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Experimental Study of the Ca Effect in the Cubic-Tetragonal Phase Transition of $Ca_{1-x}Sr_xTiO_3$

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The entropy excess corresponding to the cubic to tetragonal transition in $Ca_{0.04}Sr_{0.96}TiO_3$ perovskite has been obtained by integration of specific heat measured by conduction calorimetry. The order parameter of the transition has been obtained by means of neutron diffraction at low temperatures. Comparison of calorimetric data with the evolution of the order parameter indicates that this transition follows a mean field Landau potential as in $SrTiO_3$. The linear behaviour of the excess of entropy versus temperature suggests that a 2-4 Landau potential is sufficient to describe the transition. The Ca effect in thermodinamical properties of $SrTiO_3$ is compared with the effect of an uniaxial stress applied on pure $SrTiO_3$.

Keywords Specific heat; neutron diffraction; $SrTiO_3$; $CaTiO_3$; Landau theory

PACs: 61.12.Ld; 64.60.-i; 64.60.Fr; 65.40.Gr

Introduction

Strontium titanite, $SrTiO_3$, is a prototype material undergoing a structural phase transition. Recently we have showed that the transition at 105 K is in agreement with the mean field description, with a 2-4-6 Landau potential that indicates that this transition is near to a tricritical point [1].

Recently, we have also studied, by specific heat measurements, the cubic-tetragonal phase transition in $Ca_{0.04}Sr_{0.96}TiO_3$, and we have showed that the addition of Ca increases

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the transition temperature and the specific heat excess, but keeping its ratio constant, in agreement with Landau description [2].

In this paper, by comparing entropy excess and the order parameter we will show that this transition can be described by a 2-4 Landau potential.

According to the classical Landau theory of phase transitions, the excess free enthalpy due to the transition in a single domain is:

$$\Delta G = \frac{1}{2}A(T - T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6 + \cdots \quad (1)$$

This expression leads to a continuous phase transition for A, B, C all positive. If $B \gg C$ we obtain a second order phase transition with a (2:4) Landau potential. If the phase transition is near to tricritical point, as in the case of $SrTiO_3$, neither B or C can be neglected.

On the other hand, in a Landau potential, we have the relationship

$$\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_{Q=Q_{\text{equilibrium}}} = \frac{1}{2}AQ^2_{\text{equilibrium}} \quad (2)$$

The excess entropy ΔS is expected to be proportional to the square of the order parameter Q for any behaviour described by a Landau potential like Eq. (1). This particular relation between entropy and order parameter is in principle broken in the asymptotic regime for all other universality classes [3]. Its experimental check can be then an effective way to distinguish between genuine fluctuation-driven critical behaviour and pure Landau behaviour.

Comparison of the order parameter with that of the excess entropy is therefore a convenient way to determine whether a given phase transition follows the predictions of Landau theory, or of some other critical model.

Thus in a 2–4 Landau potential:

$$\Delta S = \frac{A^2}{2B}(T - T_c) \quad (3)$$

so, the slope of the excess of entropy versus temperature gives the relation $A^2/2B$.

Experimental and Results

Sample characteristics of $Ca_{0.04}Sr_{0.96}TiO_3$ has been described previously [2].

Neutron powder diffraction patterns were recorded using the two axis diffractometer D1B at the Institut Laue-Langevin, Grenoble, France. Neutrons of wavelength 2.52 Å were used. The sample was cooled down to 20 K and diffraction patterns were recorded continuously every 5 minutes while heating up to room temperature at 1 K min^{-1}.

A way of experimentally measuring the order parameter variation is provided through the general relationship $\langle Q \rangle^2 \propto I_k$, where I_k is the intensity of a superlattice reflection, which appears as a consequence of the transition. Figure 1 shows the variation with temperature of the square of the observed structure factors (directly proportional to the intensity) of both the 211 and 213 superlattice reflections. These have zero intensity under $Pm\bar{3}m$ symmetry and become non zero below the $Pm\bar{3}m \rightarrow I4/mcm$ transition. The pattern of intensity shows zero value from RT down to ~235 K and then increases almost linearly to ~115 K.

The specific heat has been measured by conduction calorimetry. The measurements were carried out cooling the sample from room temperature in quasiestatic conditions, at

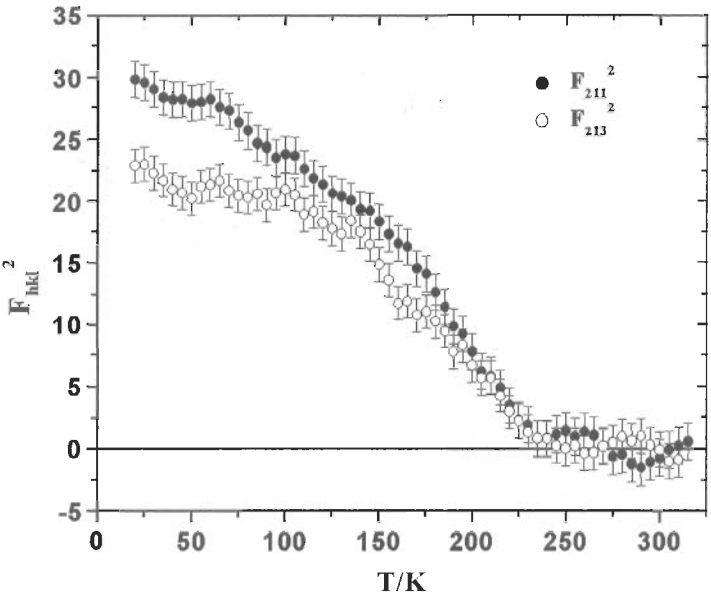

FIGURE 1 Variations in intensity of the 211 and 213 reflections with increasin temperature.

constant rate of 0.2 K h^{-1}. Specific heat data in a wide temperature range have been publishe elsewhere [2]. The entropy excess is obtained by integration of specific heat measurement taking a baseline congruent with specific heat data of pure $CaTiO_3$. Figure 2 shows th entropy excess in a temperature range that spans 30° below the transition temperature. Th entropy excess shows, in this interval, an almost linear behaviour.

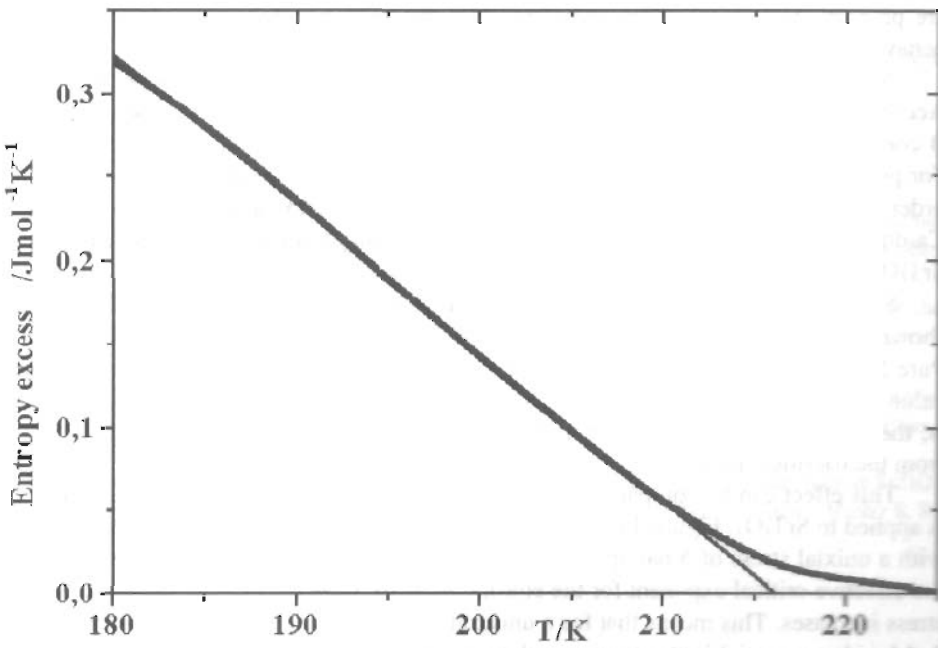

FIGURE 2 The temperature evolution of the excess entropy obtained by integration of th specific heat excess.

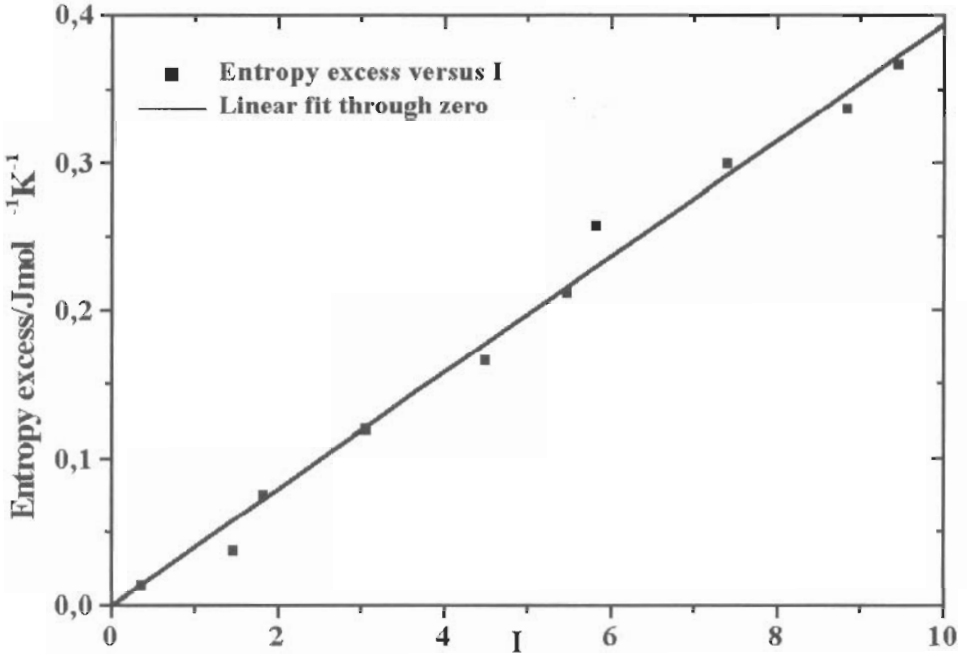

FIGURE 3 The correlation between the excess entropy and the excess intensity of neutron diffraction experiments.

For every temperature point the values of ΔS are plotted against the values of the excess intensity from the neutron diffraction data, Fig. 3. This graph shows that both quantities are proportional to each other, indicating that this transition follows mean field Landau behaviour.

At this point, the slope of ΔS versus temperature is now a significant physical quantity. According to Eq. (3) in a 2-4 Landau potential, this slope gives a relation between A and B coefficients and we obtain, from Fig. 2, a value for $A^2/2B$ of 8.8×10^{-3} JK^{-2} mol^{-1}. For pure $SrTiO_3$, $A^2/2B = 7.8 \times 10^{-3}$ JK^{-2} mol^{-1} [2]. Both coefficients are of the same order of magnitude and this fact indicates that the cubic to tetragonal phase transition in the Ca-doped $SrTiO_3$, although far from the tricritical point, is strongly related to that in pure $SrTiO_3$.

Since the transition temperature, T_c, for a pure second-order phase transition can be shown to be equal to B/A we obtain a value of $A \approx 3.9$ J mol^{-1}K^{-1}, and B ≈ 850 J mol^{-1}. Pure $SrTiO_3$ displays tricritical behaviour, with a much smaller value of B, and a larger value of C [1]. The influence of addition of Ca into the structure on the transition behaviour is, therefore, to increase the effective transition temperature and move the system away from the tricritical point.

This effect can be compared with that obtained previously [4] when a uniaxial stress is applied to $SrTiO_3$. Figure 4 shows the entropy excess for pure $SrTiO_3$ without stress and with a unixial stress of 5 bar applied to the crystallographic axis [110]. We observed that the effective critical exponent for the entropy increase from 0.37 to 0.5 when the uniaxial stress increases. This means that for a uniaxial stress the transition may be described by a 2–4 Landau potential in the same way that in doped sample.

Both, doping with Ca and uniaxial stress make the transition move further from tricritical point than in pure $SrTiO_3$.

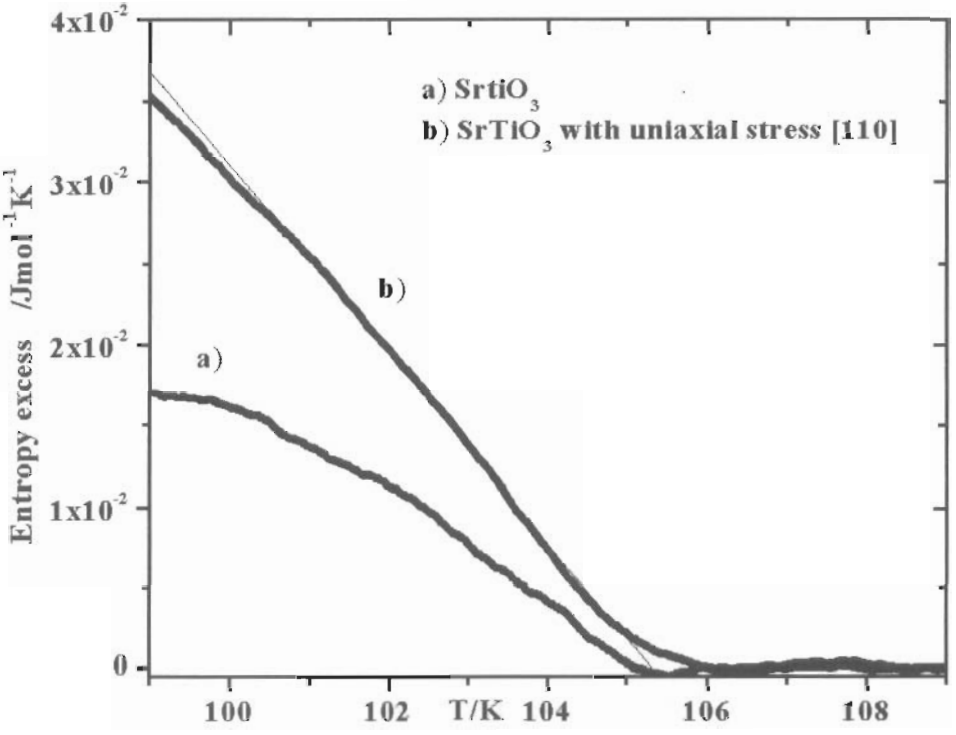

FIGURE 4 The temperature evolution of the excess entropy: a) pure $SrTiO_3$ and b) pure $SrTiO_3$ with uniaxial stress of 5 bar applied along the crystallographic [110] direction.

Acknowledgements

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