The structural phase transition in $SrTiO_3$ under uniaxial stress in the [110] direction: a calorimetric study

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Abstract. The excess specific heat of the structural phase transition of SrTiO$_3$ has been measured on single crystals under uniaxial stress along the crystallographic [110] direction and for extremely slow cooling rates. The corresponding excess entropy scales as the square of the thermodynamic order parameter. The order parameter exponent is $\beta = 0.35 \pm 0.02$ for stress-free samples and increases systematically with increasing stress. At a stress of 5 bar the exponent is $\beta = 0.5$ and the phase transition follows mean-field behaviour.

1. Introduction

Strontium titanite, SrTiO$_3$, is a prototype material as regards undergoing a structural phase transition with a relatively simple geometrical transformation pattern. The phase transition is essentially related to the tilt of TiO$_6$ octahedra in a cube cage spanned by Sr and O. Octahedra tilt transitions are most common in perovskite-type structures and systematic work on their analysis dates back several decades [1].

Despite the apparent simplicity of the transition pattern, a straightforward analysis of the transition in terms of the simplest soft-mode picture is elusive. The main difficulty relates to the coupling between the soft mode and other dynamical excitations, both fluctuations and phonon excitations. In geometrical terms, such couplings are partly indicated by the fact that the octahedra do not rotate as a strictly rigid body, but change their shape during rotation [2]. A simple correlation between the rotation angle φ and the spontaneous strain e_{sp}, beyond the lowest-order approximation $e_{sp} \propto \varphi^2$, has not been established. Furthermore, there are two sets of soft optic phonons which may potentially influence the transition behaviour. Firstly, the R phonons become soft near the transition point and act as the symmetry-breaking soft modes. Secondly, the M-point phonons also soften but do not drive the transition [3]. It is a general observation in ferroelastic and co-elastic phase transitions that such systems with a multitude of soft-phonon excitations will always show coupling phenomena ($\propto Q_1^2 Q_2^2$) which often modify the details of the transition behaviour [4]. They usually also lead to mode-crossing phenomena for $T < T_c$ [4] which could well play an important part in the 35 K anomaly in SrTiO$_3$ [5, 6, 7].

Even in the case of the simplest picture of a phase transition driven by R modes alone, the transition mechanism is complicated by the fact that the transition point is bicritical. As a consequence, uniaxial strain along the crystallographic [1 1 1] axis splits the transition

into a second-order transition at slightly higher temperature and a first-order transition at lower temperatures than in the stress-free case [8]. This bicritical behaviour also impinges on the critical behaviour of the phase transition in the following way. If the rotation axis of φ, and hence the related component of the order parameter $Q = (Q_x, Q_y, Q_z)$, are fixed in space, we would expect a simple improper ferroelastic phase transition to occur. Such phase transitions usually follow mean-field behaviour and we expect an order parameter exponent of $\beta = 0.5$ which, indeed, was found for temperatures below $T/T_c = 0.9$ by Müller and Berlinger [1]. At temperatures closer to the transition point, reorientations of rotation axes between crystallographically equivalent axes in the cubic structure correspond to the movement of domain walls. They are unlikely to occur at sufficiently low temperatures where mean-field (MF) behaviour was found. Deviations from the MF behaviour at temperatures very close to T_c were investigated using various experimental methods, although there is not full agreement between the numerical values of β derived from the experimental observations. The most relevant results for β range from 0.33 to 0.42 [1, 8, 9, 10]. Some of the differences were discussed previously as being due to variations in the defect densities in the SrTiO$_3$ samples. Although such variations will certainly exist, more systematic errors in the analysis of data, e.g. ignoring volume expansion in lattice parameters, may generate even greater errors [9]. However, great as such errors may be, the actual values of β are not too far from the theoretical value of 0.38 for a isotropic Heisenberg model [11] which relates to the reorientations of the tilt axis at temperatures close to T_c. Note that the deviation from the MF behaviour is in our discussion *not* the result of any type of expanded Ginzburg interval, but stems from the crossover from a transition mechanism with one fixed tilt axis to one in which the tilt axes can flip between the equivalent crystallographic orientations (see, e.g., [12]).

If this physical picture makes sense, we may predict the following scenario: let us apply a weak external force which prevents the tilt axis from undergoing flips into other orientations. The order parameter has then only one active component, say Q_z, whereas $Q_x = Q_y = 0$. We may then expect Q_z to show MF behaviour for $T \rightarrow T_c^-$ without any crossover. Deviations from $\beta = 0.5$, if there are any, could then be attributed to a 'true' Ginzburg interval at temperatures sufficiently close to T_c.

In this paper we argue that this prediction is, indeed, borne out in the experimental observations. The method that we used in our experimental approach was to stress a high-quality single crystal of SrTiO$_3$ weakly along the [1 1 0] direction. We then measured the excess specific heat of the phase transition over an extended temperature interval. Integrating the specific heat, we confirm for $\Delta S \propto Q^2$ an exponent $\beta \approx 0.35 \pm 0.02$ for the stress-free crystal. We also find that any stressed crystal follows MF behaviour ($\beta = 0.5$) with little indication of fluctuation corrections at temperatures close to T_c.

2. The experimental approach

Since its adaptation by Baloga and Garland [13], modulation (a.c.) calorimetry has been used for measurements under hydrostatic pressure. In our case, hydrostatic pressure does not prevent flips of tilt axes and we need to apply uniaxial stress.

Such experiments are rather difficult to conduct because the device for the application of stress disturbs the heat conduction in the sample, producing uncontrolled heat losses. Although the excess specific heat without stress has been measured by several authors [14, 15, 16, 17], there was only one study in which stress was applied to the sample [18]. No quantitative evaluation of the stress was possible from those experimental results.

In an alternative experimental approach, conduction calorimetry [19] was used. Here

the sample is placed [20, 21] between two identical fluxmeters formed by a high number of thermocouples. The details of the experimental arrangements were described previously [22, 23, 24]; here we repeat the salient points. A conduction calorimeter, where the sample is pressed between two identical fluxmeters, was constructed [24] and optimized to provide linear heat conduction and to be rigid enough to act, at the same time, as a piston which applies uniaxial stress on the sample [25]. The stress on the sample can be controlled quantitatively and absolute values of the specific heat can be measured.
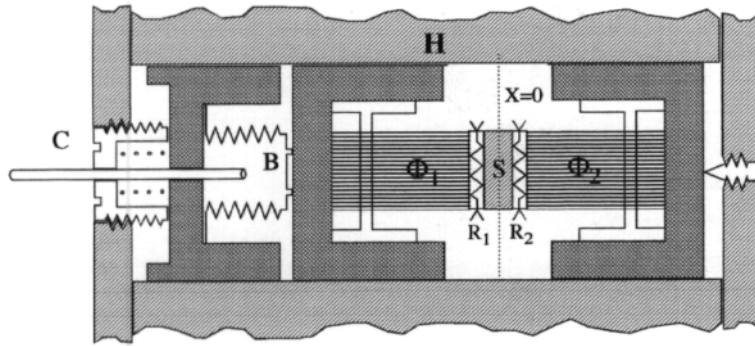

Figure 1. A diagram of the sensor: Φ_1 and Φ_2, heat fluxmeters; R_1 and R_2, heaters; S, sample; B, bellows; H, heat sink; C, capillary.

To avoid heat losses during the measurement of the specific heat under controlled uniaxial stress it is necessary that the measuring sensors be used directly to apply the stress on the sample. In our case, the sensor (figure 1) was formed of two identical fluxmeters (Φ_1 and Φ_2), two platinum resistances (R_1 and R_2), a calorimeter block (H) and a device (B) to apply an uniaxial stress to the sample (S). Each fluxmeter was made from 50 chromel–constantan thermocouples connected in series with the wires (18 mm long and 0.5 mm^2 in cross section) placed in parallel lines. On each side, every junction was glued to a thin silver plate 12 mm in diameter. The external plate was in good thermal contact with the calorimeter block and the internal plate was in thermal contact with one of the resistances R_1 or R_2. The sample was pressed between the two fluxmeters (figure 1). One of them (Φ_2) was fixed to the calorimeter block (H) while the other one (Φ_1) was pressed by bellows (B) connected through a capillary (C) to an outer pressure bottle of N$_2$. Extreme precautions were taken to achieve symmetry in the device with respect to plane $x = 0$. Thermal contact between the sample, resistance and fluxmeters was assured by means of a thermal conduction paste (beryllium oxide and silicone).

The entire assembly (figure 1) was placed in a cylindrical hole made in a cylindrical piece of bronze (10 kg) which served as the heat sink (the calorimeter block) [25]. The fluxmeters were aligned with respect to each other and, together with the bellows, were put in thermal contact with the block using graphite powder. The block and the two surrounding radiation shields were placed into a hermetic outer case under vacuum (10^{-7} Torr). The connection wires and the capillary were in good thermal contact with the outer case, the radiation shields and the block, thus producing a very good thermal stability in the sensor. The assembly, surrounded by serpentine, was placed in a Dewar jar filled with alcohol. The temperature of the alcohol bath was controlled by circulation of liquid N$_2$ through the serpentine. A Pt-100 thermometer and a Eurotherm 818 controller were used. The temperature measurement range was between liquid nitrogen and room temperature. The block temperature was

measured with a commercial platinum thermometer (Leads & Northrup (model: 8164 B) and a Thinsley resistance bridge (model: Ambassador). An HPE-1328A intensity source and an HPE-1326 multimeter were used to produce and to measure the power dissipated in the heaters R_1 and R_2 respectively. The e.m.f. produced by the fluxmeters was measured by a Keithley 181 nanovoltmeter with a frequency of four measurements per second. All the devices were controlled by an HP-75000 data acquisition system and an HP-Vectra 386 computer.

To measure the specific heat, we started from the steady state obtained when the same power W was dissipated by both resistances R_1 and R_2 (figure 1). Due to the high vacuum in the calorimeter and the small temperature difference between the sample and the calorimeter block (lower than 0.1 K) we assumed that there was no lateral heat loss, and that the temperature of the sample was uniform. At the time t_0 the power was switched off and the thermal equilibrium with the block was obtained at time t_1. The e.f.m. given by the fluxmeters $V(t)$ was measured as a function of time between t_0 and t_1. The integration of this e.m.f. between t_0 and t_1 allows us to obtain the thermal capacity of the sample [20, 22].

A sample formed from several single crystals of strontium titanate was studied. These crystals were grown by Verneuil process with a purity of 99 998%. The main impurities were 3 ppm of Fe and 2 ppm of Ni. These crystals were of the same thickness (1 mm) and had an overall surface face (110) of 25 mm^2. The flatness of this face was better than 1 μm over the full sample. The face (110) was placed perpendicular to the direction X in figure 1; thus the uniaxial stress was applied along the crystallographic [1 1 0] direction.

3. Results and discussion

With the sample under different uniaxial stresses (0, 2, 4 and 5 bar) the specific heat was measured while decreasing the temperature at a constant rate of 0.06 K h^{-1} and increasing the temperature at 0.07 K h^{-1} and 0.2 K h^{-1} for various runs. Data were obtained at intervals of 0.02 K and 0.05 K. The increase of the temperature in the sample due to the measurement process is estimated to be 0.06 K.

In figure 2, data obtained while cooling the sample are shown for various uniaxial stresses. At 105.0 K the specific heat shows a stepwise behaviour. Its specific heat jump Δc_0 is estimated to be 0.003 J g^{-1} K^{-1} which is in reasonable agreement with the values obtained by Garnier [16] and Franke and Hegenbarth [17]. Within the experimental resolution, Δc_0 remains constant for all applied stresses while the transition width increases with increasing stress.

Data obtained while heating the sample show a similar behaviour to those shown in figure 2, although, as we could expect, the transition appears to be marginally wider on heating than on cooling.

In order to analyse our results further we follow the procedure for the determination of the excess entropy commonly used for the investigation of ferroelastic phase transitions [4]. The excess entropy ΔS is calculated from

$$\Delta S = -\int_T^{T_c} \frac{\Delta c}{T}\, dt \tag{1}$$

where the excess heats have been determined with reference to a straight line adjusted for $T > 106$ K for each stress. These straight lines are represented in figure 2. The resulting excess entropies are shown in figure 3. We now correlate the excess entropy directly with the structural order parameter Q using the underlying assumption of Landau theory, namely
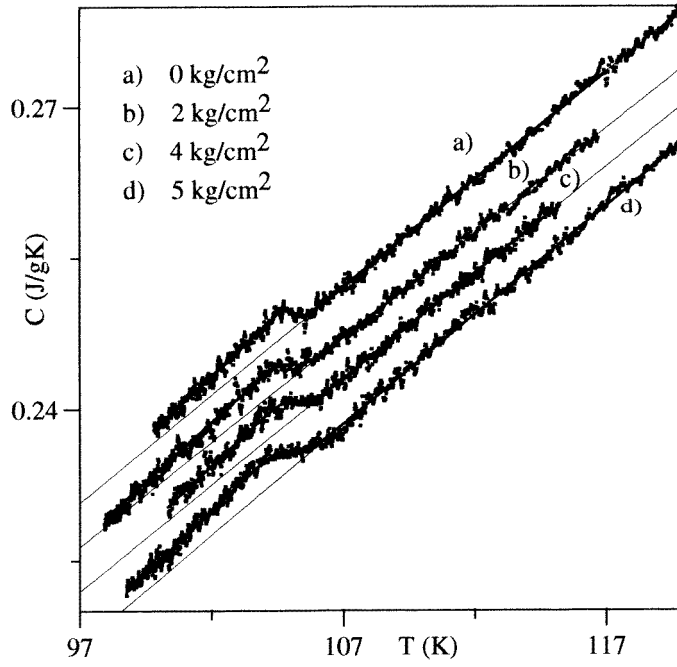
Figure 2. The specific heat of strontium titanite versus temperature (on cooling) for some applied uniaxial stresses. For reasons of clarity data under stress have been shifted in the graph.

the quadratic Q-dependence of ΔS:

$$\Delta S \propto Q^2 \qquad \text{and} \qquad \Delta S^{1/2\beta} \propto T - T_c \tag{2}$$

where β is the critical exponent of the order parameter.

Using the data in figure 3, the exponent β has been calculated for each stress in such a way as to obtain the best linear relation between $\Delta S^{1/2\beta}$ and T. These linear relations are shown in figure 4. The values of β and the corresponding linear regression coefficient are indicated for each stress in table 1.

We now turn to the discussion of the experimental observations on the stress-free crystal which we use to test the underlying assumptions of equation (2). As a first result we find the exponent β to be 0.35 ± 0.02. This value is close to the Ising value and slightly below the anticipated value for the 3D Heisenberg model. It is close to the earlier results of Müller and Berlinger [1] and Steigmeier and Auderset [10]. This agreement is taken as justification of the validity of assuming a simple quadratic scaling of the excess entropy with respect to the order parameter. Estimating the relevance of the entropy tails near T_c, we proceed as follows. The rotation angle at $T/T_c = 0.96$ is $\varphi = 0.67°$ [8]. The excess entropy at the same temperature is 7.76×10^{-5} J g^{-1} K^{-1} for the stress-free sample leading to the relation

$$\Delta S = 1.73 \times 10^{-4} \varphi^2 \ (\text{J g}^{-1} \ \text{K}^{-1}). \tag{3}$$

We may now use this estimate to calibrate the weak tails of the excess entropy at temperatures close to the transition point. The maximum amplitude of this tail is 2.3×10^{-6} J g^{-1} K^{-1}. The equivalent rotation angle is $0.013°$. Such small rotation angles may well be the signature of defects, surface heterogeneous stress fields, etc and may not relate to intrinsic effects of the phase transition. We conclude, therefore, that the exponent
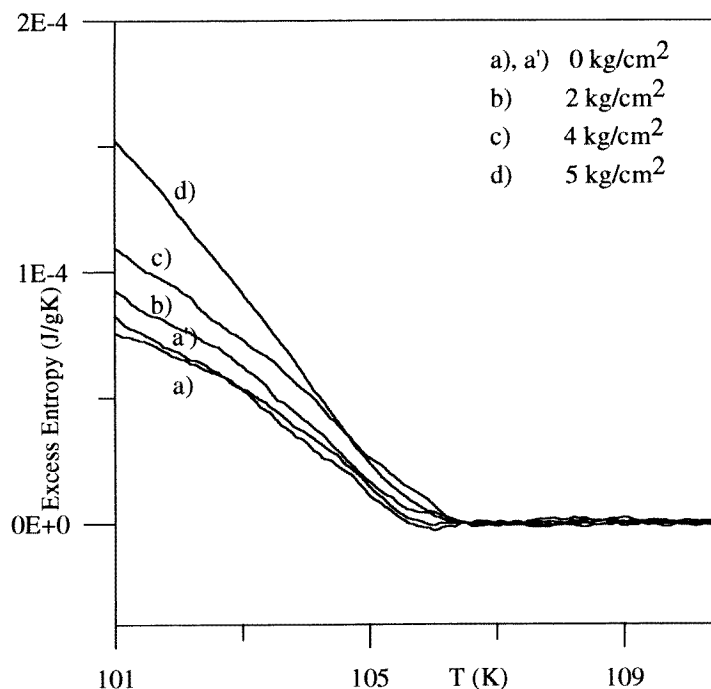
Figure 3. The excess entropy versus temperature for the different applied uniaxial stresses represented in figure 2.

β found in stress-free crystals is close to that found by other experimental methods and that there is no compelling evidence for additional fluctuation effects at temperatures close to the transition point.

Using the same scaling relation we now analyse the excess entropy of samples under uniaxial stress in the crystallographic [1 1 0] direction. Ignoring the weak tails near the transition points, all curves can be described empirically by power laws. The exponents β clearly increase with increasing stress from 0.35 to 0.5 (table 1). Simultaneously we find an increase of the transition temperature, which we define as the temperature at which the power-law entropy disappears. This temperature is 104.88 K for the stress-free sample and increases to 105.31 K for a load of 5 bar. The resulting stress dependence of the transition temperature is much greater than for the cubic–trigonal transition when stress is applied along the crystallographic [1 1 1] direction [8]. It also exceeds the slopes of the T_c versus p curves obtained by [26] for stresses much larger than those employed in our experiments. At this point, our results on the dT_c/dp slope may only be correct within some 20% and further work is clearly needed to chart the p–T field with sufficient accuracy in order to derive firm conclusions regarding the crossover behaviour for weak stresses in the [1 1 0] direction.

Such work should focus on the question of whether the transition temperature depends linearly on the external stress, as predicted by Landau theory for the uniform state, or, alternatively, whether a non-linear regime exists for small stresses. Such non-linearities were previously observed in ferroelastic materials for stress fields generated by defects. The non-linear part of the T_c versus p curve was called the plateau regime [4, 27] with
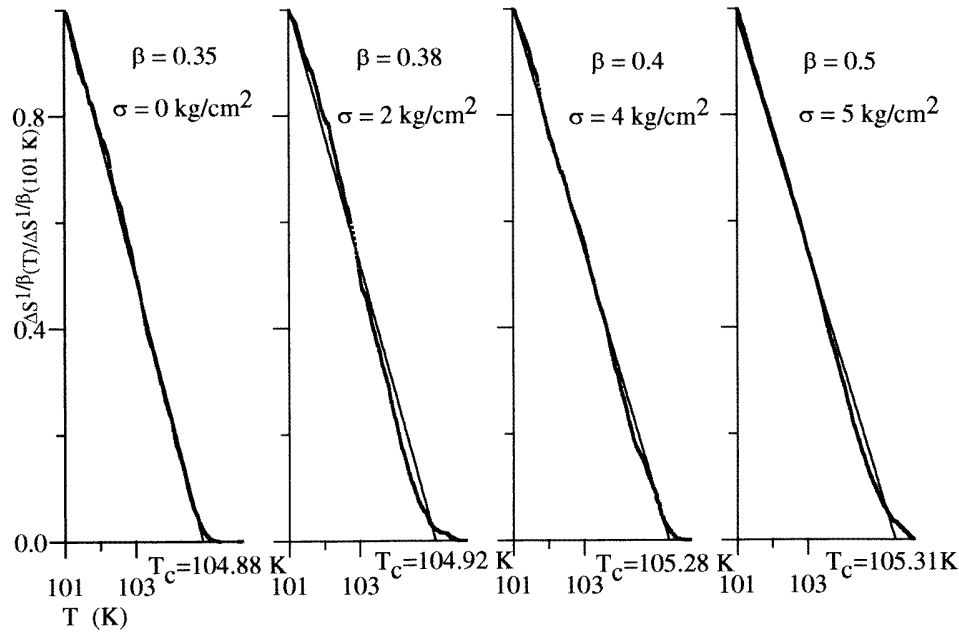
Figure 4. The best linear relation between $\Delta S^{1/2\beta}$ and temperature for the different applied uniaxial stresses represented in figure 2.

a weaker (stronger) p-dependence in the (inverse) plateau at $p = 0$. The physical origin of the (inverse) plateau lies in the heterogeneity of the sample in the presence of defects or domain boundaries. In this context the results of Fossheim and Berre [26] are most important. These authors found that external stress decreases the attenuation of ultrasonic-wave propagation near T_c. The relevant stresses were of the order of some 100 bar, i.e. much greater than in our experiments. Fossheim and Berre found no saturation of the reduction of attenuation for pressures up to $\simeq 500$ bar, and correlated this effect with a continuous decrease of the number of domain walls in the sample. This observation is at variance with the behaviour of other improper ferroelastic materials in which the coercive stress is much lower (e.g. 1 bar in Pb$_3$(PO$_4$)$_2$ at $\simeq 0.8$ T_c; [4, 28]). Further work is clearly needed to identify the characteristic coercive stress in SrTiO$_3$ at temperatures closer to T_c.

The main result of our investigation is that even small uniaxial stresses applied in the crystallographic [1 1 0] direction lead, for extremely slow cooling rates, to mean-field behaviour of the phase transition in SrTiO$_3$. We also find that the excess entropy at $T < T_c$ increases with increasing uniaxial stress. It is now tempting to speculate that the increase of ΔS is directly correlated with an increase of the rotation angle in the unidomain state. Experimental work designed to clarify this point is under way.

Acknowledgment

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