

⁶C. S. Liu, M. N. Rosenbluth, and W. M. Tang, Princeton Plasma Physics Laboratory Report No. MATT-1125, 1975 (unpublished).

⁷W. W. Lee and H. Okuda, Princeton Plasma Physics Laboratory Report No. MATT-1188 (to be published);

also private communication with M. True.

⁸J. Canosa and H. Okuda, *Phys. Fluids* **18**, 335 (1975).

⁹Y. Y. Kuo, to be published.

¹⁰B. B. Kadomtsev and O. P. Pogutse, *Nucl. Fusion* **11**, 67 (1971).

$T^{3/2}$ Contribution to the Specific Heat of Ferroelectrics at Low Temperatures

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A $T^{3/2}$ contribution to the low-temperature specific heat of the ferroelectrics triglycine sulfate, potassium dihydrogen phosphate, BaTiO_3 , and LiNbO_3 is reported. This may be a domain-wall contribution because it is not present in paraelectrics or antiferroelectrics.

The specific heats of a number of well-known paraelectrics, ferroelectrics, and antiferroelectrics have been measured in an adiabatic vacuum calorimeter in the range 2–35 K.¹ This Letter reports an unusual contribution to the specific heat found only in the ferroelectrics at the lowest temperatures.

All of the materials measured show maxima in CT^{-3} ($5.3 \leq T_{\text{max}} \leq 26.3$ K), and these maxima can be fitted very well with single Einstein frequencies.¹ At temperatures below T_{max} , the CT^{-3} curves for the paraelectrics and antiferroelectrics decrease with decreasing temperature and approach the flat T^3 Debye behavior. For the *ferroelectrics*, however, the CT^{-3} curves go through minima and *increase* with decreasing temperature down to 2 K. The measuring conditions (<5% uncertainty) and addenda were essentially the same for the paraelectrics, ferroelectrics, and antiferroelectrics.¹

The specific-heat data below the CT^{-3} minima for the ferroelectrics follow very accurately a $T^{3/2}$ law,

$$C = AT^3 + BT^{3/2}, \quad (1)$$

as shown in Fig. 1 for the displacive ferroelectrics BaTiO_3 and LiNbO_3 and in Fig. 2 for the hydrogen-bonded ferroelectrics potassium dihydrogen phosphate (KDP) and triglycine sulfate (TGS). The samples were multidomain single crystals (no attempt was made to pole the crystals).

The data in Figs. 1 and 2 were fitted by Eq. (1) and the results are summarized in Table I. The Debye temperatures in Table I were calculated from the coefficient A , and confidence limits are given on the B coefficient.

The excellent data fits leave no doubt as to the presence of the $T^{3/2}$ term and the presence of this term depends on whether the crystal is ferroelectric or not rather than whether the ferroelectric is displacive or hydrogen bonded. It is natural to ascribe this $T^{3/2}$ contribution to the presence of domain walls.

One would expect the B coefficient in Eq. (1) to be proportional to the number of domain walls present in the crystal; this can be controlled by

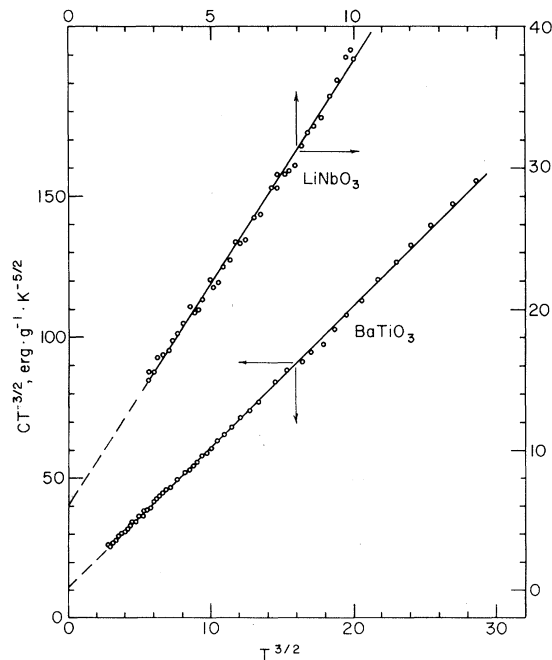


FIG. 1. Specific-heat plot according to Eq. (1) for the displacive-type ferroelectrics BaTiO_3 and LiNbO_3 .

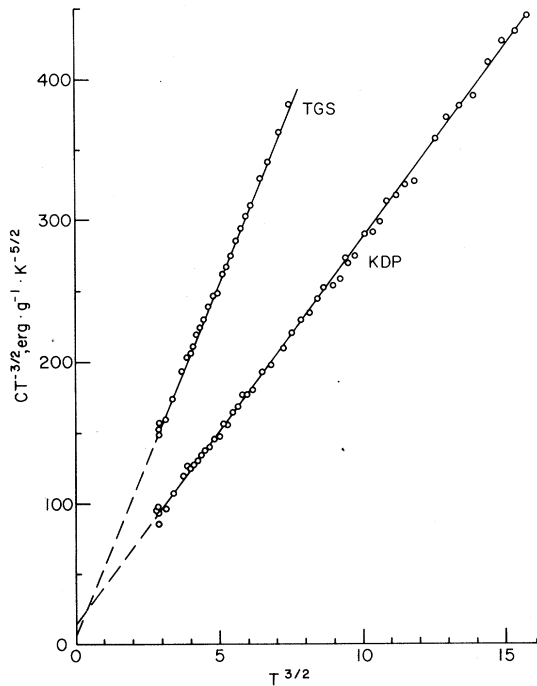


FIG. 2. Specific-heat plot according to Eq. (1) for the hydrogen-bonded ferroelectrics TGS and KDP.

poling at higher temperatures.

In ferromagnetic and ferrimagnetic materials, spin waves contribute a $T^{3/2}$ term to the specific heat. The demonstration of a $T^{3/2}$ pseudo-spin-wave contribution to the specific heat of hydrogen-bonded ferroelectrics would be a direct confirmation of the pseudo-spin-wave theory which suffers from lack of experimental contact at higher temperatures. (In fact, the assumption of well-defined pseudospin waves is valid only at low temperatures.) These findings demonstrate that

TABLE I. $T^{3/2}$ fitting results.

Crystal	Θ_D (K)	B (erg $g^{-1} K^{-5/2}$)	Residual standard deviation in $CT^{-3/2}$
BaTiO ₃	255	10.77 ± 0.12	0.86
LiNbO ₃	347	6.03 ± 0.08	0.51
TGS	107	7.65 ± 0.48	2.4
KDP	175	15.40 ± 0.50	3.6

the domain-wall contribution can mask a search for such a pseudo-spin-wave contribution, which means that such an experiment would have to be carried out on a carefully poled, single-domain crystal of, say, KDP or TGS.

Finally, it is possible to sketch the broad outline of how a $T^{3/2}$ specific-heat term might arise from domain walls. Firstly, quantized waves obeying Bose-Einstein statistics will contribute a $T^{3/2}$ or T^3 term depending on whether the dispersion relation follows $\omega \propto q^2$ (as for magnons in ferromagnets) or $\omega \propto q$ (as for low-frequency phonons and for magnons in antiferromagnets), respectively. Domain-wall oscillations are known, and if such oscillations were quantized, resulting in the dispersion relation $\omega \propto q^2$, then a $T^{3/2}$ term would follow.

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¹W. N. Lawless, to be published.