Ferroelectrics, 2002, Vol. 267, pp. 317–322
Reprints available directly from the publisher
Photocopying permitted by license only

LOW-T FERROELECTRICITY IN ANTIPHASE DOMAIN BOUNDARIES OF $SrTiO_3$

L. ARZEL[ab], B. HEHLEN[a], A.K. TAGANTSEV[c], F. DÉNOYER[d], K.D. LISS[e*], R. CURRAT[b], and E. COURTENS[a]

[a]*Laboratoire des Verres – UMR 5587 CNRS, Université Montpellier 2, F-34095 Montpellier Cedex 5, France,* [b]*Institut Laue-Langevin, BP 156, F-38042 Grenoble Cedex 9, France,* [c]*Laboratoire de Céramique, EPFL, CH-1015 Lausanne, Switzerland,* [d]*Laboratoire de Physique des Solides, Université Paris-Sud, F-91405 Orsay Cedex, France,* [e]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France.*

(Received in final form November 24, 2001)

The ferroelectric transition of *bulk* strontium titanate is suppressed by a combination of two effects: (1) the structural changes produced by the antiferrodistortive transition at T_a=105 K and (2) the quantum fluctuations. The structural changes are strongly perturbed within antiphase domain *boundaries*, and this in such a manner that a ferroelectric transition should occur in boundaries containing the tetragonal *c*-axis at T_c~ 35 to 40 K. This provides a possible explanation for a number of anomalies observed in $SrTiO_3$ at those temperatures. We report a new low-*T* anomaly on the lattice parameter *c* measured on a thin polished platelet. The above model is consistent with its sign and size, as well as with the sign and size of earlier birefringence measurements on similar samples.

Keywords strontium titanate, domain boundaries, ferroelectric transition, lattice constant, birefringence

---

*Present address: Institut für Werkstoffforschung, GKSS-Forschungszentrum, Postfach 1160, D-21502 Geesthacht, Germany.

I. INTRODUCTION

Quantum Ferroelectricity in $SrTiO_3$

Perovskites ABO_3 show *two* types of instabilities. 'Structural' ones, related to rotations of BO_6 octahedra, and ferroelectric ones, due to polar displacements within B–O bonds. These instabilities generally *compete*. Strontium titanate is a special case for which the 'tolerance factor' [1] is very close to one. Hence, both instabilities are nearly equally active. On cooling, the structural transition occurs first, at T_a = 105 K. Its order parameter is the alternate rotation angle ϕ of the TiO_6 octahedra. This cubic-to-tetragonal transition splits the soft TO branch F_{1u} of the cubic phase. In the low-T phase, the pure TO modes are either polarized in the *ab*-plane (E_u) or along the *c*-axis (A_{2u}). Near zone center, the former have a frequency ω_a, the latter ω_c. It is experimentally confirmed that under zero stress these frequencies are well represented by [2]

$$\omega_{a,c}^2 = \omega_0^2 + D_{a,c}\,\phi^2 \quad , \qquad (1)$$

where ω_0 is the frequency of the 'bare' ferroelectric mode. The *positive* constants $D_{a,c}$ express the above competition. One finds that ω_0^2 strongly bends away from the Curie-Weiss law owing to quantum effects but that it nevertheless crosses zero at $T_{c0} \sim 30$ K [2]. Hence, quantum fluctuations *alone* are not sufficient to prevent ferroelectricity. Just a slight decrease of quantum effects, replacing ^{16}O by ^{18}O seems sufficient to restore it [3]. It is of interest to analyze $D_{a,c}$ in terms of contributions due to the transition-induced strains, $\Delta a/a < 0$ and $\Delta c/c > 0$, and to pure rotations at zero strain. One finds that D_a is positive *mostly* owing to the negative $\Delta a/a$. D_c is positive *mostly* owing to the pure rotation ϕ around the *c*-axis, while the positiveness of $\Delta c/c$ reduces D_c [2].

The Structural Domains

There are two categories of domains due to the structural transition. First and most obvious are twin domains corresponding to different orientations of the tetragonal *c*-axis along any one of the former cubic axes. These can be called 'structural' domains. For reasons of strain compatibility their boundaries are (1 1 0) planes of the cubic phase.

The second category of domains occurs within singly oriented tetragonal crystals or crystallites. It results from the cell doubling occuring at the structural transition in all three cubic directions. The sign of ϕ is significant here, as it determines the phase of the rotation. A couple of antiphase domains is characterized by the same rotation axis but opposite signs, ϕ and $-\phi$. Two adjacent antiphase domains are separated by an antiphase domain boundary (APDB).

There are two extreme types of planar APDBs [4]. The '*longitudinal*' ones are perpendicular to the tetragonal *c*-axis. It is evident from the structure that these produce no disruption in the oxygen positions. Thus, they should be thin and of low energy cost, and might as well be called '*easy*' boundaries. These were observed in very thin samples with electron microscopy [5] and they were found to be extremely numerous. The other extreme planar APDBs can be called '*transverse*' as their plane contains the *c*-axis. With *c* along the third axis, the rotation of adjacent domains is characterized by $+\phi_3$ and $-\phi_3$. It is evident that the continuity of the oxygen position requires that ϕ_3 be small over an extended region near the center of such boundaries. This can only be achieved with thick boundaries of rather high energy cost which therefore can be called '*hard*' [4]. They are presumably less frequent in high quality crystals, but they will be promoted by appropriate dislocations.

Different Low-Temperature Single Crystal Varieties

Experiments on strontium titanate are currently performed on 'single' crystals, thin films, powders, and ceramics. Considering only single crystals, one should distinguish at least three distinct low-T varieties.

Most experiments are performed on crystals for which the tetragonal axis is not forced into a single direction. In some cases it would be difficult to do so owing to the particular experimental method, for example in torsion-balance measurements [6]. Such crystals obviously contain many structural domains and walls depending, among others, on the internal stresses always present in Verneuil-grown crystals. Many measurements can be strongly affected by these domains.

Another category of data is obtained on crystals that are oriented in the tetragonal phase by applying stresses upon lowering T through T_a. Since $c/a > 1$, uniaxial pressure on a (110)-cubic face can force the *c* axis in the single ⟨001⟩-direction [7]. Similarly, biaxial or cylindrical geometries can be used [8]. With uniaxial pressure, it is possible to remove the applied stress at sufficiently low T, and the orientation is preserved [9]. This allows one to measure reliably the tetragonal anisotropy of the phonon spectra. For high quality crystals, such samples are presumably the most perfect ones, although they might still contain many easy APDBs.

In a third method, a thin (~200 μm), elongated, (110)-platelet, with its axis in the ⟨001⟩-direction, is polished optically. These platelets orient spontaneously with *c* in their long direction [7]. Although the detailed mechanism is not understood, one presumes that work-hardening by polishing produces the orienting stresses. This implies a fairly high density of dislocations that might also stabilize the hard APDBs. Such platelets have been very much used for EPR experiments, among others.

II. CALCULATION OF ANTIPHASE DOMAIN BOUNDARIES

A calculation of APDBs using a Gibbs potential plus gradient terms, and including a stability analysis, is given elsewhere [4]. It shows that *longitudinal* boundaries are very thin and 'simple', *i.e.* all components of ϕ vanish in their center. They are stable against the development of a polarization P, mostly owing to $\Delta a/a < 0$ imposed by the adjacent domains.

Transverse boundaries have a structure similar to magnetic Néel walls [4]. This was shown in detail for those perpendicular to a tetragonal a axis. While $\phi_3 = 0$ in their center, a component ϕ_1 perpendicular to the wall is maximum there. These boundaries are thick (~90 Å). They develop a component P_3 at $T_c \sim 35$ to 40 K mostly owing to the fact that $\phi_3 = 0$ in their center together with $\Delta c/c > 0$ imposed by the adjacent bulk. This ferroelectricity is thus quite independent from the angular position of the boundary around the c direction. The saturation polarization is large (~4 $\mu C/cm^2$), and produces large stresses in the boundaries, which at saturation are $\sigma_3 \sim 3\times10^8$ and $\sigma_2 \sim -2\times10^7$ erg/cm^2.

A distribution of such boundaries, separated by an average distance L, strains the bulk of the sample proportionally to t/L, where t is the full boundary thickness. In particular one expects a change in Δc owing to the ferroelectric transition taking place at T_c. This change is given by

$$\delta(\Delta c)/c = (s_{11}\,\sigma_3 + s_{12}\,\sigma_2)\; t/L, \qquad (2)$$

where s is the elastic compliance tensor. We also calculated the strains in perpendicular directions. These are found to be appreciably smaller.

III. SOME LOW-T ANOMALIES OF $SrTiO_3$

Among the low-T anomalies reported on $SrTiO_3$, some can clearly relate to the rearrangement of structural domains. This is the case for the early observations of Lytle [10], as well as for several later reports of electromechanical, ultrasonic, or internal friction anomalies. It is likely that the development of polarization in domain walls modifies the domain mobility, also for structural ones, as for example in gadolinium molybdate [11]. This can lead to many effects that all occur at the same temperature. Dielectric losses [12] could also be explained by the occurence of polarization in a fairly dense set of boundaries.

There are however effects that appear to be 'bulk' ones, like the EPR observation of slight anomalies near 37 K on the crystal field parameters [13], or also the measurement of a birefringence that departs from ϕ^2 below 37 K [14]. These could be explained by bulk strains

resulting from a distribution of polar boundaries, as sketched at the end of the previous section. If so, there should be a measurable effect on c.

We have searched for it using X-ray diffraction on a platelet sample of the type described at the end of Section I. As explained there, such a sample might contain a large density of hard APDBs. The experiment was performed on the triple axis diffractometer ID15 at ESRF, Grenoble, France, using penetrating X-rays of 117 keV in a dispersionless transmission geometry. In this instrument, the angular position of the monochromator and analyzer are monitored with laser interferometers, one fringe corresponding to ~0.1". The resolution on the scattering vector in the longitudinal direction is $\sim 1\times10^{-5}$ Å^{-1}, which for the (005) reflection used translates into an accuracy on variations of c of $\sim 5\times10^{-6}$ Å. Figure 1 shows the results obtained on this platelet. Each point corresponds to one measurement which is obtained by first centering the reflection from the crystal followed by a scan of the analyzer, removing thereby the broadening due to the sample mosaicity. The tem-

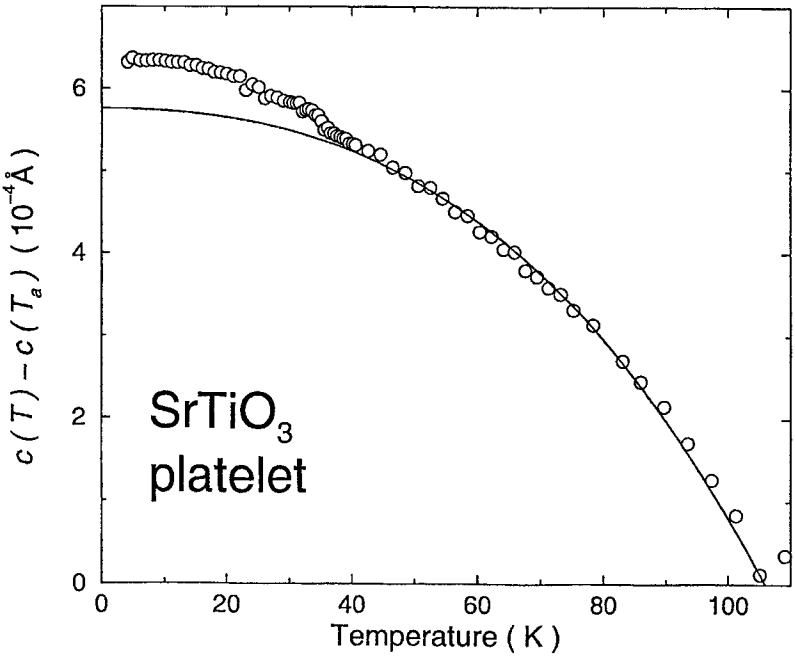

Fig. 1 Variation of the lattice parameter c below T_a. The line is in ϕ^2. It reveals the excess $\delta\Delta c$ that develops below ~ 37 K.

perature is then raised and stabilized for the following point. The solid line represents the expectation, assuming that the variation of c below T_a just follows ϕ^2. One sees that c departs from the line below ~37 K. The saturation value of this excess at low T is $\delta\Delta c \approx +5\times10^{-5}$ Å. Equation (2) predicts a positive $\delta\Delta c$. From it, one calculates $t/L\approx0.1$, so that about 10% of the volume would be occupied by polar boundaries. This is of course a very rough estimate to be taken as an order of magnitude only.

It can however be compared to the sign and size of the birefringence anomaly that was measured on a similar platelet [14]. According to the above model, the extra signal below T_c is given by

$$\delta(n_e - n_o) = \tfrac{1}{2}n^3(\Pi_{12} - \Pi_{11})(\sigma_3 - \sigma_2)\, t/L \quad , \qquad (3)$$

where n_e, n_o, and n, are the extraordinary, ordinary, and average indices, respectively, and Π is the stress-optic tensor with Π_{12}-Π_{11}=1.0×10^{-13} cgs [15]. Introducing the above value of t/L, one calculates $\delta(n_e$-$n_o)\approx 2\times 10^{-5}$ which in sign and magnitude agrees with the observation [14].

In conclusion, a low-T anomaly on the lattice parameter c has been measured on a platelet of $SrTiO_3$. It supports the prediction that APDBs can play an important role at low-T in certain types of samples, and that these APDBs can undergo a ferroelectric transition at temperatures around 35 to 40 K. This clearly has the potential to explain many observed anomalies of this material.

References

[1] H.A. Megaw, *Proc. Phys. Soc. (London)*, **58**, 133 (1946).
[2] A. Yamanaka *et al.*, *Europhys. Lett.*, **50**, 688 (2000).
[3] M. Itoh *et al.*, *Phys. Rev. Lett.*, **82**, 3540 (1999).
[4] A.K. Tagantsev *et al.*, *Phys. Rev. B.*, **64**, 1841XX (2001).
[5] R. Wang *et al.*, *Phys. Rev. B.*, **61**, 8814 (2000).
[6] A. Binder and K. Knorr, *Phys. Rev. B.*, **63**, 194106 (2001).
[7] K.A. Müller *et al.*, *Solid State Commun.*, **8**, 549 (1970).
[8] See, *e.g.* Mao Liu *et al.*, *Phys. Rev. B.*, **55**, 3480 (1997).
[9] L. Arzel *et al.*, *Ferrolectrics*, **236**, 81 (2000).
[10] F.W. Lytle, *J. Appl. Phys.*, **35**, 2212 (1964).
[11] V.A. Meleshina *et al.*, *Sov. Phys. Crystallogr.*, **18**, 764 (1974); V. Janovec, *Ferrolectrics*, **35**, 105 (1981).
[12] O.G. Vendik *et al.*, *J. Supercond.*, **12**, 325 (1999); C. Ang *et al.*, *Appl. Phys. Lett.* **76**, 1929 (2000).
[13] K.A. Müller *et al.*, *Zeit. Phys. B*, **84**, 277 (1991).
[14] E. Courtens, *Ferroelectrics*, **183,** 25 (1996).
[15] A.A. Giardini, *J. Opt. Soc. Am.*, **47**, 726 (1957).