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The spontaneous strain in $SrTiO_3$ in the quantum paraelectric regime: the dependence on sample preparation

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Abstract. The temperature dependence of the spontaneous strain in $SrTiO_3$ has been studied using triple-axis diffractometers of high momentum-space resolution for synchrotron radiation with energies above 100 keV. In the temperature range from 40 to 80 K the experimental data are in excellent agreement with a Landau theory taking into account the quantum mechanical zero-point fluctuations. At temperatures below 40 K a difference between experiment and theory of about 4% occurs which is considered as an indication for a novel phase in the quantum paraelectric regime. The difference between the fitted theory and the experimental data is nearly the same for all of the samples investigated; the biggest difference is observed in the fit parameter describing the theoretical saturation value of the spontaneous strain at zero temperature. In absolute numbers the measured spontaneous strain is strongly sample dependent, i.e. flux-grown, float-zone-grown and Verneuil-grown crystals show differences in the spontaneous strain of about 30% at 10 K. On the other hand, only small variations are observed in samples which were subjected to different heat treatments, which determine the number of oxygen vacancies.

1. Introduction

$SrTiO_3$ is a perovskite, which undergoes a structural phase transition from cubic to tetragonal structure at $98 \lesssim T_c \lesssim 105$ K. Unlike the cases for most perovskites, a ferroelectric phase transition at low temperatures is suppressed. According to measurements of the dielectric constant, $SrTiO_3$ should be ferroelectric below $T_q \approx 38$ K, if the classical mean-field theory is appropriate [1]. However, at very low temperatures the paraelectric phase is stabilized by quantum mechanical fluctuations; the temperature range below 38 K is called the quantum paraelectric regime. Saturation of the order parameter of the structural phase transitions in perovskite-type compounds was first observed by Müller *et al* [2] using electron paramagnetic resonance (EPR) spectroscopy. In 1991 the same group identified an additional contribution to the order parameter for $SrTiO_3$ below 38 K, which they considered to be due to a novel phase in the quantum paraelectric regime [3]. Courtens *et al* [4] observed anomalies around this temperature in the development of the TA-phonon branches by means of neutron and Brillouin scattering experiments.

The spontaneous strain is coupled in a linear–quadratic manner to the antiferrodistortive rotation angle of the oxygen octahedra, which is the primary order parameter. Neumann *et al* [5] detected a discontinuity in the spontaneous strain near the Curie–Weiss temperature using high-energy synchrotron radiation which was interpreted as an indication of this new low-temperature phase.

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In the present paper we present high-resolution measurements of the spontaneous strain for various $SrTiO_3$ specimens, in order to study the influence of sample quality and the effect of oxygen vacancies. After description of the experimental set-up, the differences between the low-temperature behaviours of the samples grown by different techniques or subjected to different heat treatments are illustrated. Then we report on the results from fitting an extension of the Landau theory due to Salje *et al* [6] to the data and, finally, the observed differences are discussed.

2. Experimental procedure

$SrTiO_3$ crystals grown by three different growth techniques have been investigated. One sample was grown more than two decades ago by the top-seeded method [7], and is hereafter referred to as the 'float-zone-grown' sample; another sample was grown by a high-temperature solution technique [8], and in the following is called the 'flux-grown' sample; and a set of nominally pure Verneuil-grown crystals were obtained from the company Crystal (Berlin, Germany).

The float-zone-grown sample consists of an almost ideally perfect bulk surrounded by an approximately 200 μm thick skin layer with a mosaicity of about seven seconds of arc; these values are known from x-ray [9] and γ-ray diffraction experiments [10], respectively. The mosaic spread of the flux-grown crystal was $\approx 10''$, which is still rather small compared to the typical widths of the rocking curves of Verneuil-grown samples, varying between $50''$ and $200''$.

Table 1. Specifications of the samples investigated. Specimens grown by three different techniques (bold type) were available.

Growth technique	Sample preparation	Sample colour
Flux grown	—	Brownish, transparent
Verneuil grown		
Oxidized	(48 h, O_2 atmosphere, 1 bar, 1000 °C)	Slightly rose, transparent
As grown	—	Transparent
Reduced	(5 h, H_2 atmosphere, 1 bar, 1050 °C)	Black
Strongly reduced	(5 h, H_2 atmosphere, 1 bar, 1250 °C)	Black
Float-zone grown	—	Slightly brownish, transparent

However, the almost perfect flux-grown and float-zone-grown crystals are slightly brownish, perhaps due to iron impurities [11], in contrast to the transparent as-grown Verneuil samples. In order to change the defect concentration, the Verneuil crystals have been annealed under various conditions (table 1). As a consequence of the Verneuil growth technique, the 'as-grown' samples contain a certain number of oxygen vacancies. On heating the Verneuil crystals under an oxygen or hydrogen atmosphere, the number of oxygen vacancies is changed, i.e. $V_O^{\bullet\bullet}$ defects are annihilated or produced, respectively. The optical absorption increases strongly with the number of oxygen vacancies [12]; strongly reduced samples lose their transparency. To freeze in the reduction state at high temperatures, the samples were quenched in cold water. The measurements were performed at the storage rings DORIS III (positron energy 4.5 GeV) and PETRA II (12 GeV) at DESY, Hamburg. The new high-energy beamline [13] at PETRA is equipped with an undulator; the high-field

wiggler BW5 at DORIS produces synchrotron radiation with a critical energy of 27 keV. At both beamlines three-crystal diffractometers in the horizontal Laue geometry are installed [14, 5]. At the PETRA beamline an additional monochromator is placed in the primary beam for reasons of radiation safety and background reduction. To achieve the highest photon flux on the sample, the (3 1 1) reflection of an imperfect silicon crystal was used, which also suppressed the second harmonic. In a monochromatic beam with a cross-section of 1×1 mm^2, about 10^{12} photons s^{-1} were available at the sample position at PETRA, compared to 10^{10} photons s^{-1} at BW5, in both cases with an energy resolution of $\Delta E/E \approx 4 \times 10^{-4}$. The horizontal divergence (HWHM) was $12''$ and $40''$ at PETRA and BW5, respectively. A solid-state Ge detector with a resolution of 500 eV at 100 keV was used, allowing us to separate the higher harmonics in the beam electronically. The Verneuil samples were mounted in a strain-free manner on the cold finger of a closed-cycle refrigerator, with the possibility of cooling down to 8 K. The cryostat itself was fixed on a standard Huber Eulerian cradle. For the highly perfect float-zone-grown and flux-grown crystals, the oscillations of the sample due to vibrations of the closed cycle were too large with respect to the mosaicity of the sample. Therefore these samples were investigated using a He bath 'orange' cryostat and a double cradle.

The spontaneous strain was measured in the $SrTiO_3$ (6 0 0) reflection direction using the (6 6 0) reflection of perfect silicon crystals as the monochromator and analyser at an energy of 100 keV. The small misfit of about 7% of the Bragg angles of the monochromator/analyser and the sample leads to a nearly dispersion-free set-up [15, 16] with high resolution in momentum space. The longitudinal resolution at the PETRA beamline ($\Delta q_x \approx 1.5 \times 10^{-4}$ Å^{-1}) is about three times better than that at BW5 ($\Delta q_x \approx 5 \times 10^{-4}$ Å^{-1}). The intrinsic transverse resolution was $\Delta q_y \approx 5 \times 10^{-5}$ Å^{-1} at PETRA and BW5. The large mosaicity of the Verneuil crystals, however, limited the transverse resolution to 10^{-3} Å^{-1}. The good resolution of the three-crystal diffractometer in the scattering plane allows for fine-mesh $\boldsymbol{k}$-space scanning. The resolution perpendicular to the scattering plane is typically $\Delta q_z \approx 10^{-1}$ Å^{-1}.

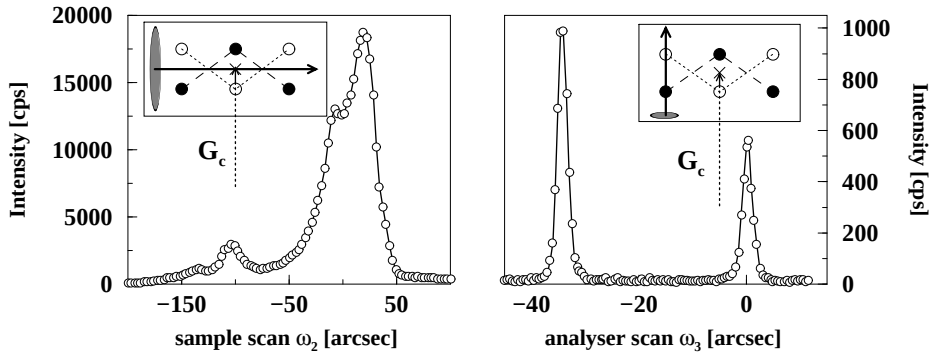

Figure 1. Typical domain patterns at $T = 8.5$ K. On the left-hand side (panel (a)) the domain structure in the transverse direction for reflection (6 0 0) is determined by rotating the sample (ω_2) in the two-crystal mode; the longitudinal splitting (panel (b)) is obtained from an analyser (ω_3) scan in the three-crystal mode. Possible $\boldsymbol{q}$-space positions of the tetragonal domains around the cubic Bragg reflection $\boldsymbol{G}_c$ are illustrated in the inset; open and filled circles represent *a–c–a* and *c–a–c* domains, respectively (the dimensions are not to scale). The arrows point in the scanning direction; the resolution volumes are drawn schematically at the bases of the arrows.

Due to there being three degrees of freedom for the rotation of the oxygen octahedra and consequently for the orientation of the tetragonal unit cell, the crystal can form up to 2×5 families of domains below the critical temperature of the structural transition [17]. The projection onto the [001] scattering plane reduces the possible number of satellites in $\boldsymbol{q}$-space to 2×3, represented by open and filled circles in the insets of figures 1(a) and 1(b). If the longest axis—by convention named the c-axis—of the tetragonal unit cell is oriented parallel to the reciprocal-lattice vector, the corresponding domain is called a c-domain; otherwise it is called an a-domain. Two domain formations each with three spots around the cubic lattice point are possible: a–c–a or c–a–c domains, which do not coexist in ideal crystals. However, in the Verneuil samples both families of domains occurred simultaneously due to their large mosaicity, but in most cases only two domains of each family could be observed. The transverse (figure 1(a)) splitting $\Delta\omega_2$ is due to the twinning angle α; the longitudinal (figure 1(b)) splitting $\Delta\omega_3$ is related to the spontaneous strain $(c/a_0 - 1)$ and is proportional to the length of the reciprocal-lattice vector. By rotating the sample in the two-crystal mode, the transverse positions ω_2 of the domains can be determined. The high resolution in the longitudinal direction obtained from analyser scans makes this method very sensitive to measurements of the spontaneous strain, as can be seen in figure 1(b). The distance $\Delta\omega_3 = 34''$ of the two clearly separated peaks in this example with $\boldsymbol{G} = (6\ 0\ 0)$ is equivalent to a spontaneous strain of $c/a_0 - 1 = 5.7 \times 10^{-4}$ with a relative error of about 0.3%. Similar accuracy is obtained for the more perfect crystals, where only one family of domains occurs at a time and therefore two analyser scans at different ω_2-positions are necessary.

3. Discussion

Salje *et al* [6] describe the order parameter saturation within the Landau theory, however, by taking into account the quantum mechanical zero-point fluctuations. In figure 2 the order parameter evolution is classified into three parts. In the critical region close to T_c, fluctuations dominate the system and the Landau theory is inapplicable. The critical exponent describing the temperature dependence of the order parameter for $SrTiO_3$ has been determined to be $\beta = 0.34$ [18]. The transition temperature T_c^{class} expected from mean-field theory is lowered due to quantum fluctuations to T_c^{qm}; in fact the transition takes place at $T_c < T_c^{qm}$ because $\beta < 0.5$. Far away from T_c, the system evolves in a Landau-like fashion with $\beta = 0.5$, i.e. Q^2 is linear in T. However, at $T = \Theta_s$ saturation sets in and at $T = 0$ K the saturation value Q_s^2 is reached. Q_0^2 is the extrapolated value at $T = 0$ K with saturation not taken into account. Using the equations from [6], it should be possible to describe the temperature evolution of the spontaneous strain in the QM and in the Landau region. In the case of $SrTiO_3$, which is a displacive system, only three free parameters are needed to fit the data, e.g. Q_s^2, Q_0^2 and T_c^{class}. From these values, the characteristic temperatures T_c^{qm} and Θ_s, and the dimensionless parameter η, which is a measure of the quantum mechanical influence ($0 \leqslant \eta \leqslant 1$; $\eta = 0$ yields the classical result), can be calculated.

As shown in figure 3(a), the measured spontaneous strain is strongly sample dependent, i.e. flux-grown, float-zone-grown and Verneuil-grown crystals show differences in the spontaneous strain at 10 K of about 30%. On the other hand, only small differences are observed for the various Verneuil crystals (figure 3(c)). In order to make sure that the influence of critical fluctuations is negligible, the fitting range had to be cropped at $T > 80$ K, but in contradiction to the theoretical expectations, reasonable fits could be obtained only after further narrowing the fitting range. The lower limit had to be set to at least 30 K; in fact all data-sets have been fitted over the range from 30 to 80 K.

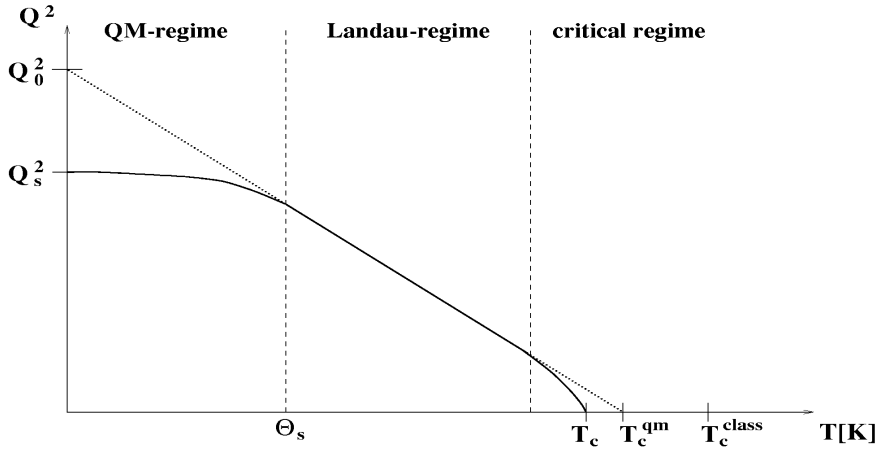

Figure 2. A schematic view of the theoretically expected temperature evolution of the squared order parameter. The transition temperature T_c^{class} expected from mean-field theory is lowered by quantum mechanical effects to T_c^{qm}; in fact the transition takes place at $T_c < T_c^{qm}$ because $\beta < 0.5$. In the Landau regime the critical exponent $2\beta = 1$ leads to a linear slope, but at temperatures lower than Θ_s saturation sets in. The saturation value for $T = 0$ K is Q_s^2; Q_0^2 is the extrapolated value at $T = 0$ K for Landau behaviour.

Table 2. Fit parameters (columns 1–3) and resulting quantities for different samples. The critical temperature T_c is shown for comparison.

	Q_0^2 (au)	Q_s^2 (au)	T_c^{class} (K)	T_c^{qm} (K)	Θ_s (K)	η	T_c (K)
Flux grown	1.16	0.62	120.0	111.4	54.2	0.45	102.5
Verneuil grown							
Oxidized	1.59	0.56	133.5	112.6	85.6	0.64	105.7
As grown	1.45	0.54	136.2	116.4	84.5	0.62	105.8
Reduced	1.37	0.53	134.7	116.5	81.0	0.60	104.8
Strongly reduced	1.34	0.50	129.5	110.3	81.0	0.63	101.0
Float-zone grown	1.24	0.48	125.5	108.1	76.2	0.61	99.5

In table 2 the fit parameters obtained are shown. The largest differences are observed in the saturation values Q_s^2. The more oxygen vacancies in the Verneuil crystals, the lower the saturation value; i.e. these defects reduce the maximum rotation of the oxygen octahedra at $T = 0$ K. The fact that the saturation value is lowest for the most perfect, float-zone-grown sample suggests the existence of defects in this crystal, which do not influence the mosaicity. On the other hand, the saturation value is largest for the flux-grown sample and only for this crystal is a linear relation between Q^2 and T observable. The QM region starts below $\Theta_s = 54.2$ K; for all of the other crystals the value for Θ_s is of the order of 80 K. It was shown in [19] that, in a picture of only one soft mode driving the phase transition, the characteristic frequency $\Omega_0 = 2k_B/\hbar\Theta_s$ should correspond to the frequency ω_{soft} of the soft mode at $T = 0$ K, and for strong coupling of the soft mode with all other phonons, one would expect $\Omega_0 \approx \omega_E$, where ω_E is the Einstein frequency of the system. For the displacive phase transition of quartz, $\Omega_0 \approx \omega_E$ was found [19]. In $SrTiO_3$ we find

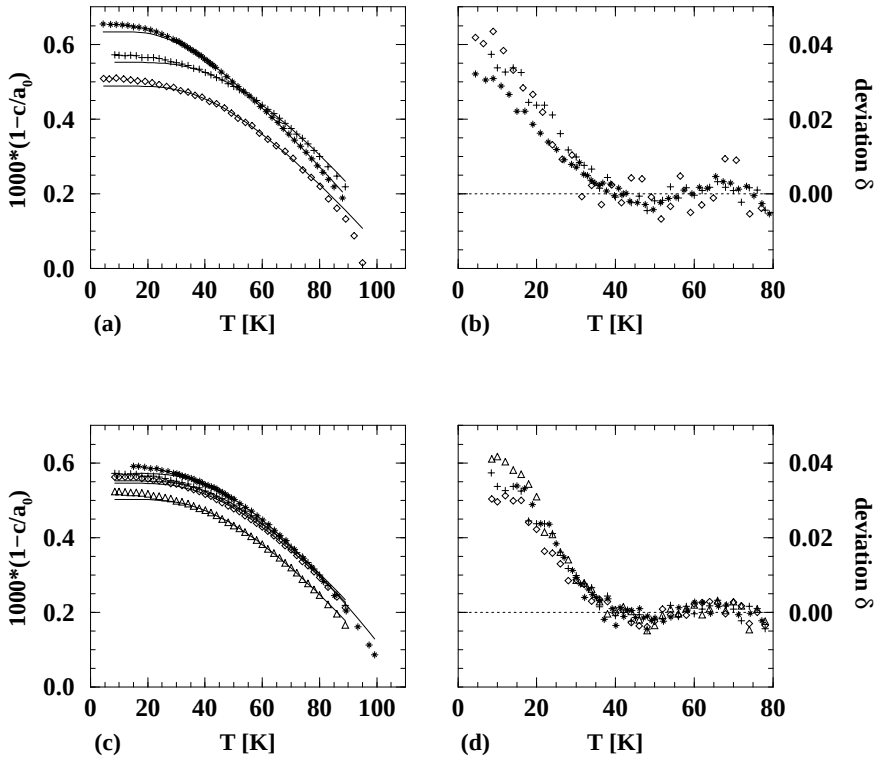

Figure 3. The spontaneous strain versus the temperature measured for float-zone-grown (◊), flux-grown (∗) and Verneuil-as-grown (+) crystals (a), and measured for different Verneuil crystals: oxidized (∗), as grown (+), reduced (◊) and strongly reduced (△) (c). Solid lines represent least-squares fits to the experimental data as described in the text. On the right-hand side ((b) and (d)) the deviations δ between fit and the data, normalized to the respective saturation values for the spontaneous strain at $T = 0$ K, are displayed.

$\omega_{soft} \ll \Omega_0 \ll \omega_E$, which confirms the observation in [20] that the coupling between the soft mode and other phonons affects the transition, but it is much weaker than in quartz. The weakest coupling can be seen for the flux-grown crystal; similarly the parameter η describing the quantum mechanical influence is lowest for the flux-grown sample and nearly constant otherwise.

The deviation δ between the experimental data and theory is shown in figures 3(b) and 3(d). In the range from 40 to 80 K the temperature dependence of the spontaneous strain is in excellent agreement with the theoretical predictions, but below 40 K for all of the samples the data deviate from the fit in the same manner. The deviation starts at around 38 K and increases with falling temperature to its maximum value of about 4%. This behaviour confirms the observations made in [3]; the continuous increase below T_q is considered as an indication for an additional phase transition at $T_q \approx 38$ K. It is surprising that the transition temperature and the maximum deviation are almost constant for all of the different samples. If the deviations originated from the formation of polarized clusters, as suggested in [21], the existence of polar oxygen vacancies would affect the low-temperature anomaly.

Another model for explaining the observations has been suggested by Scott [22] and is still under discussion [23, 24]. The frequencies of the ferroelectric and the antiferrodistortive optical modes become degenerate at approximately 37 K. Coupling of these modes, e.g. via defects, could influence the order parameter evolution, but one would expect a strong defect dependence of the coupling constant.

Further theoretical work is necessary to explain the experimental observations made.

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