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Low-temperature calorimetric study of SrTiO₃

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Abstract

The specific heat of SrTiO₃ shows an anomaly at 105 K due to a structural transition from the tetragonal to cubic phase. The shape of the anomalous specific heat, $\Delta C_p(T)$, measured previously using quasi-static conduction calorimetry is confirmed and compared with results from rapid AC calorimetry (scanning rate ~ 30 K h⁻¹). The close agreement of both data sets proves that slow relaxational processes (e.g. the rearrangement of dense domain patterns) do not influence $\Delta C_p(T)$ significantly in SrTiO₃. Measurements at low temperatures do not reveal any further anomaly. The freezing temperature reported around 30 K due to quantum saturation of the order parameter does not produce any anomalous effect in the heat capacity.

1. Introduction

The structural phase transition near 105 K in SrTiO₃ is one of the most thoroughly studied transitions of all non-metallic systems. Previous results were summarized by Cowley in 1996 [1] who puts some emphasis on the criticality of the transition. Although truly critical behaviour may be relevant at $T > T_c$, its effect at $T < T_c$ was subsequently shown to be, at best, limited to a very narrow temperature interval of < 1 K [2]. The seemingly unusual temperature evolution of the order parameter at $T < T_c$ was shown to be related to the vicinity of a tricritical point and the effects of quantum saturation rather than criticalities. It was shown that the experimental results obtained by Müller and collaborators [3–5] could be analysed within the same framework of mean field theory [6–8].

Similar results were obtained for the structurally closely related transition in KMnF₃, [9] with the additional benefit that this transition can be shifted through the tricritical point by appropriate doping with Ca [10].

One of the cornerstones of the arguments in favour of a tricritical mean field behaviour of SrTiO₃ is the experimental observation that the excess specific heat, and hence the excess entropy ΔS , follows $\Delta S \propto Q_i^2$, where Q_i is the relevant component of the order parameter. This relation leads to the exponent $\gamma = 1$ and the corresponding Landau potential as given by [2]. The calorimetric data were obtained for different samples with different crystallographic orientations. In several experiments uniaxial stress, perpendicular to (100) face, was applied, its effect on the specific heat anomaly was rather small.

In all cases, a Landau step of about 1.5% of the background specific heat was observed with the same temperature evolution of $\Delta C_p(T)$ also in agreement with Franke and Hegenbarth [11]. This anomaly is clearly rather small and it is little surprise that Todd and Lorenson [12] and Strukov *et al* [13] failed to find the anomaly altogether. With the availability of large single crystals of SrTiO₃ and improved calorimetric facilities, quasi-static experiments became possible and led to the reassessment of the transition behaviour.

Disagreement exists, however, between these results and some previous AC calorimetric measurements. While Garnier [14] found that sample annealing simply smeared the transition over a larger temperature interval, Hatta *et al* [15], in an extensive study found a bewildering complexity of transition behaviour depending on the structural state of the sample. While a monodomain sample showed a peak near 107 K but no anomaly at lower temperatures, a polydomain sample showed a very broad anomaly near 98 K. The background heat capacity chosen by Hatta *et al* [15] was a straight-line and it was chosen in such a way that the critical exponent of the heat capacity is $\alpha = 0.125$ in agreement with the three-dimensional Ising system. Nevertheless, although this base line has the same slope as the specific heat data far and above T_c , it does not have the same absolute value. Monodomain sample showed a maximum excess value of ΔC_p of about $1.5 \text{ cal mol}^{-1}\text{K}^{-1} \sim 6.3 \text{ J mol}^{-1}\text{K}^{-1}$ and $0.35 \text{ cal mol}^{-1}\text{K}^{-1} \sim 1.5 \text{ J mol}^{-1}\text{K}^{-1}$ for the polydomain which is almost twice as large as the sample measured quasi-statically ($0.7 \text{ J mol}^{-1}\text{K}^{-1}$). This disagreement could be due to a high degree of impurities in the sample of Hatta *et al* [15] or some unknown experimental difficulty. It could also be that high defect densities (antiphase or twin boundaries) contribute differently to both experimental techniques. In order to clarify this point the quasi-static measurements were repeated and new AC measurements were undertaken using a small fraction of the same single crystal.

We will show in this paper that all calorimetric measurements lead to the same excess specific heat ΔC_p .

In the AC experiment, the sample was also measured over a large temperature interval below T_c in order to check if any anomaly could be found related to previously reported anomalies between 30 and 65 K [5, 15–20]. We will show that, within experimental resolution, no such anomaly was found.

2. Experimental techniques

We use two different experimental techniques, namely quasi-static conduction calorimetry and AC calorimetry.

The sample was a single crystal SrTiO₃ and was Verneuil grown with a purity of 99.998%. The main impurities were 3 ppm of Fe and 2 ppm of Ni. The large face of the crystal was the crystallographic (100) plane. The same sample was also used by Chrosch and Salje [21] for x-ray diffraction analysis of its domain structure of $T > T_c$. It was found that only very coarse twin and anti-phase domains were formed in this sample which excludes significant contribution from domain boundaries to the experimental values of C_p .

2.1. Conduction calorimetry or microcalorimetry

The experimental arrangement has been described in detail [22]. The sample is pressed between two identical heat fluxmeters which are made from 50 chromel–constantan thermocouples connected in series with the wires placed in parallel lines. The fluxmeters which have a circular section of 1 cm², are rigid enough to apply a controlled uniaxial stress on the sample in the range between 0 and 12 bars [22]. Two electrical resistances (heaters) are placed between each face of the sample and fluxmeters. The entire assembly was placed in a cylindrical hole made in a cylindrical piece of bronze (10 kg) which served as the heat sink (the calorimeter block). The block and two surrounding radiation shields were placed into a hermetic outer case under vacuum (10⁻⁷ Torr).

The high vacuum in the block, the high numbers of thermocouples and the symmetry in the fluxmeters and sample distribution, assure the unidimensional heat conduction through the fluxmeters. In these conditions the system has a sensitivity of 0.1 μW. The measurements are carried out on quasi-static conditions changing the temperature of the block at a very low constant rate ($\partial T/\partial t < 0.1 \text{ K h}^{-1}$).

The system allows the measurements of latent heat and absolute value of specific heat in different experiments but in the same thermal conditions following the procedure previously described [10, 23, 24].

2.2. AC calorimetry

Dynamic specific heat measurements were made with a modified Sinku Riko ACC-1VL calorimeter between 4 and 120 K. The sample used for the measurements was a single-crystal slab of around 2 × 2 × 0.2 mm³, cut from the same sample used in conduction calorimetry. The sample is excited with a square wave heating produced by a chopped light from a halogen lamp. An optical fibre is used to drive the power onto the sample, producing a temperature oscillation of a few mK. The experimental method and instrument are similar to the ones described by Garfield *et al* [25].

With appropriated excitation frequencies the specific heat is inversely proportional to the oscillation amplitude. Heating and cooling scanning rates between 10 and 30 K h⁻¹ and frequencies between 1.5 and 30 Hz were used at different temperatures. No differences were found in the specific heat results at different rates. The heating and cooling results coincided without any detectable hysteresis.

The AC measurements provide relative specific heat values that were scaled with an absolute value taken from the conduction calorimetry measurements.

3. Results

The raw data of the absolute specific heat of SrTiO₃, for a typical run between 85 and 120 K obtained at constant rate of 0.06 K h⁻¹ by conduction calorimetry are shown in figure 1.

The results of the AC measurements are shown in figure 2 for the whole temperature range.

In order to obtain the specific heat baseline we used the procedure as explained in Salje *et al* [2]. The second order polynomial makes self-consistent the same linear temperature evolution of the square of the order parameter found in all other experimental observations in the temperature interval between 80 and 90 K with the entropy excess. This polynomial is also shown in figure 1.

This base line, although fitted for conduction calorimetry data between 80 and 90 K, may be extended for AC data, with physical sense, thirty degrees below this range. This fact gives validity to the procedure used to calculate the base line.

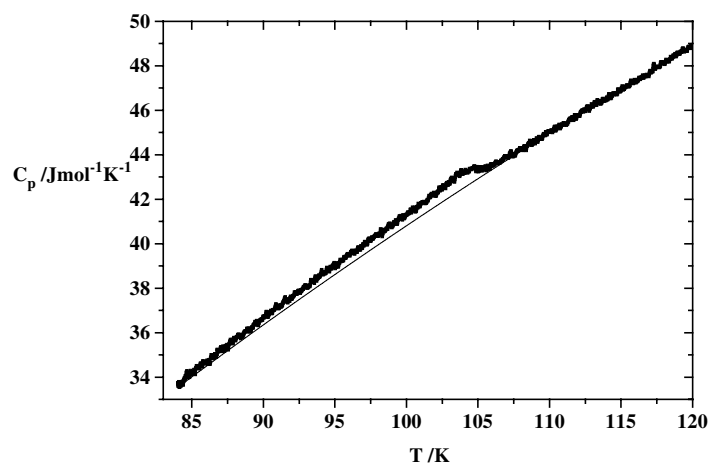


Figure 1. SrTiO₃ specific heat obtained by conduction calorimetry at a constant rate of temperature change of 0.06 K h⁻¹. We obtain a data every 0.02 K. The base line is calculated following the procedure by Salje *et al* [2].

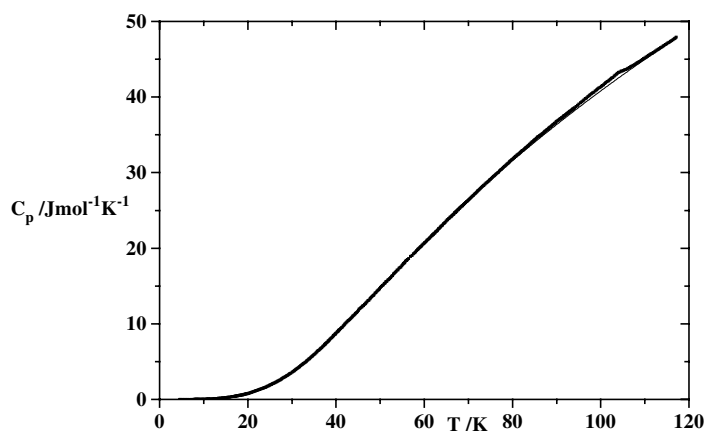


Figure 2. SrTiO₃ specific heat obtained by AC calorimetry at a constant rate of temperature change of 30 K h⁻¹. The base line calculated by Salje *et al* [2] is also shown in a wide temperature interval.

The conduction calorimetry specific heat excess, shown in figure 3, is clearly non-symmetrical which disagrees with the almost symmetrical critical behaviour obtained by Hatta *et al* [15]. A small cusp is seen between 103 and 105 K. At lower temperatures a smooth and continuous decay of ΔC_p is found.

The step at transition temperature is about 0.7 J mol⁻¹K⁻¹, which corresponds to 1.7% of the normal specific heat. The data agree perfectly with those published by Gallardo *et al* [26] and Salje *et al* [2].

The excess of specific heat for AC data are shown in figure 3. The chosen base line is the same one used in conduction calorimetry. Within experimental resolution the data agree very well with those of the quasi -static measurements obtained by conduction calorimetry. However, they disagree with the earlier data of Hatta *et al* [15]; even if we choose the same base line for Hatta experiment, the shape and the specific heat excess are quite different,

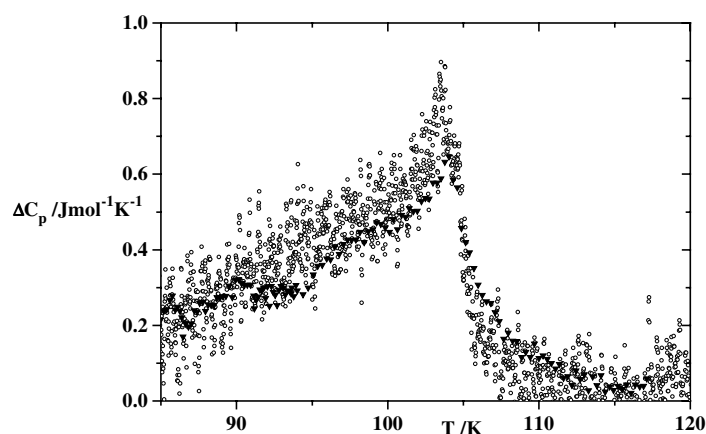


Figure 3. SrTiO₃ specific heat excess obtained by conduction calorimetry (open circles) and by AC calorimetry (filled down triangles).

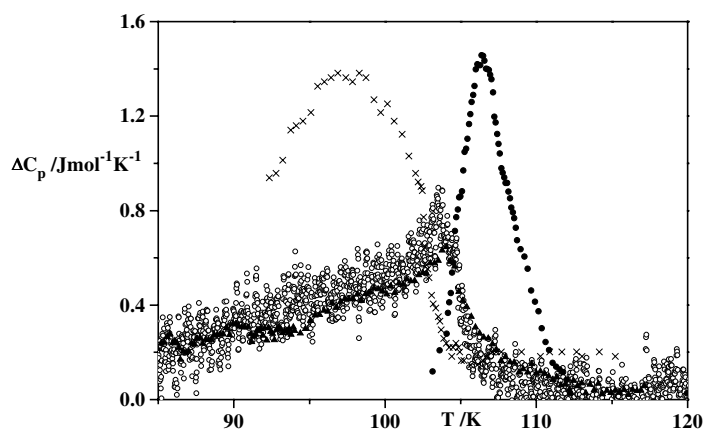


Figure 4. SrTiO₃ specific heat excess obtained by conduction calorimetry (open circles), by AC calorimetry (filled up triangles), by AC calorimetry by Hatta *et al* [15] in the monodomain sample (filled circles) and in the polydomain sample (crosses), with the same base line used for our data.

see figure 4. No sharp maximum was found while the continuous decay of the excess specific heat at low temperatures is clearly visible. This result confirms the earlier observations of Gallardo *et al* [26] and Salje *et al* [2].

The low-temperature measurements down to 4 K show a very smooth variation without any detectable anomaly, see figure 2.

Quantum mechanical effects produce a coherent quantum state in strontium titanate at low temperature [5]. The order parameter saturates giving entropy saturation below a freezing temperature $T_s = 30$ K [2, 8]. This effect implies the absence of any anomalous specific heat contribution below this temperature and a very gradual increase above it. In any case, this specific heat component is much smaller than the lattice phonon contribution and cannot be separated due to its smoothness. Accordingly, one cannot expect any anomalous behaviour at this temperature, as is shown by the experimental results. The precision of the specific heat measurements, around 0.1% above 80 K and a bit worse at liquid helium temperatures, assures that any possible anomalous peak should be much lower than 1% of the total specific heat.

Acknowledgments

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