Heat Capacity in Magnetic and Electric Fields Near the Ferroelectric Transition in Tri-Glycine Sulfate

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Specific-heat measurements are reported near the Curie temperature ($T_C = 320$ K) on tri-glycine sulfate. Measurements were made on crystals whose surfaces were either non-grounded or short-circuited, and were carried out in magnetic fields up to 9 T and electric fields up to 220 V/cm. In non-grounded crystals we find that the shape of the specific-heat anomaly near T_C is thermally broadened. However, the anomaly changes to the characteristic sharp λ -shape expected for a continuous transition with the application of either a magnetic field or an electric field. In crystals whose surfaces were short-circuited with gold, the characteristic λ -shape appeared in the absence of an external field. This effect enabled a determination of the critical exponents above and below T_C , and may be understood on the basis that the surface charge originating from the pyroelectric coefficient, dP/dT, behaves as if shorted by external magnetic or electric fields.

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The discovery of a continuous-phase transition in tri-glycine sulfate, $[(CH_2NH_2CO_2H)_3 \cdot H_2SO_4]$ (TGS) showing the dielectric analog of ferromagnetism, was made fifty-years ago at Bell Laboratories¹. This transition was considered ideal in that critical exponents, as determined from the electric polarization, P, and the dielectric constant, ϵ , are equal both above and below $T_C^{2,3}$. Today pyroelectric sensors based on TGS have technological importance for the development of flat-panel displays⁴ and room-temperature detectors of far-infrared laser radiation^{5,6}. Their sensitivity originates from a large pyroelectric coefficient⁷, dP/dT, low Curie temperature, $T_C = 320$ K, and low coercive electric field¹, $E_c = 220$ V/cm.

In an earlier review of the critical exponents for TGS, Gonzalo³ pointed out that although they are well-behaved above and below T_C in P and ϵ measurements, the paucity of data points in the vicinity of T_C have prevented a determination using specificheat data. Consequently, many high-quality specificheat measurements have been made to characterize T_C and to complete the set of critical exponents for TGS^{7,8,9,10,11,12,13,14,15,16,17,18}. Adiabatic measurements⁷ made near T_C on powdered TGS samples were puzzling in the sense that for the first time, in the field of ferroelectrics, the specific-heat anomaly for a continuous transition was not of the λ type. Instead the transi-

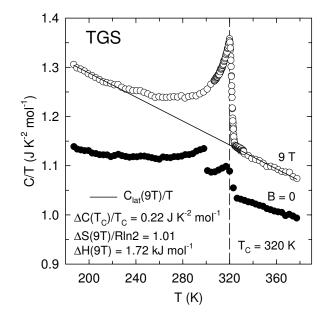


FIG. 1: The temperature dependence of C/T at 0 T (solid black circles) and 9 T (open circles) in the regime of $T_C=320$ K for a non-electrically grounded (free-standing) TGS single crystal. Data from measurements in fields as low as 3 T, not shown, are congruent with those for 9 T.

tion was thermally broadened, giving an entropy change,

 $\Delta S=2$ J K $^{-1}$ mol $^{-1}$, that was much less than the expected $R\ln 2^{19}$. High-sensitivity ac measurements of the Seidel type 20 made on short-circuited crystals, showed a pronounced λ anomaly at T_C^{-12} . Shortly afterward, high-precision ac measurements reproduced the λ anomaly, and the specific-heat data were shown to depend logarithmically on $(T-T_C)$ in a range $T-T_C \leq 20~\mathrm{K}^{14}$ above T_C . Seeking to clarify the experimental situation, Strukov 16 performed high-accuracy adiabatic specific-heat measurements and set limits on the relative measurement accuracy needed for observing critical fluctuations near T_C . In the low-temperature limit, specific-heat measurements 21,22 demonstrated the surprising result that surface excitations, (up to 250 microns thick) cause a $T^{3/2}$ term in the bulk heat capacity.

It was therefore anticipated that because: (a) surface excitations are known to affect the bulk thermodynamic properties at low-temperature giving rise to a $T^{3/2}$ term²², (b) non-grounded powders do not give the expected λ anomaly at $T_C^{\,7}$, (c) ac measurements show a pronounced λ anomaly with a logarithmic critical fluctuations^{14,18}, and (d) high-precision adiabatic measurements show a smearing of the transition and do not have a logarithmic singularity¹⁶, surface excitations generated from the pyroelectric coefficient, dP/dT, were affecting the nature of the specific-heat anomaly near T_C .

In this Letter, we report measurements of the specific heat made on crystals whose surfaces were either non-electrically grounded (free standing) or short circuited with a thin layer of gold. The data for non-electrically grounded crystals in zero magnetic or electric fields show that the shape of the specific-heat anomaly

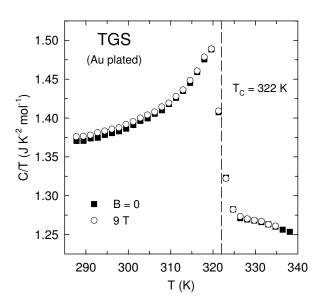


FIG. 2: The temperature of C/T near T_C is shown for short-circuited (gold plated) TGS crystals at 0 T (solid squares) and 9 T (open circles). One sees that when the surface charge is shorted with a thin layer of gold, the characteristic λ -shape appears and shows no magnetic-field dependence.

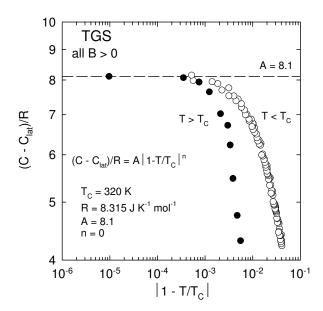


FIG. 3: Log-log plot of the excess heat capacity versus reduced temperature showing the λ anomaly above T_C (solid circles) and below T_C (open circles). Results for the critical exponents obtained on each side of T_C are given in the plot legends. As an independent check, $RA/T_C = 0.21$ J K⁻² mol⁻¹, which is equal to the value of the specific-heat discontinuity at T_C given by $\Delta C(T_C)/T_C$, shown in Fig. 1

near T_C is thermally broadened, giving an entropy change smaller than the expected $R \ln 2$, in agreement with previous results of Hoshino $et~al.^7$. The anomaly changes into the characteristic λ -shape expected for a continuous transition with the application of either magnetic or electric fields giving an increased entropy change $\Delta S = 5.8~\mathrm{J~K^{-1}~mol^{-1}} = R \ln 2$. In crystals whose surfaces were short-circuited with gold, the characteristic λ -shape appeared at T_C with no applied magnetic or electric fields.

The TGS crystals used for the experiments were grown from supersaturated solutions of the components by evaporation. Crystal quality was checked by examining the sharpness and reversibility of the transition at T_C as determined by variable-temperature capacitance measurements²³. Specific-heat measurements were made using a thermal-relaxation technique²⁴. Thermal-relaxation calorimetry provides a means of determining a sample's specific heat by measuring the thermal response of a sample/calorimeter assembly to a change in heating conditions. Crystal dimensions for the TGS used in the magnetic field measurements were 2.85 mm x 3.78 mm x 1.11 mm with a mass of 17.89 mg. Crystal dimensions for the TGS used in electric field measurements were 3.74 mm x 3.55 mm x 1.15 mm with a mass of 22.38 mg.

Figure 1 shows the temperature dependence of C/T versus T in the vicinity of T_C , for 9 T on non-grounded (free-standing) TGS crystals with the magnetic field applied parallel to the easy b-axis. At zero magnetic field (solid circles), there is a broad anomaly separated into

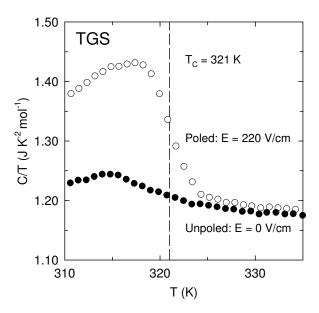


FIG. 4: Temperature dependence of C near T_C as a function of electric field, 0 V/cm (solid circles) and 220 V/cm (open circles).

two peaks near T_C . These zero-field results are strikingly similar to those reported nearly fifty years ago by Hoshino et al.⁷. A previous theory developed for Rochelle salt¹⁹, showed that the free energy for a continuous transition could be approximated by a polynomial in the second and fourth power of the order parameter-the electric polarization along the easy b-axis. Applying these results to TGS. Hoshino et al. found a linear decrease of P^2 as a function of temperature approaching T_C . Using polarization and dielectric susceptibility data, Hoshino et al. were able to identify the numerical values of the parameters in Mueller's model¹⁹. However, the experimental entropy change at T_C was 33 percent lower than the theoretical value. In those measurements the TGS was made into a powder, and the sample was not electrically grounded. In agreement with our zero-field results on a non-electrically grounded crystal, their results had an entropy change of 2 J K⁻¹mol⁻¹, and did not have the characteristic λ shape. After cooling the non-grounded crystal back to room temperature and applying a 9 T magnetic field at 300 K, the characteristic λ shape reappears (open circles), see Fig. 1. Integration of 9 T the C/T versus T curve gives the entropy change previously unaccounted for in our zero magnetic field data in addition to the earlier data by Hoshino et al.⁷, specifically $\Delta S = 5.8 \text{ J K}^{-1} \text{ mol}^{-1} = R \ln 2$, as indicated in the legend of Fig. 1.

This result, combined with Lawless's observation²² that surface excitations significantly contribute to the bulk heat capacity, suggested that the surface charge emanating from the pyroelectric coefficient, dP/dT, was behaving as though being shorted by the external magnetic field. In order to test this hypothesis, TGS crystals were short-circuited by coating all sides with a thin layer

of gold. The same measurements shown in Fig. 1 were made on these gold-coated crystals. Figure 2 shows the temperature dependence of C/T in the vicinity of T_C for magnetic fields on short-circuited (gold-plated) TGS crystals in zero magnetic field (solid squares) and 9 T (open circles) with the magnetic field applied parallel to the easy b-axis. The results show that the λ anomaly appears in the absence of a magnetic field in the short-circuited (gold-plated) TGS crystals. There is no additional magnetic-field dependence to within experimental error.

Figure 3 shows the excess specific heat, defined as the quantity $(C - C_{lat})$, normalized to the universal gas constant, R, versus reduced temperature, $(1 - T/T_C)$, on a log-log scale. The lattice specific heat, C_{lat} , was represented by a linear fit from the ferroelectric phase to the paraelectric phase, as indicated in the 9 T curve of Fig. 1. The curves above and below T_C approach the same horizontal line with n = 0 and $A = 8.1 \text{ J K}^{-1} \text{ mol}^{-1}$ in the expression $(C - C_{lat})/R = A|1 - T/T_C|^n$. As an independent check of the critical exponents, we note that $RA/T_C = 0.21 \text{J K}^{-2} \text{ mol}^{-1}$ (obtained from the fit), is equal to the value of the specific-heat discontinuity at T_C given by $\Delta C(T_C)/T_C$, shown in Fig. 1, and an exponent of n = 0 signifies a logarithmic singularity above and below T_C^{25} . The latter result appears to be consistent with renormalization group theory in which a single unstable fixed point determines the exponents 26 .

Lastly, we provide another verification of this effect in electric field²⁷, as shown in Fig. 4. Measurements of non-grounded (free-standing) TGS crystals in zeroelectric field (solid circles) and in an applied electric field of 220 V/cm (open circles) are shown in this figure. Qualitatively mirroring the magnetic field results shown in Fig. 1, the anomaly is broad near T_C in zeroelectric field, while the characteristic λ -shape appears, albeit more broadened than those observed in magnetic fields, in a modest electric field. In context of our data the magnetic field dependence appears to be extrinsic in origin. Because the specific-heat data in magnetic field enabled a determination of the critical exponents, it is not exactly an artifact. We note that similar observations involving the magnetic response of space charges at the surface of a dielectric have been made by Catalan²⁸. It was shown that the space charge at surfaces²⁹ contributes to an extrinsic magnetic field effect in dielectrics.

In summary, we have demonstrated that the surface charge on non-electrically grounded TGS crystals interacts with external magnetic and electric fields. This effect may be understood on the basis that the surface charge originating from dP/dT behaves as if shorted by the external fields. Because many heat capacity measurements involve measuring a temperature-time derivative, added contributions originating from dP/dT are easily realized. Using data obtained in magnetic fields, critical exponents were derived corresponding to the expression $(C-C_{\rm lat})/R = A|1-T/T_C|^n$, thereby completing the set for TGS³. An exponent of n=0 signifies a logarithmic

singularity above and below T_C . The ability to effectively "short" the surface charge with an external magnetic or electric field on free-standing crystals overcomes experimental difficulties from additional background subtractions and heat leaks from the electrical grounding leads. Our observations appear to be consistent with a recent detailed model that explains the magnetic response of space charge at a surface of a dielectric material²⁸.

Acknowledgments

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