Brief Reports

Origin of the $T^{3/2}$ specific-heat term in triglycine sulfate at low temperatures

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Two sets of specific-heat experiments on single crystals of ferroelectric triglycine sulfate (TGS) at low temperatures are reported aimed at discriminating between bulk and surface contributions to the unusual $T^{3/2}$ specific-heat term. In the first set, two large crystals with small surface-to-volume ratios (S/V) were measured, where one (poled) crystal was single domain and the other crystal multidomain. In the second set, two assemblies of small TGS crystals with large S/V values were measured. The data demonstrate that a *surface* excitation is responsible for the $T^{3/2}$ term in TGS, and an unusually thick ($\simeq 0.02$ cm) surface layer is indicated.

I. INTRODUCTION

A well-defined $T^{3/2}$ specific-heat term has been demonstrated below about 5 K in the ferroelectrics BaTiO$_3$, LiNbO$_3$, triglycine sulfate (TGS), and potassium dihydrogen phosphate (KDP).[1] This contribution, which is in excess of the usual T^3 Debye term, was originally believed due to domain-wall oscillations.[1] However, subsequent measurements on relatively *small* samples of the *incipient* ferroelectrics SrTiO$_2$ and TiO$_2$ also revealed a $T^{3/2}$ term, and a surface excitation was postulated.[2]

Radebaugh[3] has suggested on thermodynamic grounds that in zero electric field the spontaneous polarization and specific heat should *both* be proportional to the same power of the temperature (as $T \rightarrow 0$). Subsequently, Vieira *et al.*[4] measured the spontaneous polarization difference $P_s(T = 0)$ $- P_s(T)$ in TGS and found a $T^{3/2}$ dependence below 4 K, in agreement with Radebaugh's theory. Also, Vieira *et al.* have recently reported similar measurements on BaTiO$_3$ and LiNbO$_3$ which further demonstrate the $T^{3/2}$ term.[5]

Therefore, while there is considerable experimental evidence for a $T^{3/2}$ specific-heat term in ferroelectrics, there is virtually no understanding of the origin of this unusual excitation. The theoretical models, to which we shall return below, deal exclusively with *bulk* phenomena. The purpose of this paper is to report specific-heat measurements aimed at discriminating between bulk and surface phenomena contributing to this $T^{3/2}$ term. The ferroelectric chosen here is TGS, for the following reasons: First, large single crystals of TGS are easily grown, and complete poling of TGS at room temperature can be accomplished

with modest electric fields. Second, TGS has the largest low-temperature specific heat of the ferroelectrics mentioned above so that addenda corrections are minimized.

II. EXPERIMENTAL METHODS AND RESULTS

Two sets of measurements were made, the first set on two large single crystals wherein one crystal was poled; and the second set on two assemblies of small TGS crystals. The purpose of the former experiments was to study the $T^{3/2}$ term in both a multidomain and a single-domain crystal wherein the surface-to-volume ratios (S/V) were small. The purpose of the latter experiments was to study the $T^{3/2}$ term at large S/V values. All crystals studied were from the same batch grown by the method of Nitsche.[6] (The TGS crystal reported in Ref. 1 was also from this batch.)

The two large crystals were shaped pellets approximately 1.5 cm in diam, 0.7 cm thick, and Manganin heaters (370 Ω) were wrapped on the periphery. The major faces were perpendicular to the polar axis, and silver electrodes were painted on the faces of one of the crystals. Carbon-chip resistance thermometers (14 mg) and Manganin thermal links were fixtured to the samples with GE 7031 varnish, and thin Manganin voltage leads were silver epoxied to the electroded sample. Addenda weights were determined by cumulative weighings. The addenda constituted 2.31 and 5.25 wt.% to the unelectroded and electroded samples, respectively. As a percentage of the total heat capacity of the samples, the addenda contributed 4–8% and 6–10%, respectively. The S/V values for these two TGS pellets were about the same, 6.26 and

TABLE I. Specific-heat coefficients of TGS samples.

Sample	S/V (cm^{-1})	m[a]	B[b]
Single-domain crystal	6.43 ± 0.06	46.38 ± 0.62	−4.68 ± 1.66
Multidomain crystal	6.26 ± 0.06	43.59 ± 0.68	0.90 ± 1.84
Multidomain crystal[c]	12.8 ± 0.13	48.67 ± 0.51	7.65 ± 0.48
Assembly of small crystals	24.7 ± 2.7	21.42 ± 1.76	27.4 ± 4.6
Assembly of small crystals	33.2 ± 3.6	18.20 ± 2.20	40.8 ± 5.7

[a]erg g^{-1} K^{-4}.   [b]erg g^{-1} K$^{-5/2}$.   [c]Reference 1.

6.43 cm,[1] respectively (determined from the pellet dimensions).

For the assemblies of small TGS crystals, several large crystals were pulverized, and small crystals ≃0.2 and ≃0.3 cm were selected. By counting the crystals and measuring their weight, the S/V value was determined using the density (1.721 g/cm^3). The resulting S/V values were 24.7 ± 2.7 and 33.2 ± 3.6 cm^{-1}; these values were estimated based on both cubes and spheres, averages taken, and the uncertainties represent the spread in S/V from the two estimates.

The small crystals were assembled into two pellet samples with GE 7031 varnish, and Manganin heaters, resistance thermometers, and thermal links were fixtured as mentioned above. For both samples, the addenda constituted about 12 wt. % and contributed about 55–60% of the total heat capacity.

The addenda corrections for all four samples were made using literature data. For the varnish addendum, which dominates the heat capacity of the large S/V samples, the heat-capacity data of Cude and Feingold were used.[7]

Specific-heat data were measured by the method reported previously.[1] The calorimeter had high-
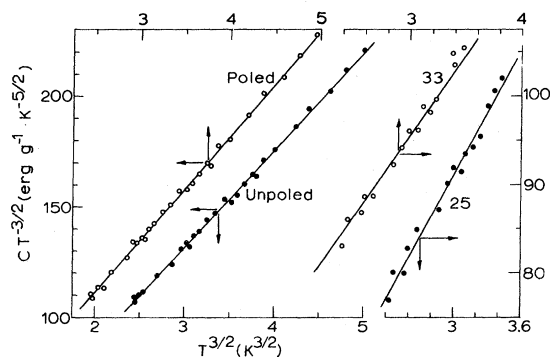

FIG. 1. Specific-heat data for the two sets of TGS crystals plotted according to Eq. (1). The curves labeled poled and unpoled refer to the large single-domain and multidomain crystals, respectively. The curves labeled 33 and 25 refer to the assemblies of small TGS crystals of surface-to-volume ratios 33.2 and 24.7 cm^{-1}, respectively.

voltage leads, and an electric field of 0.29 kV/cm was applied to the electroded TGS crystal overnight at room temperature. This corresponds to several thousand switching times for TGS in this field region, according to which[8]

$$t_s \simeq 4e^{\alpha/E} \ (\mu s) \ , \tag{1}$$

where $\alpha \simeq 3.8$ kV/cm. This field strength was maintained during cooldown and removed when the sample reached 10 K (Ref. 9); there is no doubt that the crystal was single domain.

Specific-heat data for the four samples are shown plotted in Fig. 1 as $C/T^{3/2}$ vs $T^{3/2}$, according to

$$C = mT^3 + BT^{3/2} \ . \tag{2}$$

The curves labeled poled and unpoled refer to the large crystals, and the curves labeled 25 and 33 refer to the S/V values of the assemblies of small crystals.

The low-temperature tail of an Einstein term[1] in TGS limited the $T^{3/2}$ region for the large crystals to $T^{3/2} \leq 5$, and to $T^{3/2} \leq 3.6$ for the small crystals. It is not clear why this Einstein frequency is reduced in the small crystals, and specific-heat data were not measured at sufficiently high temperatures to resolve these frequencies.

All four samples display the $T^{3/2}$ behavior, and in Table I are given the fitted values for m and B of Eq. (2). The uncertainties in m and B given in Table I result from least-squares fittings.

III. DISCUSSION

The original suggestion[1] that the $T^{3/2}$ specific-heat term in TGS is due to domain-wall oscillations now appears invalid because the large, multidomain crystal in Table I has a B coefficient that is essentially zero. This is in agreement with the experiments of Vieira et al.[4] wherein a thin, single-domain crystal (i.e., poled above the Curie temperature) exhibited the $T^{3/2}$ dependence of the spontaneous polarization at low temperatures, as noted above.

The negative B coefficient of the large, single-domain crystal in Table I is difficult to understand and may, in fact, not be a real effect. That is, this
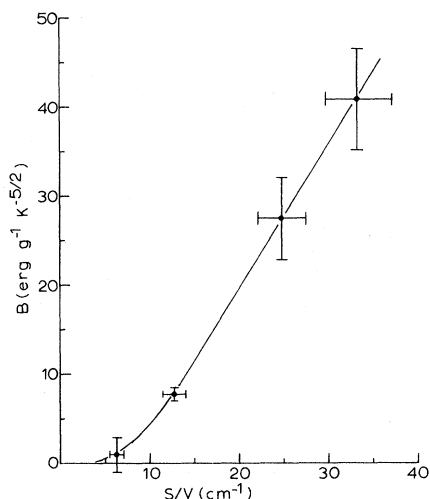
FIG. 2. (Fitted) B coefficients according to Eq. (1) plotted vs the surface-to-volume ratio, S/V. The point at $S/V = 12.8$ cm^{-1} is from Ref. 1, and the point at $S/V = 6.26$ cm^{-1} is for the multidomain crystal.

crystal had the larger addenda (owing to the electrodes), and the resolution of the (small) B coefficient depends on the addenda subtraction. What is clear is that the two large crystals in Table I qualitatively have about the same B coefficients and S/V values, thus further eliminating a domain-wall explanation.

The B coefficients in Table I are plotted versus the S/V values in Fig. 2 (except for the poled crystal). The increase of B with S/V clearly indicates that the $T^{3/2}$ specific-heat term in TGS at low temperatures is due to a *surface excitation*. Additional evidence for a surface effect comes from the m coefficients in Table I: For the three large crystals, the coefficients are in reasonably good agreement (46.2 ± 5.5%; note that the uncertainty in the measurements is $\simeq \pm 5\%$), whereas the smaller crystals have considerably reduced m coefficients. Considering a model of spherical crystals with a surface-layer thickness δ and assuming that the T^3 term arises from the bulk material, the $T^{3/2}$ term from the surface layer, it is straightforward to show that

$$m = m'[1 - (S/V)\delta/3]^3 , \qquad (3)$$

where m' is the T^3 coefficient for the bulk material. Equation (3) shows that m decreases with S/V, and adopting $m' = 46.2$, we find that $\delta = 0.027$ and 0.024 cm from the $S/V = 24.7$ and 33.2 cm^{-1} data in Table I, respectively. This same model yields

$$B \propto \{1 - [1 - (S/V)\delta/3]^3\} ,$$

which semiqualitatively agrees with the Fig. 2 data.

While there is satisfactory agreement between these two estimates of δ, these surface layers are much thicker than the surface layers estimated for TGS from dielectric data[10] ($\sim 10^{-5}$ cm). It is probable that the small crystals studied here were strained, and there is evidence from birefringence data that surface strains can extend up to ~ 0.1 cm into bulk SrTiO$_3$ crystals.[11]

Theoretically, a bulk excitation with a dispersion relation $\omega \propto k^2$ leads to a $T^{3/2}$ specific-heat term (e.g., spin waves in ferromagnets), and Gonzalo[12] has proposed a model along these lines involving amplitude modulation of long-wavelength Bloch waves to explain the $T^{3/2}$ effect in ferroelectrics. Kirkpatrick and Varma[13] have shown that a random Ising model with R^{-3} interactions also leads to a (bulk) $T^{3/2}$ specific-heat contribution. For surface contributions, it is well known that the Debye theory predicts a T^2 term, and modern treatments[14] also lead to a T^2 contribution. Experimentally, this has been demonstrated in the case of finely divided MgO particles.[15] A $T^{3/2}$ *surface* term requires an $\omega \propto k^{4/3}$ dispersion relation.[2]

The studies here demonstrate that a surface-layer excitation is responsible for the $T^{3/2}$ specific-heat term in TGS at low temperatures, but the layer thickness indicated, ~ 250 μm, is orders of magnitude greater than the dimensions commonly associated with two-dimensional phenomena. Moreover, a rough estimate of the $T^{3/2}$ effect observed in the other ferroelectric-type materials[1,2] similarly suggests thick surface layers. What, then, is the nature of the excitation found in the surface regions of ferroelectrics, regions which are sufficiently extensive to be thought of as bulklike? It is tempting to ascribe the effect to a large density of strain-induced domain walls in the surface region, but were this the case, one would expect a more pronounced difference between the two large crystals measured here. Also, while the small crystals reported here were probably highly strained due to the pulverization,[16] not all the crystals measured to date have been so strained.

Finally, the incipient ferroelectrics SrTiO$_3$ and KTaO$_3$ are difficult to reconcile: The $T^{3/2}$ term has been demonstrated in SrTiO$_3$,[2] but neither KTaO$_3$ nor the quantum ferroelectric (at the critical concentration[17]) KTa$_{0.988}$Nb$_{0.012}$O$_3$ display the $T^{3/2}$ term down to 1.7 K for S/V values $\simeq 15$ cm^{-1}.[18]

Future work here should be devoted to lower-temperature measurements and to larger-S/V-value crystals under more strain-free conditions.

ACKNOWLEDGMENTS

[1]W. N. Lawless, Phys. Rev. Lett. 36, 478 (1976); Phys. Rev. B 14, 134 (1976).

[2]W. N. Lawless and A. J. Morrow, Ferroelectrics 15, 167 (1977).

[3]R. Radebaugh, Phys. Rev. Lett. 40, 572 (1978).

[4]S. Vieira, C. de las Heras, and J. A. Gonzalo, Phys. Rev. Lett. 41, 1822 (1978).

[5]S. Vieira, C. de las Heras, and J. A. Gonzalo, in Proceedings of the Fourth European Meeting on Ferroelectricity, Portoroz, September 1979 [Ferroelectrics (in press)].

[6]R. Nitsche, Helv. Phys. Acta 31, 306 (1958).

[7]J. L. Cude and L. Finegold, Cryogenics 11, 394 (1971).

[8]E. Fatuzzo and W. J. Merz, Phys. Rev. 116, 61 (1959).

[9]Low-temperature electrocaloric effects in TGS were also examined by switching this field off and on after the specific-heat data were taken. No heating or cooling effects were observed, 4–20 K.

[10]A. G. Chynoweth, Phys. Rev. 117, 1235 (1960).

[11]K. Aso, J. Appl. Phys. 15, 1243 (1976).

[12]J. A. Gonzalo, Ferroelectrics, 20, 159 (1978).

[13]S. Kirkpatrick and C. M. Varma, Solid State Commun. 25, 821 (1978).

[14]L. Dobrzynski and A. A. Maradudin, Phys. Rev. B 14, 2200 (1976); I. A. Privorotskii, Phys. Lett. 60A, 361 (1977).

[15]W. H. Lein and N. E. Phillips, J. Chem. Phys. 33, 1415 (1958).

[16]There is also the possibility of a chemical reaction between the small TGS crystals and the GE 7031 varnish. The crystals were disassembled with the varnish solvent after the specific-heat measurements and weighed; the weights before and after were identical.

[17]U. T. Hochli and L. A. Boatner, Phys. Rev. B 20, 266 (1979).

[18]W. N. Lawless, Phys. Rev. B 16, 433 (1977); data on the KTN quantum ferroelectric are unpublished.