Checks on the reproducibility were made by comparing the charge released for a given temperature increase with that recovered by coming back to the initial temperature, with no significant error. Before cooling, the sample was heated to $T > T_c \simeq 322$ K, and then cooled down under a dc field of ~ 400 V/cm in order to induce a single-domain state.

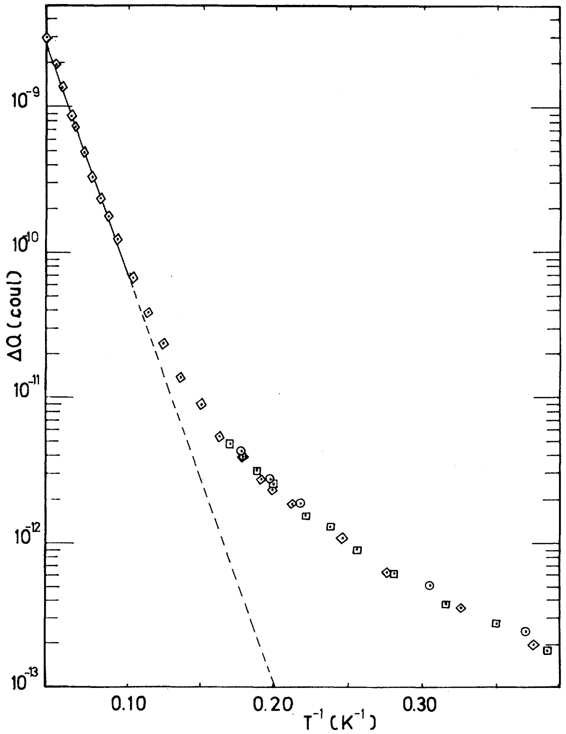

FIG. 1. Log ΔQ (charge released upon heating from 2.2 K) as a function of the inverse absolute temperature for triglycine sulfate. (The experimental points correspond to several heating and cooling runs.)

Figure 1 shows a semilog plot of the charge released, $\Delta Q = S\Delta P$, versus the inverse absolute temperature. For a two-level system involving the reversal of a dipole moment in a (spontaneous) field we have

$$P = (N_1 - N_2)\mu_s = (N - 2N_2)\mu_s = [1 - 2\exp(-2\mu_s E_s/kT)]N\mu_s, \quad (1)$$

where $N_1 \geqslant N2$ is the number of dipoles (per unit volume) of moment μ_s pointing in one direction and N_2 is the corresponding number of dipoles pointing along the opposite direction ($N_1 + N_2 = N$). Hence,

$$\Delta P \equiv P_0 - P = 2N\mu_s e^{-\Delta/kT}, \quad P_0 \equiv N\mu_s, \quad (2)$$

at temperatures low enough to justify neglecting contributions to the change in spontaneous polarization other than those due to the μ_s dipoles. Then, using $S = 5.17$ cm^2 and $\Delta Q = S\Delta P = e^{-a/T}$, we obtain

$$N\mu_s = C/2S = 14.0 \text{ esu/cm}^2; \quad \Delta = ka = 9.08\times10^{-15} \text{ erg}. \quad (3)$$

From the energy Δ we can get an associted Einstein frequency $\nu_E = \Delta/h = 45.7$ cm^{-1} in very good agreement with the Lawless value ($\nu_E = 46.9$ cm^{-1}).

It can be seen in Fig. 1 that the data fulfill Eq. (2) very well above ~ 9 K, but show a systematic deviation at lower temperatures, indicating that

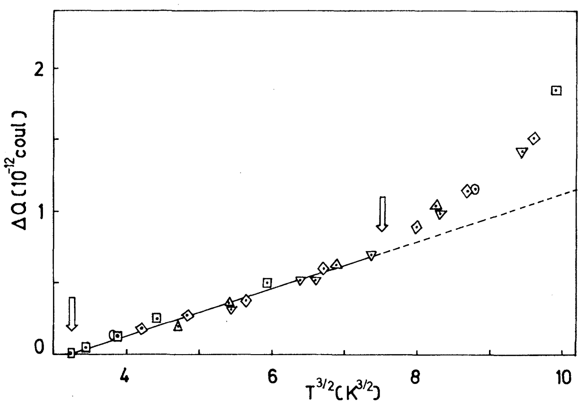

FIG. 2. ΔQ as a function of $T^{3/2}$. The two arrows mark the temperature interval within which the Lawless specific-heat data (Refs. 1 and 2) also fulfill a $T^{3/2}$ law. Note that since ΔQ is the charge released from 2.2 K, $\Delta Q = 0$ at this temperature. Extrapolating the straight line to $T = 0$ one can easily obtain the extra charge expected to be released between 0 and 2.2 K, which is $\Delta Q(0 \rightarrow 2.2 \text{ K}) = 0.54\times10^{-12}$ C.

there is another contribution to ΔP becoming dominant as $T \to 0$. Figure 2 shows a plot of the lower temperature data as a function of $T^{3/2}$. We can see that the data are consistent with

$$\Delta P = AT^{3/2},$$
$$A = (0.997 \pm 0.004) \times 10^{-4}\ \mathrm{esu/cm^2\ K^{3/2}}, \tag{4}$$

in an interval 2.2–4 K, which exactly overlaps the region where Lawless[1,2] observed the $T^{3/2}$ temperature dependence of the specific heat.

Following the same reasoning used by Radenbaugh,[3] we can check whether the value of A is compatible with the value[1,2] of the coefficient B in the expression for the zero-field specific heat:

$$C_0' = B'T^{3/2},$$
$$B' = (7.65 \pm 0.48)\ \mathrm{erg/g\ K^{3/2}}. \tag{5}$$

The third law of thermodynamics would require that, if P (the contribution to the polarization due to the μ_s dipoles) and C_0 (the specific-heat unit volume) are given, respectively, by $P/P_0 = 1 - AT - AT^{3/2} \exp(-\mu_s E/kT)$ and $C_0 = \rho C_0' = BT^{3/2}$, then the following inequality must hold:

$$A \leqslant \tfrac{4}{15} \mu_s B/k. \tag{6}$$

To evaluate the right-hand side of Eq. (6) we need a numerical value for μ_s. Assuming that the same dipoles (corresponding to internal degrees of freedom and hence not to be confused with the largest "ferroelectric" dipoles) are involved in both contributions to C_0, one can get N from the Lawless[2] data:

$$N = N_A(\rho/M)r = 0.247 \times 10^{22}\ \mathrm{dipoles/cm^3}, \tag{7}$$

where N_A is Avogadro's number, $\rho = 1.69\ \mathrm{g/cm^3}$, $M = 323\ \mathrm{g/mol}$, and $r = 0.786$ is extracted from the Schottky anomaly (or Einstein-mode contribution) of the specific heat. This leads to

$$\mu_s = P_0/N = 5.65 \times 10^{-21}\ \mathrm{esu\ cm}. \tag{8}$$

Using this value in the right-hand side of Eq. (6), one gets

$$A \leqslant 1.40 \times 10^{-4}\ \mathrm{esu/cm^2\ K^{3/2}},$$

which is compatible with the experimental value of Eq. (4).

We finally note that a recently proposed model,[4] based on the amplitude modulation of the dipole amplitude by long-wavelength Bloch waves, leads to expressions for C_0 and ΔP of the form

$$C_0 = \frac{Nk}{4\pi^2} b\left(\tfrac{5}{2} I_{3/2}\right)\left(\frac{T}{\theta}\right)^{3/2} = BT^{3/2} \tag{9}$$

and

$$\Delta P = \frac{N\mu_s}{4\pi^2} a(I_{1/2})\left(\frac{T}{\theta}\right)^{3/2} = AT^{3/2}, \tag{10}$$

where

$$\begin{aligned} I_{3/2} &= \int_0^\infty x^{3/2}(e^x - 1)^{-1}\,dx = 0.0452 \times 4\pi^2, \\ I_{1/2} &= \int_0^\infty x^{1/2}(e^x - 1)^{-1}\,dx = 0.0587 \times 4\pi^2, \end{aligned} \tag{11}$$

and b and a are dimensionless constants. From (9) and (10) one can get

$$\mu_s = \frac{5}{2} \frac{b}{a} \frac{A}{B} \frac{I_{3/2}}{I_{1/2}} k, \tag{12}$$

which reproduces the value given in Eq. (8) if we take $b/a = 2.77$.

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