Specific heat of $RbCaF_3$ below 300 K

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Specific-heat measurements between 2 and 260 K have been made on polycrystalline $RbCaF_3$. Specific-heat anomalies are seen at all three transitions previously inferred from dielectric, optical, and EPR measurements, showing that lattice cooperative effects are indeed observed at quite low temperatures. We find a small first-order transition at 198 K with a latent heat of 36 J/mole, a broad transition at $\simeq 50$ K with an apparent latent heat of $\simeq 7$ J/mole, and a transition at $\simeq 7$ K, which has a very small latent heat (if any) and may be higher order than first. In all three cases, the different lattice phases are clearly seen as a change in slope of C/T vs T across the transition.

INTRODUCTION

It has recently become possible to prepare large single crystals of $RbCaF_3$ by the Bridgman method. A series of preliminary measurements[1] has shown that this material undergoes a lattice transition from cubic to tetragonal at 198 K, in a manner which appears to be entirely analogous to the well-studied soft-mode transitions in $SrTiO_3$ at 105 K,[2,3] and $KMnF_3$ at 186 K.[4-6] Additional transitions were detected at $\simeq 43$ and $\simeq 10$ K in some of the measurements made on $RbCaF_3$, but were not visible in others. Although EPR and optical birefringence definitely show the 198-K transition to be from cubic to tetragonal, structural information could not be obtained about the lower-temperature phases. In fact, optical-birefringence changes were minimal at these temperatures, while the EPR splittings exhibited hysteretic effects and unexplained loss of intensity. The main evidence for these lower-temperature transitions came from audio-frequency dielectric-constant and loss measurements.

Similar lower-temperature lattice transitions have been seen in[7,8] $SrTiO_3$ and $KMnF_3$,[9] but because of the antiferroelectric and antiferromagnetic ordering which develop, respectively, in these crystals,[10,11] their effects are often only indirectly or poorly seen. Another well-studied perovskite lattice exhibiting a soft-phonon-mode transition is $LaAlO_3$,[10,11] which appears to have no additional lattice transition below its 797-K transition from cubic to trigonal. A review of these and related matters can be found in Ref. 12. $BaTiO_3$ is another perovskite lattice for which specific heat has been measured, and it exhibits three separate lattice transitions at relatively high temperatures,[13] 388, 276, and 199 K, each accompanied by an apparent latent heat and significant thermal-expansion coefficient anomalies.

$RbCaF_3$ has reasonable electric and magnetic susceptibilities throughout the entire temperature range from 1 to 300 K, exhibits well-defined domain structure (including single domain under appropriate conditions[14]), and can be conveniently investigated by a variety of techniques. Thus it is important to establish the reality of all three previously seen transitions as true lattice phase changes, as well as to determine whether latent heats accompany the phase changes. Studies of critical dynamics and scaling behavior near each of these transitions will require a knowledge of the extent to which residual first-order contributions might be influencing fluctuation behavior near T_c. Previously, a comparison of the temperature dependence of the order parameter of $RbCaF_3$ near its cubic-to-tetragonal phase change with that of $SrTiO_3$ and $LaAlO_3$ (second-order transitions) and $KMnF_3$ (small first-order contribution) has shown it to be intermediate in its behavior to these two cases, with a somewhat smaller critical exponent.[1]

EXPERIMENTAL

Heat capacities of a 10-g polycrystalline sample prepared by the Bridgman method were measured by adiabatic calorimetry. The sample temperature determinations were based on the electrical resistance of a Cryo-Cal germanium thermometer for the range 2–25 K and of a Minco platinum thermometer for the range 25–300 K. Pulsed Joule heating was obtained by passing a current through a manganin wire, which, along with the thermometer, was thermally anchored to the sample. Their heat capacities were measured for addenda corrections. For the whole temperature range the heat capacity of a high-purity copper

sample was also measured as a check of the experiment. The data obtained in this check were in good agreement with the literature values.

Because the three expected transitions occur at distinctly different temperatures, measurements were carried out in three ranges: (a) 80–260 K, (b) 30–90 K, and (c) 2–25 K. Liquid-nitrogen coolant was employed for the first range, and liquid helium for the last two.

RESULTS AND DISCUSSION

For clarity the results will be presented separately for each of the three different temperature ranges covered by an individual set of experiments.

(a) 80–260 K. As shown in Fig. 1, a sharp spike with half-width $\simeq 0.5$ K occurs in the C-T curve at 198 K, indicating a first-order phase transition. Its gross appearance resembles that reported by Furukawa *et al.*[15] for $KMnF_3$. By drawing a smooth curve through the data points in the transition region, as in Fig. 2, we obtain an estimate of the latent heat at this transition, 36 J/mole. Further evidence of a structural change is demonstrated by the inset in Fig. 1, which shows a slope change in the log-log plot of C/T versus T at T_c.

The linearity of this $\log(C/T)$ vs $\log(T)$ plot encourages one to extrapolate the data into the region of T_c from both sides of the transition in order to obtain the specific-heat jump ΔC_p. A simple least-squares procedure gives the result

$$\Delta C_p = 0.0062 \pm 0.0004 \text{ J/g K at } T_c = 198.0 \pm 0.3 \text{ K},$$

with the larger value of C_p below T_c. This value can be used to obtain an estimate of the coherence length characteristic of the transition. We expect the order parameter to correspond to the rotation angle ϕ of the fluorine octahedra, in analogy to the transitions in $SrTiO_3$ and $LaAlO_3$.[11] Using the result of Ginzberg[16] as applied by Müller and Berlinger,[11] the zero-temperature coherence length is

$$l = (k/\rho \Delta C_p)^{1/3} \epsilon_c^{-1/6},$$

where ϵ_c is the fractional temperature range over which deviations from mean-field behavior are observed. From Ref. 1, $\epsilon_c \simeq 0.25$. The density of $RbCaF_c$ is 3.426 g/cm^3, and the lattice parameter in the cubic phase above T_c is 4.452 Å. Using these values, $l \simeq 10.9$ Å. This result is in excellent agreement with twice the lattice spacing, 8.9 Å, which would characterize the optic-mode condensation at the zone boundary. Thus $RbCaF_3$ at 198 K appears to furnish another example[11,17] of a large critical region near T_c as a consequence of short range coherence length.

(b) 30–90 K. The existence of a cusplike specific-heat anomaly between 48 and 52 K is apparent in Fig. 3. As expected, one also sees the difference in slopes of the two lattice specific heats just above and below the transition at $\simeq 50$ K. (The

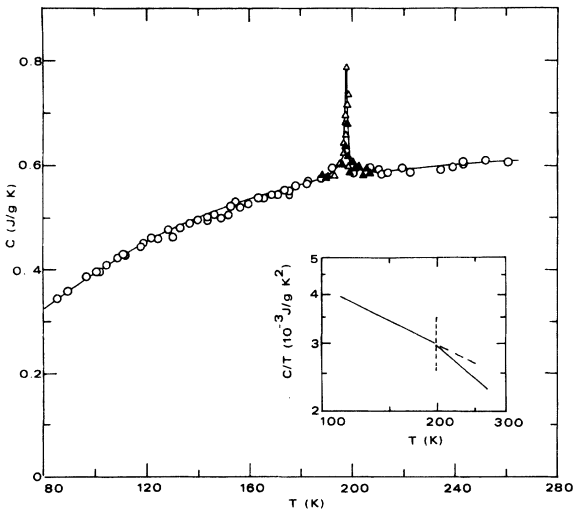

FIG. 1. Specific heat of $RbCaF_3$ versus temperature in the range 80–260 K. Different symbols represent different temperature increments for each heat capacity determination: ○—$\Delta T \simeq 5$ K, ▲—$\Delta T \simeq 1$ K, △—$\Delta T \simeq 0.2$ K. The inset, in terms of C/T vs T and based on a smooth curve drawn through the data points, clearly shows a slope change at the transition temperature.

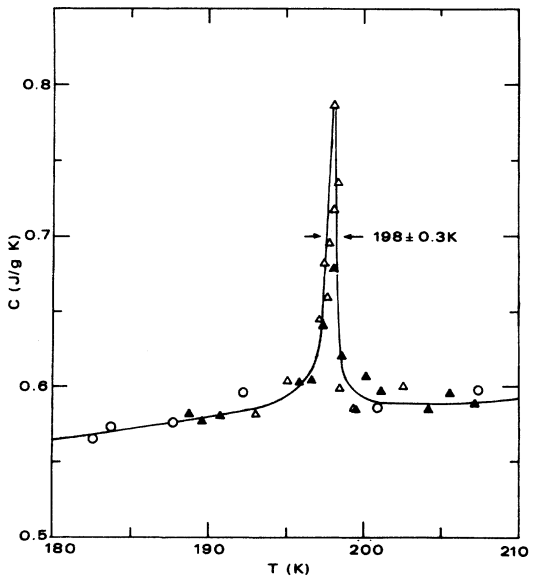

FIG. 2. Specific-heat anomaly at 198 K in $RbCaF_3$. For different symbols see caption of Fig. 1.

specific heats are expected to be nearly linearly dependent on temperature throughout this range.) Owing to the broadening of the transition and the relatively small specific-heat peak, the latent heat can only be approximately determined as $\simeq 7$ J/mole. In this case the discontinuity in specific heat is

$$\Delta C_p = 0.005 \pm 0.001 \text{ J/g K at } T_c = 50.4 \pm 0.8 \text{ K},$$

with the smaller value of C_p below T_c. The transition temperature and width measured for this sample differ significantly from that inferred previously from single-crystal EPR studies,[1] where 43 ± 0.2 K was observed. The broadening is presumably a consequence of internal stress and compositional inhomogeneity of the polycrystalline boule used.

The latent heat observed is quite small, but not unreasonably so. Even smaller latent heats have been observed for similar low-temperature structural transformations (cubic β-tungsten to tetragonal) in other compounds, for example V_3Si ($T_c \simeq 20$ K)[18,19] and Nb_3Sn ($T_c \simeq 43$ K).[20] Moreover, it was found in these cases that the transitions are highly stress sensitive, and a wide variety of transition temperatures were reported for different specimens. In view of these results, we believe that the $\simeq 7$ J/mole latent heat is the consequence of a weak first-order transition from tetragonal to some as yet unspecified symmetry in $RbCaF_3$, and that the discrepancy between our observed transition temperature and the previous single-crystal result is due to sample differences.

We have also attempted to check the suggestions made earlier[1] that thermal hysteresis accompanies this transition, and that the lattice phase below $\simeq 40$ K may be different depending on whether or

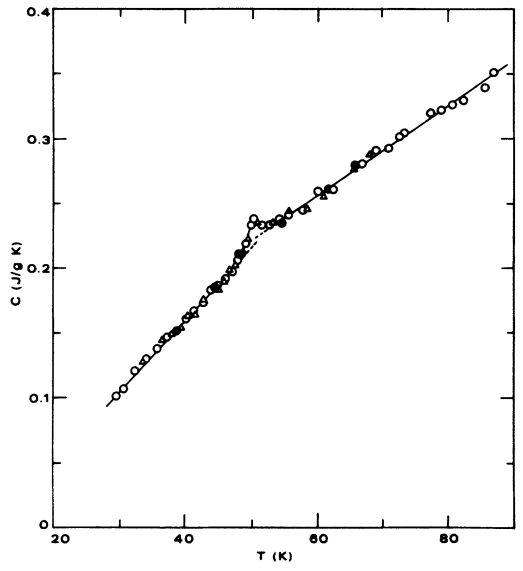

FIG. 3. Specific heat of $RbCaF_3$ versus temperature in the range 30–90 K. A clear break in the slope occurs at the transition between 48 and 52 K. Different symbols represent different thermal history of the specimen: ○—data taken on heating after the specimen was cooled down from room temperature to 4 K, △—data taken on heating after the specimen was cooled down from room temperature to only 20 K, ●—data taken along step cooling from room temperature.

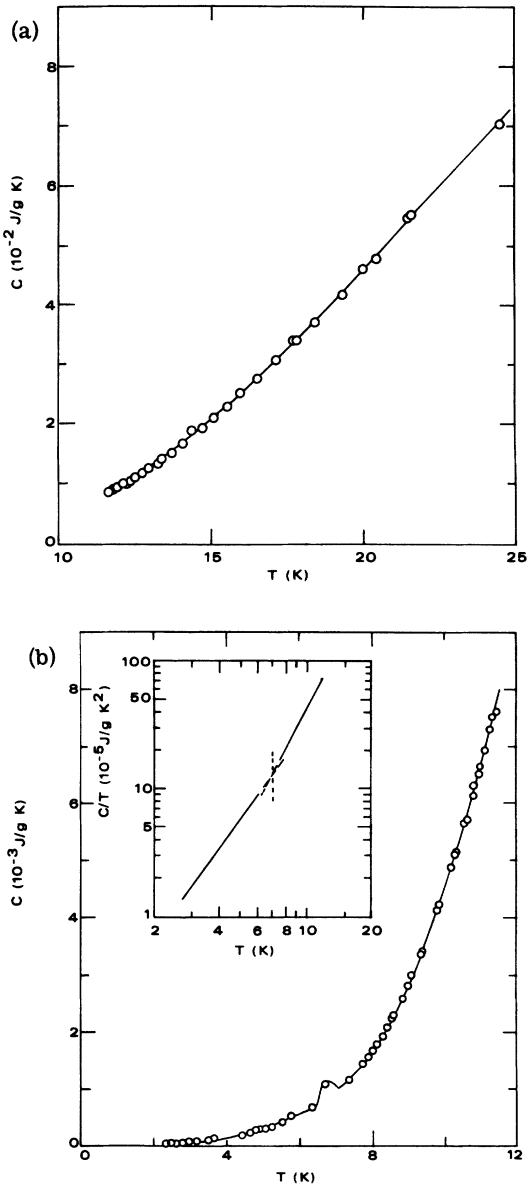

FIG. 4. (a) Specific heat of $RbCaF_3$ versus temperature in the range 12–25 K. (b) Specific heat of $RbCaF_3$ versus temperature in the range 2–12 K. An anomaly is seen at 7 K. It is further demonstrated in the inset similar to that in Fig. 1.

not the sample is first cycled through the ≃7 K transition. The first of these possibilities was checked by making measurements both for monotonic heating of the sample through T_c and for cooling (plus momentary heating) from above T_c. In order to check the second possibility, the sample was cycled first to 4.2 K for some of the data, but only to ≃20 K for other measurements. As can be seen in Fig. 3, all the data obtained in these various ways are in agreement. We conclude that neither of these effects is seen in our sample.

(c) 2–25 K. Figure 4 shows a very small specific-heat anomaly at ≃7 K. This lattice transition is seen most strikingly in the inset to the figure, where a log-log plot of C/T vs T clearly shows the different temperature dependences of the two lattice phases, intersecting at the temperature where the anomaly is indicated. The single point plotted at 6.8 K falls far outside the errors of the experiment, and represents a real deviation from the trend of C/T through this temperature. Much more detailed data would be required to determine whether this transition is in fact accompanied by a significant latent heat. But the existence of a transition (possibly higher order) at this temperature is consistent with the EPR and dielectric measurements made earlier[1] with less reliable thermometry, in which a transition at ≃10 K was suggested.

The measured specific heats near the two low-temperature transitions can be compared with tabulated values of the Debye function.[21] The qualitative behavior of the effective values of Θ_D determined in this way is consistent with the occurrence of phase changes in both cases. At the ≃50 K transition, Θ_D is 270 K just above and 273 K just below the transition. This increase in Θ_D is consistent with the loss of a lattice mode as the crystal is cooled through ≃50 K. The weak temperature variation of Θ_D at low temperatures also changes abruptly at 7 K. The calculated effective Θ_D rises from 220 to 270 K as the crystal is cooled from 11 to 7 K, then increases much less rapidly (with a factor of ≃2 change in slope) to $\Theta_D = 300$ K as the temperature is further lowered to 3 K. Again, this relatively more rapid increase in Θ_D as 7 K is approached from above is consistent with the loss of a lattice mode as the crystal is cooled through this temperature.

In conclusion, the specific-heat measurements reported here definitely establish all three transitions previously seen in $RbCaF_3$ as bulk lattice effects. The large critical region previously observed for the cubic to tetragonal transition at ≃198 K is seen to be consistent with the small coherence length expected for the transition. It seems reasonable to expect that the two lower-temperature lattice transitions at ≃50 and ≃7 K should be visible in diffraction or light-scattering experiments. If the ≃50 K transition is also characterized by a small coherence length, the observed specific-heat jump implies that a rather large critical region may be seen for this transition in other experiments. At present, no information is available as to the symmetries likely to be encountered at these lower-temperature transitions.

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