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The cubic–tetragonal phase transition in strontium titanate: excess specific heat measurements and evidence for a near-tricritical, mean field type transition mechanism

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Abstract. The transition between the cubic and tetragonal phase in SrTiO₃ shows an excess specific heat of 0.0035 J g⁻¹ K⁻¹. Comparison between the temperature evolution of the excess entropy $\Delta S = \int (C/T) dT$ and the structural order parameter Q shows $\Delta S \propto Q^2$ within experimental errors ($\gamma = 1.004 \pm 0.006$). The apparent order parameter exponent $\tilde{\beta} = 0.35 \pm 0.02$ was confirmed and analysed using a Landau-type expression for the excess Gibbs free energy $\Delta G = A\theta_s(\coth(\theta_s/T) - \coth(\theta_s/T_c))Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6$ with $A = 0.70$ J K⁻¹ mol⁻¹, $B = 31.22$ J mol⁻¹, $C = 42.17$ J mol⁻¹, $T_c = 105.65$ K and $\theta_s = 60.75$ K. The closeness to the tricritical point is seen by $B < C$; all thermodynamic data between 85 K and T_c could be described selfconsistently using this approach although small deviations cannot be excluded in a temperature interval of less than 1 K around T_c and a small tail of excess entropy at $T > T_c$.

1. Introduction

The phase transition at 105.5 K in SrTiO₃ has great historical significance because almost every development in the theory of structural phase transitions measured its success on the ability to correctly describe experimental observations in SrTiO₃. It was the first material for which soft modes were clearly measured [1–3], observations on SrTiO₃ were one of the main justifications for the development of renormalization techniques for the description of (real or perceived) critical fluctuations and it was also the first material for which a two-length-scale behaviour was postulated [4–8]. Most recently, the appearance of quantum coherent states brought SrTiO₃ back into scientific controversy [9–11]. Despite major efforts over the last 30 years to understand this apparently simple phase transition, much ‘progress’ had to be revised, because it was based on incorrect experimental observations. It is much clearer now that the significance of criticalities has to be seen in the context of similar effects due to lattice imperfections, for example [12, 13]. It is the purpose of this paper to revisit the phase transition and present, for the first time, absolute values for the excess specific heat of the transitions. We shall argue that these results can be understood within mean field theory with little (if any) contribution from non-mean-field critical fluctuations. In the classification scheme of Cowley [14], this paper belongs firmly to the classical era.

Starting points of this investigation are the previous observations that, firstly, the excess entropy of a slab of SrTiO₃ with large (110) faces appeared to follow the same temperature dependence as the square of the static order parameter as measured by ESR [15, 16]. The

second observation is that a coarse domain structure (twins and antiphase domains) appears under cooling at $T \lesssim T_c$ with no indication of interchanges of rotation axes which could be statistically relevant [17]. This means that the degeneracy of the order parameter ($n = 3$) is lifted at temperatures just below T_c . The Slonczewski–Thomas Gibbs free energy [18] with the three-component order parameter $Q = (Q_1, Q_2, Q_3)$ is then reduced to a scalar order parameter if the effect of domain boundaries and antiphase boundaries is ignored:

$$G = G_0 + \frac{1}{2}A\theta_s \left(\coth \frac{\theta_s}{T} - \coth \frac{\theta_s}{T_c} \right) Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6. \quad (1)$$

In this form, quantum saturation is taken into account in the displacive limit [19–21]. The usual strain relaxations are understood to be incorporated into the various parameters of G . In contrast to Slonczewski and Thomas, the sixth-order term is considered here explicitly because we shall argue that the phase transition is close to a tricritical point with $B/AT_c < C/AT_c$.

This approach is different from the currently held views (the ‘critical era’ in Cowley’s classification) of the transition as multicritical with an $n = 3$ -fold degenerate R_{25} soft mode and a Heisenberg-type effective Hamiltonian [22]. This Hamiltonian contains the flip motion of rotation axes and a cubic anisotropy part which characterizes the soft mode dispersion. It has been used for the analysis of various stress dependent measurements [23, 24] and appears to describe well the results of neutron scattering experiments at $T > T_c$ with the critical exponent $\gamma = 1.4 \pm 0.1$. There is little doubt that critical fluctuations lead to non-mean-field behaviour in the cubic phase but it is less clear what happens in the tetragonal phase.

The theoretical situation for the cubic $n = 3$, $d = 3$ systems is also somewhat confused. Aharony [25] predicted an order parameter exponent $\beta = 0.365$ and $\gamma = 1.386$ while Nattermann [26] argued that these exponents would only occur very close to T_c and that, in the presence of cubic anisotropies, all the exponents might be larger. Bruce [27] and Nattermann [26] concluded that the system had probably a first-order transition, although this first-order step might be too small to be seen experimentally.

In this paper we show that there is no experimental evidence for any latent heat and, consequently, the transition is continuous within accessible resolution. Furthermore we shall show that $\gamma = 1.004 \pm 0.006$ at $T < 0.99 T_c$ in agreement with the mean field description for such temperatures but in disagreement with previous prediction of renormalization group approaches (e.g. [11, 23]).

2. Experimental techniques

The experimental arrangement of the specific heat measurement has been described in detail [28]. The sample is pressed between two identical heat fluxmeters which are made from 50 chromel–constantan thermocouples [29] connected in series with the wires placed in parallel lines. One of the fluxmeters is fixed to a calorimeter block while the other is pressed by a bellow. The fluxmeters which have a circular section of 1 cm^2 , are rigid enough to apply a controlled uniaxial stress on the sample in the range between 0 and 12 bars. Two electrical resistance (heaters) are placed between each face of the sample and fluxmeters. These resistances can dissipate a uniform heat power on the sample faces or measure the temperature of the fluxmeter junctions near the sample.

The block temperature is measured with a commercial platinum thermometer (Leads and Northrup (model 8164B)) and a Tinsley resistance bridge (model Ambassador). This bridge is also used to measure the resistances of the heaters thus determining the temperature

at the internal junction of the fluxmeters. A HPE-1328A current source and a HPE-1326 multimeter are used respectively to produce and to measure the power dissipated in the heaters. The e.m.f. produced by the fluxmeters is measured by a Keithley 181 nanovoltmeter with a repetition rate of four measurements per second. All the devices are controlled by an HP-75000 data acquisition system.

The specific heat of the sample is measured using the following procedure [30]. We start from the steady state obtained when the same power W is dissipated in both heaters. This heat power W crosses through the fluxmeters producing an e.m.f. V_0 . At the initial time the power is cut off and the e.f.m. V is integrated up to the time t_1 when the thermal equilibrium with the block is obtained and the e.m.f. reaches the value V_1 .

If the measurements are carried out on quasistatic conditions changing the temperature of the block at very low constant rate ($\partial T/\partial t < 0.1 \text{ K h}^{-1}$), the e.m.f. V_1 is very small and practically constant. It is proportional to the heat flux crossing the fluxmeters to produce a change of the sample temperature at the rate of the block temperature. When there is a dissipative effect in the sample or a first-order transition is produced, V_1 changes with time and it is proportional to the dissipative power or the heat power necessary to change the transition enthalpy of the transition. This means that we can detect when a first-order transition is produced and to distinguish when the specific heat data are affected by the latent heat [31]. The measurements were carried out at constant rate of about 0.06 K h^{-1} thus a data point was obtained every 0.02 K . The increase of the temperature in the sample due to the measurement process is estimated to be 0.06 K .

The sample was a single crystal of SrTiO₃. The same sample was used by Chrosch and Salje [17] 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 contributions from domain boundaries to the experimental values of C_p . The sample was Verneuil grown with a purity of 99.9998%. The main impurities were 3 ppm of Fe and 2 ppm of Ni. The large face of the crystal was the crystallographic (100) plane instead of the (110) plane used in earlier experiments [16].

3. Results

The raw data of the absolute specific heat for a typical run between 85 and 120 K are shown in figure 1. No variation of the e.m.f. V_1 has been detected at any run, thus there is no indication for a first-order type phase transition.

In order to obtain the specific heat baseline the following procedure was adopted. In the temperature interval between 80 and 90 K, all other experimental observations [15, 17, 28, 33] find the same linear temperature evolution of the square of the order parameter. We therefore constrain the temperature dependence of the excess entropy to show the same linear dependence as the square of the order parameter at low temperatures [15, 32]. Thus x-ray data allow us to evaluate that the specific heat excess at 85 K is about $4 \times 10^{-4} \text{ J g}^{-1} \text{ K}^{-1}$ (0.2%) which is lower than our experimental error ($\pm 0.4\%$). Considering this value together with data between 108 and 120 K we have fitted a second-order polynomial function to obtain the baseline of the specific heat. This curve is also represented in figure 1.

The excess of specific heat in figure 2 was identical within the experimental scatter for all six experimental runs under different uniaxial pressure ranging between 0 and 12 bars. This result is different to that obtained previously on face [110] where a stress of this order of magnitude clearly affects the specific heat behaviour. This result is in agreement with x-ray

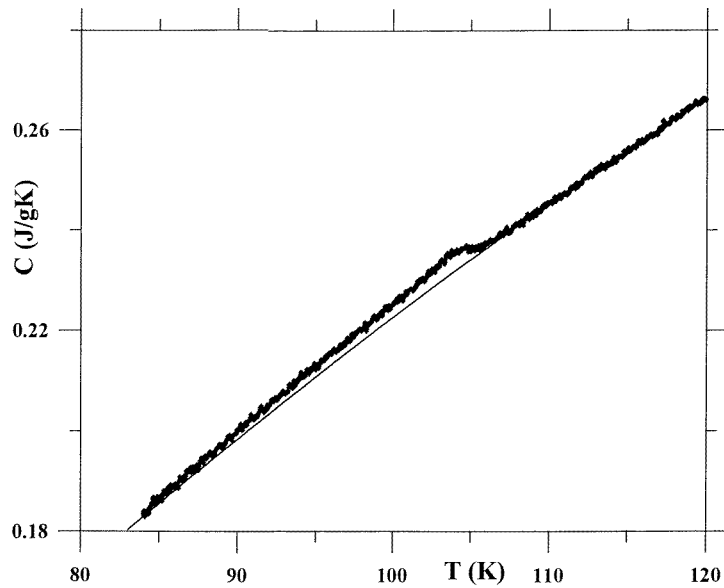


Figure 1. Experimental data of the total specific heat of SrTiO₃ between 85 and 120 K. The baseline for the extrapolated specific heat of the cubic phase is shown as a line $c = aT^2 + bT + e$ and $a = -8.01 \times 10^{-6} \text{ J g}^{-1} \text{ K}^{-3}$, $b = 0.00395 \text{ J g}^{-1} \text{ K}^{-2}$, $e = 0.0926 \text{ J g}^{-1} \text{ K}^{-1}$.

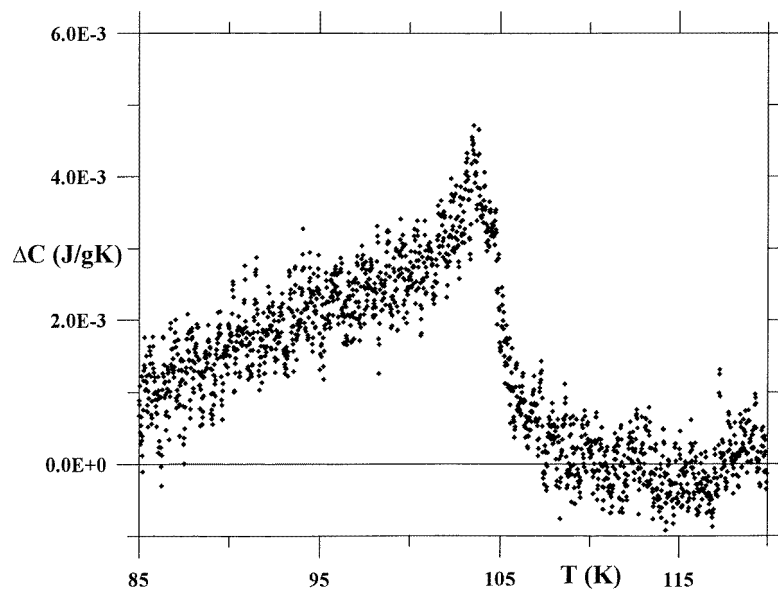


Figure 2. Excess specific heat with a Landau step at T_c of $0.0035 \text{ J g}^{-1} \text{ K}^{-1}$. A small cusp is seen in this data set at 104 K and a weak tail between 105 and 107 K; these two features are sample dependent.

study [17] which shows that uniaxial stress perpendicular to (110) generates stress dependent domain boundaries while little effect was found for stresses perpendicular to (100).

The only variation was found in the slope of the specific heat versus temperature near 105 K. In all experiments a weak rounding was found which could well be related to structural imperfections. This effect was always limited to a maximum temperature interval of 2 K. In some experiments, but not all, a small cusp is seen between 103 and 105 K. At lower temperatures a smooth and continuous decay of ΔC_p is found.

In order to compare these results with those of the temperature evolution of the structural order parameter, the excess entropy was calculated by integration of the excess specific heat data [13, 16]. The result is shown in figure 3. The same procedure was carried out for experiments where the sample was subject to uniaxial stress. While the raw data are almost indistinguishable, systematic variations may be seen after integration of ΔC_p and calculations of the excess entropy. As seen in figure 4 the absolute values of the excess entropy vary between experiments by $7 \times 10^{-5} \text{ J g}^{-1} \text{ K}^{-1}$, although the relative temperature evolution remains the same for all experiments. Ignoring the tails at $T > 104.7 \text{ K}$, all ΔS curves can be well described at $100 \text{ K} < T < 104.7 \text{ K}$ by a power-law temperature dependence with an effective exponent $2\tilde{\beta}$, and $\tilde{\beta} = 0.35 \pm 0.02$. Small variations of base line do not affect the value of β but only the absolute values of the excess entropy at low temperatures.

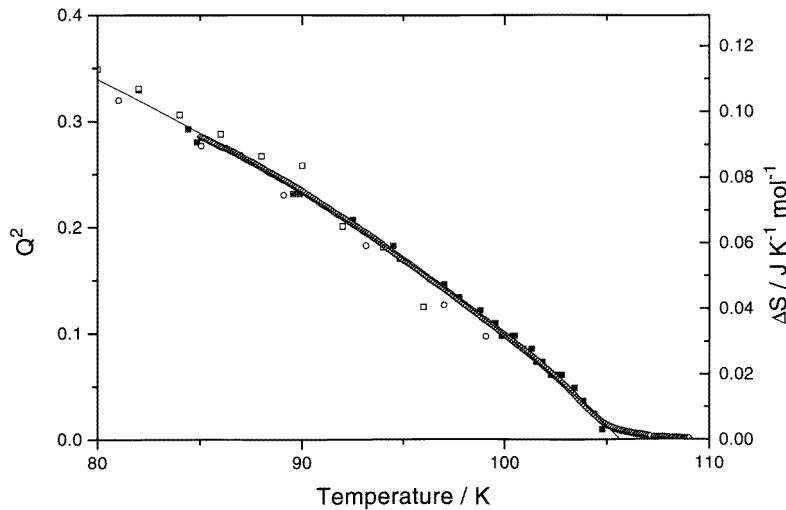


Figure 3. Temperature evolution of the excess entropy (diamonds) and the square of the static order parameter as determined from ESR measurements (full squares), synchrotron measurements of excess intensities (circles) and rocking XRD experiments (open squares). The line is the best fit for a mean field type order parameter with $\frac{1}{2}A\theta_s(\coth(\theta_s/T) - \coth(\theta_s/T_c))Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6$ and $A = 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$, $B = 31 \text{ J mol}^{-1}$, $C = 42 \text{ J mol}^{-1}$, $T = 105.65 \text{ K}$ and $\theta_s = 60 \text{ K}$.

4. Conclusion

The effective exponent $\tilde{\beta}$ is close to the experimentally observed order parameter exponent β [15, 16]. This conclusion is rather independent of the actual choice of the baseline because the values of ΔS are only taken at temperatures close to T_c . The question arises of whether a similar agreement exists also at lower temperatures, i.e. whether the reported crossover between the regime of $\beta \approx 0.35$ and the regime with linear temperature dependence of Q_2 is reproduced by the experimental data. In order to answer this question, for each

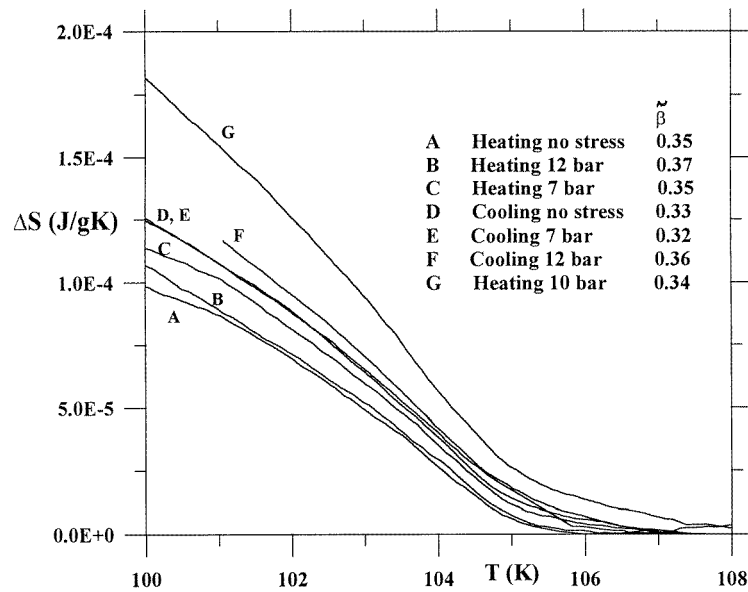


Figure 4. Stress dependence of the temperature evolution of the excess entropy for: A: heating, no stress; B: heating, 12 bar; C: heating, 7 bar; D: cooling, no stress; E: cooling, 7 bar; F: cooling, 12 bar; G: heating, 10 bar. All curves can be rescaled within experimental errors to one master curve by multiplication of ΔS with an appropriate factor.

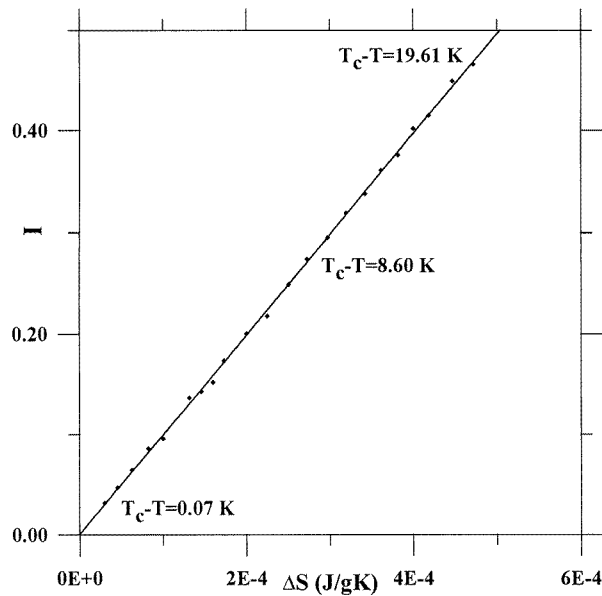


Figure 5. Correlation between the excess entropy and the excess intensity of x-ray diffraction experiments. The temperature of several data is also represented in the graph. The straight line adjusted to the data is $I = a + b\Delta S$ and $a = 8.5 \times 10^{-5}$, $b = 991 \text{ J}^{-1} \text{ g K}$.

temperature point the values of ΔS are plotted against the values of the excess intensities of x-ray diffraction data in figure 5 [33]. The diffraction data are, in turn, identical with

results from rocking curve measurements on the identical sample used for the measurements of the specific heat [17]. This graph shows clearly that both quantities are proportional to each other. In figure 6 the correlation $\ln(\Delta S/I)$ is plotted against $\ln(T_c - T)$. With $\ln(\Delta S/I) = \ln \Delta + (\gamma - 1) \ln(T_c - T)$ we find $\gamma = 1.004 \pm 0.006$ and $T_c = 104.75$ K (for a stress $\sigma = 10$ kg cm⁻²). Similar values were found for other stresses. This observation shows that γ is practically identical with the mean field values for all temperatures below 104 K. This does not rule out that non-mean-field behaviour exists in a small interval *very* close to T_c but we can exclude this possibility for any interval larger than 1 K.

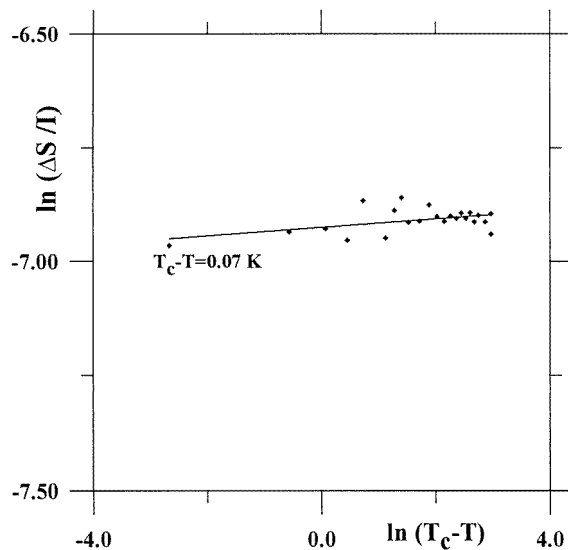


Figure 6. Determination of the exponent γ from the plot $\ln(\Delta S/I)$ versus $\ln(T_c - T)$ with $\gamma = 1.004 \pm 0.006$.

We now discuss the apparent puzzle that the effective order parameter exponent is 0.35 while $\gamma = 1$. Starting from the mean field expression (1) we analyse all available experimental data in the temperature interval between 80 and 110 K. The graph in figure 3 shows that the normalized rotation angle of the octahedral TiO₆ groups (from ESR measurements [15]), the excess diffraction intensities from synchrotron experiments [33], the twin angle between microdomains as measured by x-ray rocking curve experiments [17] and our data of the excess entropy are all identical within experimental errors. This experimental result shows that the entropy scales as the square of the structural order parameter, at least at temperatures below 105 K. The second question is whether the temperature evolution of these experimental quantities can be described by an appropriate numerical expression of the excess Gibbs free energy in equation (1). Fitting the parameters A , T_c , B , C and θ_s to the experimental data leads to the following solution

$$A = 0.70 (\pm 0.1) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$B = 31.22 (\pm 0.45) \text{ J mol}^{-1}$$

$$C = 42.17 (\pm 1.75) \text{ J mol}^{-1}$$

$$T_c = 105.65 (\pm 0.17) \text{ K}$$

$$\theta_s = 60.75 (\pm 1.51) \text{ K}.$$

We shall show in a forthcoming paper that these parameters also describe all experimental data points at lower temperature correctly. Two conclusions can be drawn from these parameters. Firstly, the transition is second order but rather close to a tricritical point. We find $B < C$. Another measure [13] for the closeness of a tricritical point is the ratio $B^2/4AC = 8.2 \text{ K} \ll T_c$ which indicates that a shift of T_c by only 8.2 K would produce a tricritical phase transition. The interval in which a simple second-order phase transition with $\beta = 0.5$ can actually be observed is very small and close to T_c . The second conclusion is that the empirical value of θ_s is higher than expected in a soft mode picture where no coupling occurs between the soft mode and other lattice excitations. Following [20] the characteristic temperature below which the order parameter becomes rather independent of temperature is in displacive systems $T_s \approx \frac{1}{2}\theta_s = 30 \text{ K}$. At this temperature all entropy changes are frozen out. In a picture of only one soft mode driving the phase transition without any coupling with other degrees of freedom (e.g. other phonons), the temperatures T_s and θ_s are determined by the bare frequency of the soft mode. In the other extreme, the soft mode may couple strongly with all other phonons. Entropy saturation is then expected when the average phonon frequency is equal to the freezing temperature. It was shown in [20] that this latter scenario leads to $\theta_s \approx \frac{1}{2}\theta_E$ where θ_E is the Einstein temperature of the material. Experimentally $\theta_s \approx \frac{1}{2}\theta_E$ was found for the displacive phase transition in quartz [20, 34]. In SrTiO_3 , we find $\theta_s \ll \frac{1}{2}\theta_E$ which shows that the coupling between the soft mode and other dynamical excitations in SrTiO_3 is weaker than in quartz although it still leads to an increase of θ_s compared with the expected value for the bare soft mode frequency.

In summary, we find that the excess specific heat data of SrTiO_3 show a mean field behaviour [12, 21] close to a tricritical point with possible influence of impurities at $T > T_c$ [35]. Entropy saturation occurs at temperatures higher than expected from the bare soft mode frequency but lower than the average phonon frequency.

Acknowledgments

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