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Twin structures in tetragonal $SrTiO_3$: The ferroelastic phase transition and the formation of needle domains

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Direct optical observation of the twin domains in ferroelastic strontium titanite at $8\,K<T<105\,K$ show that twin boundaries in the bulk do not change at temperatures below 103.4 K. At temperatures between 103.4 K and $T_c=105.65\,K$ the contrast between the birefringences of two adjacent domains is too weak to allow the visual observation of the domain wall. The temperature independent, coarse domain structure in the bulk of the crystal is in strong contrast with a fine domain structure and strain relaxations near the crystal surface. No indication for wall flip motion was found for repeated, slow cooling, and heating through the transition point. © *1999 American Institute of Physics.* [S0021-8979(99)01915-5]

I. INTRODUCTION

Early research on the phase transition of $SrTiO_3$ near 105 K focused on the multicritical character of the transition with an $n=$three-fold degenerate R_{25} soft mode. Traditionally, the transition was analyzed using renormalization group techniques starting from an $n=3$ Heisenberg-type effective Hamiltonian and a cubic anisotropy part which characterizes the soft mode dispersion. It was noted at a very early stage that in large, stress-free crystals the effect of the anisotropy was to lift the order parameter degeneracy and the applicability of $n=1$ Ising type behavior, as opposed to the $n=3$ Heisenberg case, was hotly debated.[1–6]

Recently, the analysis of the tetragonal phase at $T<T_c$ became more prominent, mainly in the context of research on mesoscopic domain structures in ferroelastic materials. It was found that surface near regions in $SrTiO_3$ crystals are finely twinned with additional high densities of antiphase boundaries.[7–10] The domain pattern reacted sensitively to weak external uniaxial stresses showing all the hallmarks of a ''normal'' improper ferroelastic material.[9] As most of these materials follow Landau–Ginzburg behavior in the low-symmetry phase, the thermodynamic properties of this phase were reinvestigated. High-resolution specific heat measurements[11] showed that the experimental observations were compatible with a near-tricritical, mean field behavior of the ferroelastic phase. The maximum temperature interval in which nonfield field fluctuations may play a role was limited to 1 K. Subsequently, Hayward and Salje[10] reviewed all available experimental data in the light of this observation and concluded that the order parameter behavior in the ferroelastic phase follows well from a macroscopic Gibbs free energy $G=1/2AQ_s(\coth Q_s/T-\coth Q_s/T_c)Q^2+\frac{1}{4}BQ^4+1/6CQ^6$ with $A=0.7\,J\,K^{-1}\,mol^{-1}$, $B=31\,J/mol$, $C=42\,J/mol$, $T_c=105.65\,K$, and $Q_s=60\,K$ as first determined by Salje *et al.*[11]

Some apparent inconsistency may now be perceived between the observation that surface near areas of $SrTiO_3$ show very fine twin structures (but no indication of flip motions of the twin walls) while larger single crystals used in electron paramagnetic resonance (EPR) experiments were reported to be single crystals at $T<T_c$. First, the question of the length scale over which twinning occurs appears to be potentially controversial. Second, the question arises if orientational fluctuations have any influence on the domain structure even though their thermodynamic relevance has been ruled out on the basis of the specific heat data. It is the purpose of this article to describe new experimental observations using the same crystal as Chrosch and Salje[7] and Salje *et al.*[11] It will be shown, first, that the optically observed twin structure in the bulk of the crystal is, indeed, very coarse and different from the surface-near regions. Second, it will be shown that the domain structure remains unchanged between 8 K and T_c with no indications for any domain reorientation.

II. EXPERIMENT

Single crystal of $SrTiO_3$ were grown using the Verneuil method and cut (110) cubic facet (5.1×3.1 mm with a thickness of 1 mm). The crystal's final thickness was 980 μm. The effects of cutting were apparent as far as 2 mm from the sides of the crystal slab, as shown by a first order white-gray crystal at 45° between cross polars at room temperature. The crystal was inserted into an Oxford Instruments CF204 (modified) helium flow cryostat. The cryostat is fixed be-

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cause of the weight of the helium transfer tube. A Leitz Orthoplan Pol microscope with crossed polars and 10× oculars, was used for the observations under white light (100 W halogen lamp). Objectives: Leitz Pol 3.2×0.12 and a Zeiss–Jena Pol 8×0.10. A Wild Photoautomat camera for black and white Polaroid pictures ($3\frac{1}{4}\times 4\frac{1}{4}$) completes the microscope. A sample holder inside the cryostat allowed 360° rotation of the crystal plate in its plane and perpendicular to the microscope axis.

Polaroid photographs of the (110) cubic cut $SrTiO_3$ crystal, at 45° between crossed polars, with magnification of 32× (objective 3.2× with ocular 10×) or 40× (4×10), were taken at regular time intervals during heating the crystal from 8 K through T_c ($T_c = 105.65$ K, as determined by calorimetric measurements), at a rate 0.62 K/min from 35 to 95 K and 0.23 K/min from 95 to 110 K. Below T_c only two types of domain walls were observed, i.e., rather large and blurred (110) walls and rather sharp (100) walls (orientation with respect to cubic axes). As expected from symmetry arguments, the angles between the traces of the walls and a (001) side were 35° and 90°, respectively. On heating, the domains disappeared gently without wall movements, as expected for a second order phase transition. Confirmation was obtained after a second cooling to 80 K and subsequent heating at a rate of 0.25 K/min, from 95 to 110 K. Large parts of the crystal were untwinned.

A heavily twinned area was selected on these photographs and each photo was digitized at 600 pi. Where necessary these images were rotated to correct for any slight misorientation of the twin planes; rotations were in the range 1°–3°. Each image was then integrated line by line, hence enhancing the birefringent effect of the domains, to produce a profile of image brightness perpendicular to the domain boundaries. The profiles were then aligned using a particularly prominent domain. In order to compensate for the variable exposure times of the original photographs the intensity profiles were normalized to this index twin. This procedure was repeated on another area of the crystal.

In order to investigate the persistence of the domains as T_c was approached an average intensity profile was produced over the temperature range 80–104 K and each of the profiles compared with this using the Pearson correlation coefficient as an indicator for possible movements of domain walls. Because the illumination over the sample was uneven the domains on the profiles were superposed on an uneven background. To remove this effect a square filter was applied to the profiles before the correlation coefficients were calculated. As well as suppressing the low frequency background this had the effect of enhancing the features produced by the domain boundaries. Photomicrograph extracts and the corresponding intensity profiles are shown on Fig. 1.

The digitized area from which the other set of profiles were produced had five particularly prominent domain boundaries in addition to the index twin. A gaussian curve was fitted to each of these features in the set of profiles and the offsets of the centroids from the index twin were determined at each temperature. For each of the five marker twins the offsets were standardized by expressing them as a ratio to the mean offset for the particular domain over the whole temperature range (Fig. 2).

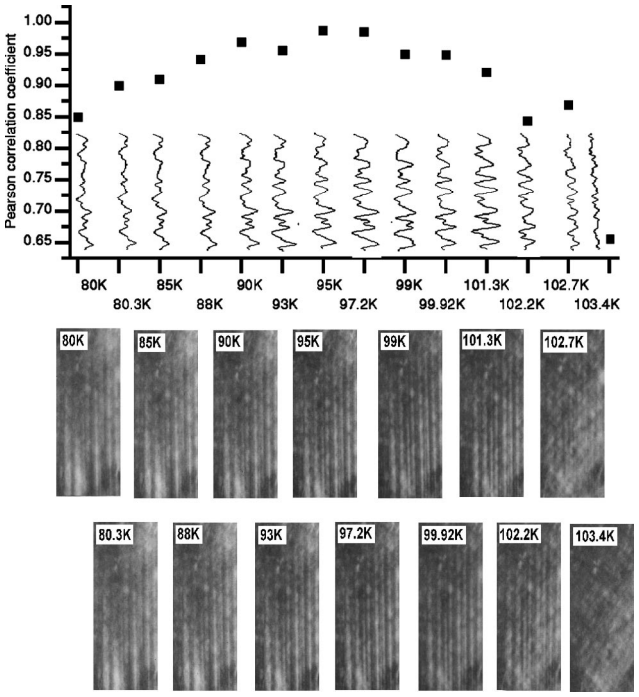

FIG. 1. The solid squares on the graph show the strength of the Pearson correlation coefficient between each intensity profile and an average of these profiles. Note the abrupt change between 102.7 and 103.4 K. Also shown on the plot are the intensity profiles used in calculating these coefficients. The vertical length of each profile is 150 μm. The profiles shown have been processed with a square filter. At the bottom of the figure are the raw images from which the profiles were initially extracted. Each image is 150 μm wide.

III. RESULTS

The optical birefringence of $SrTiO_3$ at room temperature shows a strong noncubic lattice distortion near the surface of the crystal. The rim of the birefringence in Fig. 3 extends some 100 μm into the crystal. This observation confirms earlier reports[7] on a variety of crystals all showing strong parasitic birefringence close to the surface of the samples. It appears that this birefringence is only weakly dependent on the actual surface structure. Sawn surfaces and cut and polished ones show strong parasitic birefringence although its extent inside the crystal varies from sample to sample. In view of this observation it becomes obvious that diffraction experiments related to surface near regions and the bulk of the sample lead to rather different conclusions.[7,12,13] The parasitic birefringence depends little on temperature and, in particular, shows almost no change at the transition to the ferroelastic phase. Similar parasitic birefringence was observed in $BaTiO_3$.[14]

The domain structure in $SrTiO_3$ consists in the bulk of the sample of coarse twin domains. We found almost no memory of the domain patterns under repeated heating and cooling through the transition point. Large areas of the crystal consist of one single twin domain. The most common structures were arrays of parallel domain walls leading to the formation of needle domains near to the crystal surface.

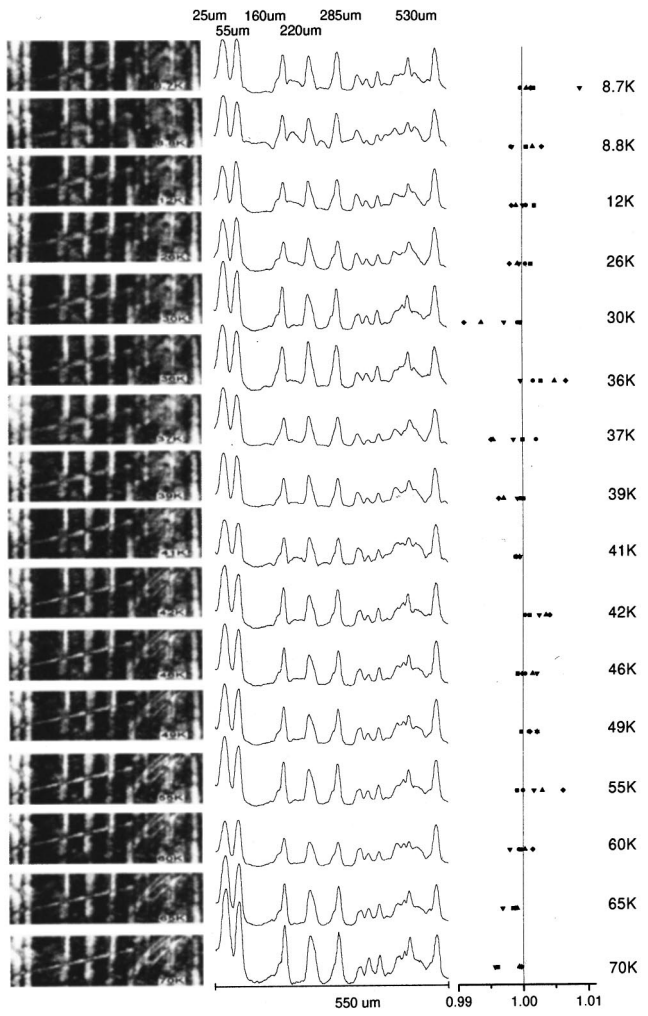

FIG. 2. The photomicrographs on the left show a twinned area at different temperature increments. Each image is 550 μm wide and some surface scratching is also visible. In the center are the intensity profiles extracted from these images. The deviations of the center of key twins from an index twin (at 530 μm) are shown to the right. These are expressed as a ratio of the offset against the mean offset for the twin over the temperature range. All offsets are less than 1%. (Symbols: square, 25 μm; circle, 55 μm; up triangle 160 μm; down triangle, 220 μm; diamond, 285 μm).

These domain walls showed no temperature dependence. Any deviations from the marker twin being attributable to measurement errors, consistently less than 1% and occurring randomly over the temperature range (Fig. 2).

A crucial part of the investigation was focused on the persistence of domain structures when heating the crystal through the transition point. The transition temperature of the sample was determined by calorimetric measurements as 105.65 K. Heating the sample slowly through the transition point showed that the birefringence contrast between two adjacent domains became increasingly faint. Increasing exposure time was used to compensate for this effect and, indeed, the domain boundaries were clearly visible up to a temperature of 102.7 K then disappearing over the next 0.7° interval (Fig. 1). This observation shows clearly that no reorientation of domain boundaries occurs in the ferroelastic phase of $SrTiO_3$.

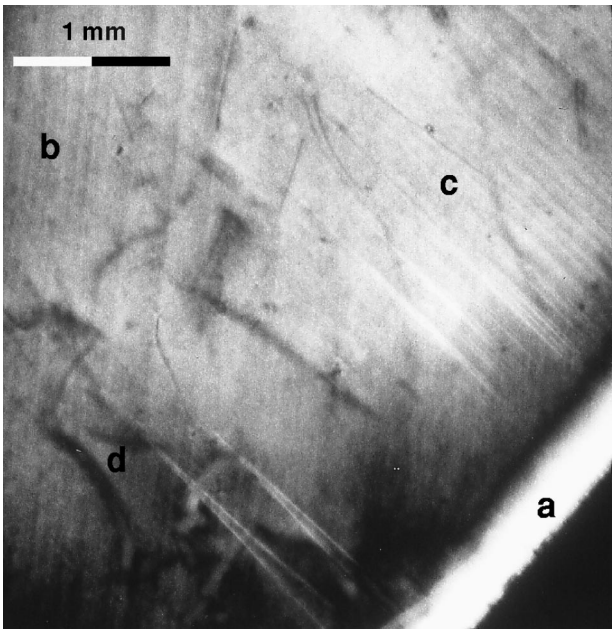

FIG. 3. Photomicrograph of a $SrTiO_3$ crystal at 84 K showing rim of strong parasitic birefringence within 100 μm of the edge of the sample (a). Multiple (110) twins oriented oblique to the crystal edge can also be seen (b) and (100) twins, including two well defined needle twins, perpendicular to the crystal edge (c). Needle *d* is analyzed in Fig. 4.

IV. DISCUSSION

The phase transition in $SrTiO_3$ is correlated with the appearance of microstructures which are the hallmark of a classic improper ferroelastic transition. It differs from other ferroelastics with respect to the importance of surface relaxations. Such relaxations are expected on theoretical grounds to exist in all ferroelastics,[9,15–17] although the characteristic length scale at $T \ll T_c$ is expected not to exceed some 10 nm. In $SrTiO_3$ the effect is both stronger as assessed from the high level of parasitic birefringence and also spreads more widely into the inner part of the sample. In all samples we found a rim of relaxed material, virtually independent of the preparation of the crystal surface. This observation agrees well with the reported nonuniformity of the diffraction pattern which showed surface related secondary length scales.[12,13]

The surface-near regions appear not to alter the thermodynamic behavior of the transition as far as seen by the measurements of the specific heat. They do change the domain structures, however. Surface-near structures seem to be twinned on a submicron level while the bulk of the crystal is only coarsly twinned. The observations in this article clearly indicate that the twin domains in the bulk of the material correspond fully with those observed in other ferroelastic materials. The main domain structure consists of needle domains having linear trajectories and tip angles in the range 4.3°–5.5° (Fig. 4).[17–19]

The persistence of the domain structure up to a temperature very close to the transition point, as seen by independent calorimetric measurements, is a clear indication that in these materials flips of rotations axes or tumbling motions of the TiO_6 octahedra do not build up to a macroscopic scale. It is

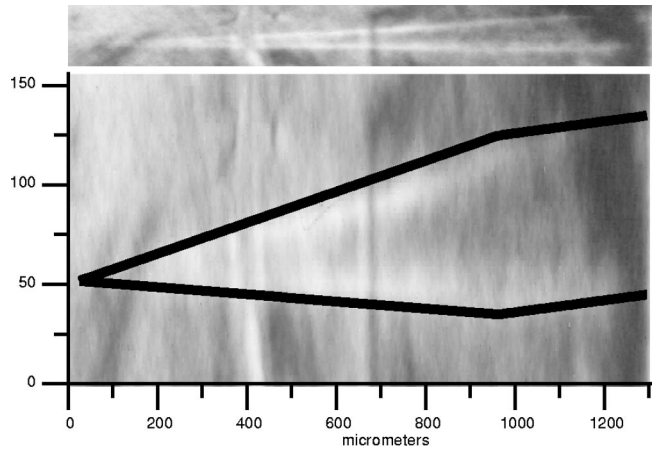

FIG. 4. Detail of needle domain in $SrTiO_3$ (extracted from Fig. 3). Upper image shows true aspect ratio. The lower image has the *y* axis expanded to demonstrate the linear nature of the needle tip, both axes have the same units. The apparent asymmetry in the latter is due to the nonlinear expansion. Fuller description of the fitting procedure is given in Salje *et al.* (see Ref. 18).

important to note that this situation may be changed under suitable external stresses. Pertsev, Zembligotov, and Waser have shown that the stresses exerted by substrates on thin films of perovskites can lead to the reestablishment of order parameter degeneracies which, in turn, would allow fluctuations to explore the full parameter space.[20] In this case the energy barrier for tumbling motions of the octahedra could well be reduced in $SrTiO_3$ so that Heisenberg-type fluctuations may occur well within the ferroelastic phase. In this case, the order parameter evolution in $SrTiO_3$ under such constraints would not follow the observed mean field behavior and twin structures would disappear on a macroscopic scale at temperatures well below T_c. Furthermore, domain reorientations and heavily curved twin walls would be expected. This is not what was found in the large single crystal used in this study, however, where no indication for deviations from a simple ferroelastic behavior was observed.

The observation that the coarse twin structure of the bulk is independent of temperature is also in contrast with the previous observation that the fine domain structure near the surface changes strongly over several tens of degrees below T_c.[7] The temperature independence of bulk domains is not due to strong pinning effects as indicated by the almost complete lack of memory effect and the high mobility of domain walls under unixial stress.[21] Movements of twin walls were also observed in EPR experiments[22] and optically.[23] Our results are also in good agreement with the observation by neutron and x-ray diffraction that structural defects and secondary length scales exist near the surface of $SrTiO_3$ crystals but not in the bulk.[24,25]

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