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Low-temperature pyroelectric anomalies in single domain crystals of triglycine sulphate

H. M. AL-ALLAK*, R. DEWSBERRY
Viriamu Jones Laboratory, Physics Department, University College Cardiff, South Glamorgan, CF1 1XL, UK

The pyroelectric coefficient along the ferroelectric axis, of single-domain samples of triglycine sulphate has been determined on heating by means of the static technique from 85 K to within a few degrees below the Curie point, T_c. Dielectric and ferroelectric measurements carried out on some representative specimens in the vicinity of T_c revealed a normal second-order ferroelectric transition. Anomalies in the pyroelectric signal were observed at temperatures of the order of 125, 165 and 270 K which have analogues in previous electrical and structural measurements.

1. Introduction

The ferroelectric nature of triglycine sulphate (TGS), $(NH_2CH_2COOH)_3H_2SO_4$, was first discovered in 1956 by Mathias *et al.* [1]. The crystal is one of a very few ferroelectrics known to exhibit a second-order phase transition. Hoshino *et al.* [2] suggested that the main reversible dipole is associated with the non-planar glycine ion, G_I, and this is now generally accepted. This reversal is thought to be associated with the flipping motion of the weakly hydrogen-bonded NH_3^+ group to the opposite side of the $C–CO_2$ plane through a rotation of the $C–C^N$ bond [3–5].

Previous pyroelectric measurements on crystalline triglycine sulphate by Chynoweth and Feldman [6], using the dynamic technique and carried out to temperatures down to 133 K, have failed to reveal anomalous behaviour. Mangin and Hadni [7, 8] using a similar technique but down to liquid helium temperatures, have reported anomalous behaviour at about and below 16 K, but not above this temperature.

Despite these negative results, there is evidence of various anomalies in the behaviour of TGS in the temperature range 16 K to room temperature and these will be commented on later in this paper. Hence, it was decided that pyroelectric investigations should be undertaken in this laboratory as part of a comprehensive study of the electrical properties of the material. In the present investigation the pyroelectric current under short circuit conditions was measured on heating, employing the static technique and a current measuring instrument similar to that described by Lines and Glass [9]. The theory of the experiment is also given in this reference which indicates that the area under the current–time curve for a small temperature increment, ΔT, and corresponding time increment, Δt, is the corresponding change in the spontaneous polarization, ΔP_s, scaled by the electrode area. The pyroelectric coefficient, λ, is then given by the ratio $\Delta P_s/\Delta T$, provided that λ is constant.

2. Experimental procedure

The investigated samples were clear, free from cracks, and were cut with their main faces perpendicular to the ferroelectric axis. Silver evaporated electrodes were deposited on these main faces so that the samples were in the form of parallel plate capacitors. The samples had areas in the range 0.86–0.45 cm^2 and thicknesses in the range 0.037–0.1 cm.

The experiments were carried out in a storage cryostat, especially designed to minimize thermal shock. Temperature control, involving a copper–constantan thermocouple mounted on the cryostat finger at the base of the sample, was by means of a Thor temperature controller Model 3010 II in conjunction with an electronic ramp-generating programmer which allowed accurately controlled heating and cooling regimes and temperature stability to within $\pm$ 0.05 K. The samples were mounted in an unclamped fashion.

The pyroelectric current was measured using a current to voltage convertor of high stability and fast response based on National Semiconductor operational amplifier type LP351N feeding a Hewlett–Packard $X–Y$ recorder type 7035A with external timebase, type Hewlett–Packard 17108A. The limit to the accuracy of measurement of ΔP_s, and hence λ, of $\pm$ 5% resulted from current fluctuations from the sample which far outweighed inaccuracies inherent in the current measuring apparatus.

Before each pyroelectric investigation, the samples were poled by heating to above the ferroelectric phase transition temperature, T_c, within the cryostat and then cooling through T_c while maintaining a large d.c. field (between 680 and 1800 V cm^{-1}) across the

* *Present address*: Department of Physics, University of Durham, Science laboratories, South Road, Durham DH1 3LE, UK.

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samples. This field was removed when room temperature was reached during the sample cooling-down procedure to low temperatures which employed a cooling rate of 0.2 K min^{-1}.

After reaching the desired low temperature the pyroelectric current was measured on heating as follows. The temperature was increased by one degree at the conveniently slow rate of 0.5 K min^{-1} while recording the pyroelectric signal. Because the sample temperature always lagged behind that of the cold finger during ramping, the pyroelectric current was recorded for a longer period (generally around 1 min) until it approached zero when temperature equilibrium was finally reached. This procedure was then repeated at different temperatures within the range of measurements. The heating rate between temperature intervals was again kept at 0.5 K min^{-1}. Before each measurement was made the temperature was maintained for about 5 min to ensure temperature homogeneity within the samples.

3. Experimental results

In order to assess the ferroelectric quality of the crystal used, several representative samples were used to investigate the temperature dependence of the spontaneous polarization, P_s, and the relative permittivity, ε', using the well-known Sawyer–Tower method and an a.c. bridge, respectively. P_s was found to decrease continuously to zero on approaching T_c, giving a linear relationship between P_s^2 and temperature, T, in the vicinity of T_c following the prediction of the Devonshire theory [10–12] for the second-order ferroelectric phase transition. The value of P_s at room temperature is about 2.85 $\mu C\,cm^{-2}$ in agreement with the results of Tsedrick *et al.* [13], Hoshino *et al.* [14] and Jona and Shirane [15].

The anomalous rise of ε' with temperature was continuous when heating through T_c, again indicating a second-order ferroelectric transition. The material showed a transition temperature of ≈ 322.4 K, a value very close to those already reported in the literature [14, 15]. The values of the Curie constants above $T_c(C_p)$ and below T_c (C_f), 3500 and 1500 respectively, are similar to those reported previously by other workers such as Gonzalo [16], Hoshino *et al.* [14] and Felix *et al.* [17]. This gives a value of 2.5 for C_p/C_f which is very close to the theoretical value of 2.4 for adiabatic conditions [18].

A typical pyroelectric signal recorded at 91.5 K is shown in Fig. 1. Region A extends for a period of 2 min and corresponds to the temperature ramping-up time. As the sample temperature finally reaches that of the cold finger, the pyroelectric signal gradually decreases to zero, giving rise to Region B. It should be noted that low-frequency current oscillations of about 0.17 Hz (probably of a piezoelectric nature) are present on the signal as the temperature is ramped up. However, at temperatures above about 115 K, the pyroelectric signal became sufficiently large to mask off these oscillations.

The temperature dependence of λ over the range 85 K to within few degrees of T_c is shown in Fig. 2, as a semi-log plot of λ versus T. The value of λ at 318 K of $9.5 \pm 0.6 \times 10^{-8}$ C $cm^{-2}K^{-1}$ is in good agreement with those calculated from the results of Krem-

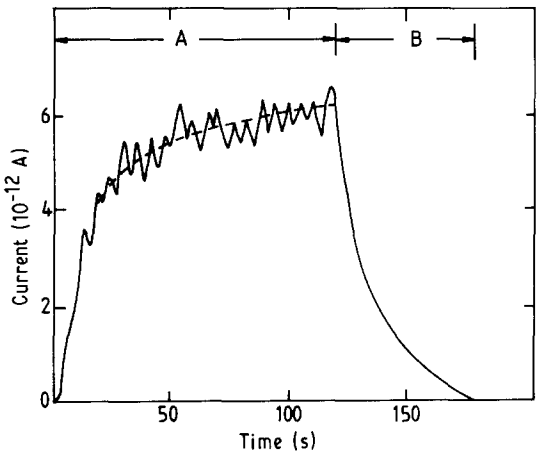

Figure 1 Showing a representative pyroelectric signal recorded at 91.5 K.

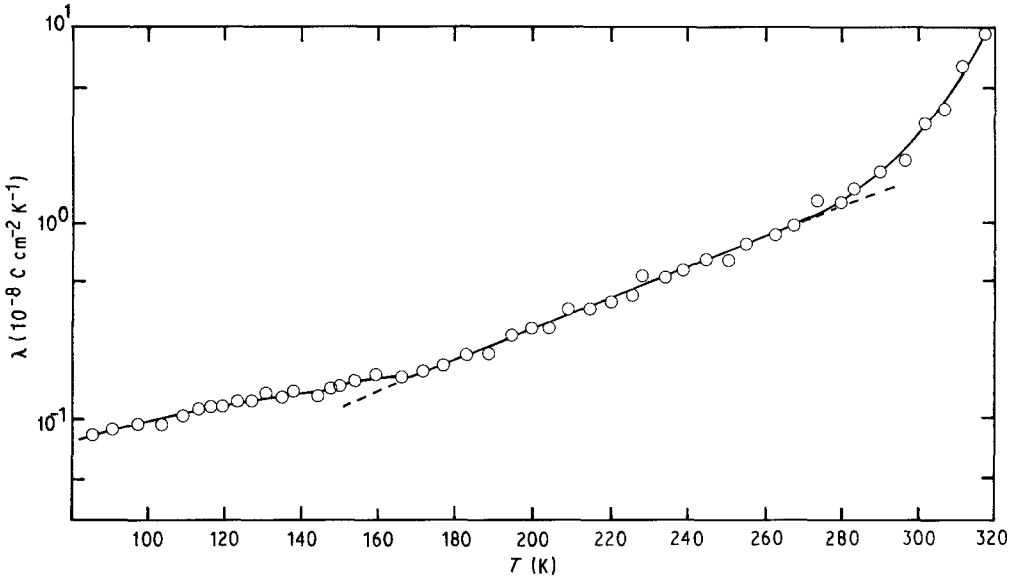

Figure 2 Dependence of log λ on temperature.

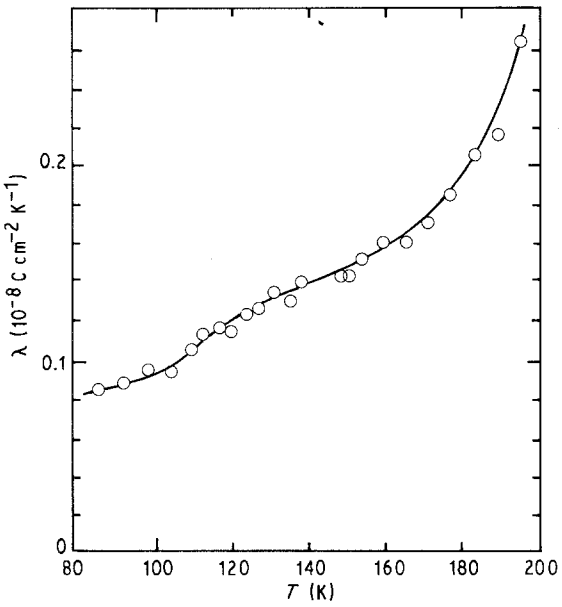

Figure 3 A plot λ versus T Showing a small bulge centred around 125 K.

enchugskii and Samoilov [19] and of Felix *et al.* [17] using the dynamic and the static techniques, respectively. However, comparison at lower temperatures was not possible because the cited data were in arbitrary units. The plot is seen to be linear over the temperature range 165–270 K. If a plot of λ versus T at the lower temperature end is made, a small bulge can then be seen more noticeably around 125 K, Fig. 3. The position and magnitude of this bulge varied somewhat between samples.

Preliminary experiments carried out at the lower temperature end, before the linear ramping of temperature was adopted as the standard heating technique, involved much more rapid heating of the sample. The temperature programmer was set so as to give a temperature increment of 1 K as a discontinuity. The ratio of rise in temperature of the sample was therefore dependent on the thermal response of the total system involving both the cryostat cold finger and sample in a much more dramatic fashion than for the linear ramping method. When using this method, the resulting plot of λ versus T showed a monotonic increase in λ with temperature with barely detectable anomaly bulge at about 100 K. Furthermore, no low-frequency oscillations on the pyroelectric signals were observed. This set of experiments demonstrates that the anomalous behaviour, observed in a more pronounced fashion in the temperature-ramping experiments, can be masked by inappropriate temperature regimes.

4. Discussion

Before commenting more fully on the present pyroelectric measurements, attention will be given to previous appropriate studies of the behaviour of TGS down to low temperatures. Blinc *et al.* [20], who carried out proton magnetic resonance studies, observed that the temperature dependence of the second moment of the absorption lines shows two anomalies, one at the Curie point and the other centred on about 153 K. This lower temperature effect was attributed to a simple reorientation process of the NH_3^+ group. Hoshino [21], on the other hand, proposed a 35° flipping motion for the G_I dipole between two sites, related by the mirror plane perpendicular to the b-axis, as a mechanism to account for the value of the second moment at 160 K because this was held to be too low to be associated with the freezing in of the NH_3^+ group.

Al-Eithan [22] carried out Raman studies on TGS and concluded that the NH_3^+ stretching vibrational mode (associated with G_I), in addition to other internal modes, shows a linewidth anomaly at about 110 K, indicating a phase transition. Corresponding work on deuterated TGS showed a linewidth transition at about 134 K. The large isotropic shift was considered to be a good indication that the NH_3^+ and corresponding ND_3^+ groups were intimately bound up in the transition. It is further stated that these structural changes are intimately connected with NH_3^+ group orientation and that this is supported by results of ultrasonic investigations, as will be noted below. The Raman investigation also showed that the lattice vibrational mode (around the 1 0 0 direction) was affected by the transition, as well as the linewidth anomaly for the internal SO_4 mode at 90 cm^{-1}. This last point was said to be due to a change in the bond system, resulting in changes in G_I behaviour. Corresponding ultrasonic measurements showed that small changes in sound velocity, elastic constants and increased attenuation were associated with the proposed phase transition indicating a small cooperative change in the molecular dynamics of the NH_3^+ groups. Thermal expansion experiments indicated changes in behaviour at about 120 K and also at about 270 K.

As explained in Section 3, our graphs of log λ versus T show linear behaviour in the temperature range $\sim$ 165 to $\sim$ 270 K. The deviation from linearity at about 165 K may well be related to the same structural changes reported by Blic *et al.* at about 153 K. While the change in shape of the graphs at about 270 K relates well to the reports of several workers, Roder *et al.* [23], who studied the domain structure of TGS down to low temperatures using scanning electron microscopy, found that the domain structure did not change with temperature below 260 K, and correspondingly, Domansky [24] reported a large increase in the coercive field. The change in behaviour at 270 K reported by Al-Eithan has been mentioned above.

The bulge in our curves at about 125 K also relates reasonably well with the work of Al-Eithan but, as already mentioned, shows some variation between samples. This variation may be due to differences in thermal history or variation in the impurity content between samples influencing the behaviour of the G_I dipole.

Our data indicate a slow increase in the spontaneous polarization down to 85 K (Fig. 4) also in agreement with the previous works of Chynoweth and Fieldman [6] and Mangin and Hadni [7, 8]. (The values of P_s in Fig. 4 were obtained by measuring the

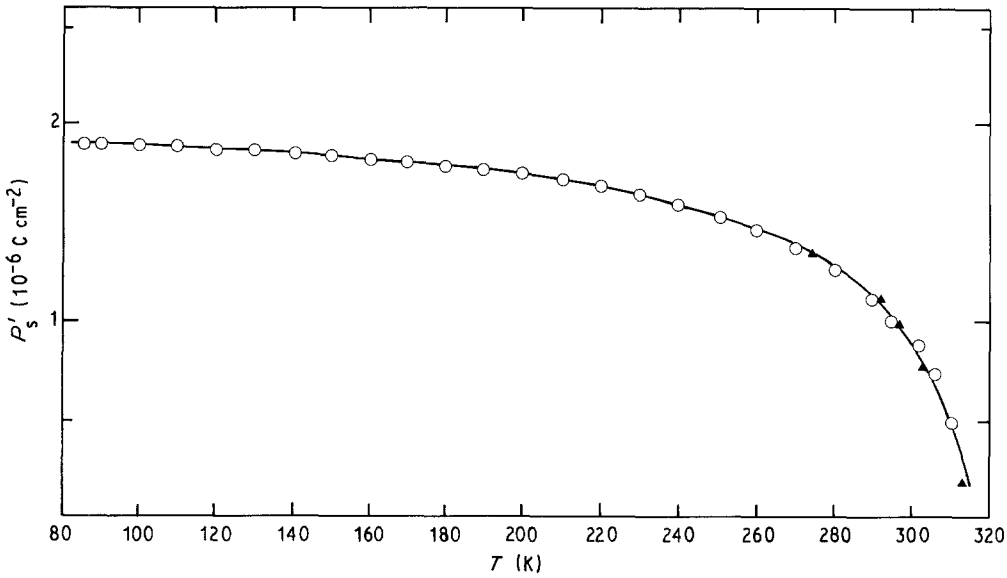

Figure 4 The behaviour of P_s with temperature. (○) Pyroelectric measurements, (▲) data obtained using the Sawyer–Tower technique.

charge under a plot of λ versus T, not shown here.) Also shown in Fig. 4 are the data obtained using the Sawyer–Tower circuit in the vicinity of T_c, which are seen to be very similar to the pyroelectric measurements. This further confirms the validity of the pyroelectric technique used in this work and indicates efficient poling procedure. The suggestion made by Ganesan [25] that TGS might have a phase transition at low temperatures, like that of Rochelle salt, to become paraelectric, is clearly not borne out over the temperature range of our experiments.

The present work has clearly indicated the value of pyroelectric investigation as pointer to the presence of anomalous behaviour which may then be investigated by more appropriate techniques. It has also demonstrated that careful control of the temperature regime is extremely important and that the static method does have an advantage over and above the dynamic method. This is particularly the case if the thermal capacity of the sample is a function of temperature.

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References

1. B. T. MATHIAS, C. E. MILLER and J. P. REMEIKA, *Phys. Rev.* **104** (1956) 849.
2. S. HOSHINO, Y. OKAYA and R. PEPINSKY, *ibid.* **115** (1959) 323.
3. M. I. KAY and P. R. KLEINBERG, *Ferroelectrics* **5** (1973) 45.
4. K. ITOH and T. MITSUI, *ibid.* **5** (1973) 235.
5. S. R. FLETCHER, E. T. KEVE and A. C. SKAPSKI, *ibid.* **14** (1976) 775.
6. A. G. CHYNOWETH and W. L. FELDMAN, *J. Phys. Chem. Solids* **15** (1960) 225.
7. J. MANGIN and A. HADNI, *J de Phys. Lett.* **39** (1978) 447.
8. *Idem, Phys. Rev. B* **27** (1983) 7730.
9. M. E. LINES and A. M. GLASS, "Principles and Applications of Ferroelectrics and Related Materials" (Claredon Press, Oxford, 1977) p. 143.
10. A. F. DEVONSHIRE, *Phil. Mag.* **40** (1949) 1040.
11. *Idem., ibid.* **42** (1951) 1065.
12. *Idem., Adv. Phys.* **3** (1954) 85.
13. M. S. TSEDRIK, G. A. ZABOROVOSKI, N. P. DEMILDOVICH and L. N. MARGOLIN, *Kristal Technik* **10** (1975) 55.
14. S. HOSHINO, T. MITSUI, F. JONA and R. PEPINSKY, *Phys. Rev.* **107** (1957) 1255.
15. F. JONA and G. SHIRANE, *ibid.* **117** (1960), 139.
16. J. A. GONZALO, *ibid.* **144** (1965) 662.
17. P. FELIX, P. GAMOT, LACHEAU and Y. RAVERDY, *Ferroelectrics* **17** (1978) 543.
18. S. TRIEBWASSER, *I.B.M.J. Res. Develop.* **2** (1958) 212.
19. L. S. KREMENCHUGSKII and V. B. SAMOILOV, *Sov. Phys. Crystall.* **12** (1968) 543.
20. R. BLINC, S. DETONI and M. PINTAR, *Phys. Rev.* **124** (1961) 1036.
21. R. HOSHINO, *J. Phys. Soc. Jpn* **17** (1962) 119.
22. F. Y. Al-EITHAN, PhD thesis, University of Wales (1983).
23. A. RODER, C. SCHEIDING and H. MAACK, *Ferroelect. Lett.* **44** (1982) 641.
24. S. DOMANSKI, *Proc. Phys. Soc. London* **B27** (1958) 306.
25. S. GANESAN, *Acta. Crystallogr.* **15** (1962) 81.

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