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Abstract
A birefringence-imaging study of a crystal of SrTiO$_3$ shows a purely second-order phase transition close to 105 K with no measurable indications of critical fluctuations. The near perfectly linear development of the birefringence near the $m\bar{3}m\,F4/mmm$ phase transition is consistent with normal Landau mean-field behaviour with an order-parameter critical exponent close to 0.5.

1. Introduction

The ferroelastic (or antiferrodistortive) phase transition in strontium titanate (SrTiO$_3$) is one of the most widely studied structural phase transitions in the literature. The nature of the symmetry change and its relationship to the angle of tilt of the oxygen octahedra at the transition was first shown by Unoki and Sakudo [1]. In addition, Fleury *et al* [2] showed that condensation of a soft phonon component at the R point of the cubic Brillouin zone occurred at the transition, thus doubling the unit-cell dimensions, in agreement with the tilted octahedra model. Later, critical behaviour at the transition was demonstrated in the classic work of Müller and Berlinger [3], who showed by ESR that crystals of SrTiO$_3$ seemed to show an order parameter variation with a critical exponent β of around 0.33(2), consistent with a microscopic model involving critical fluctuations. This discovery resulted in a huge number of publications generally supporting this finding.

In more recent times, the idea that SrTiO$_3$ might show critical fluctuations has been questioned, since a number of experiments measuring various physical quantities, such as excess entropy [4–6], indicate that the transition can be explained via a classical mean-field approach, with a critical exponent β consistent with a tricritical value tending towards 1/4. It is interesting to note in contrast that Kozlov *et al* [7] were able to show that it was possible to fit the observed order parameter measurements to a conventional Brillouin function over the entire temperature range from 0 K to the transition temperature, corresponding to a mean-field exponent $\beta = 1/2$.

However, very few optical birefringence measurements of the phase transition have been published up to now, despite this being one of the most sensitive and simplest ways

to study structural changes in optically transparent crystals. The first and most significant of these studies was by Courtens [8] who, using a very careful and precise compensator method, found that the birefringence also suggested critical behaviour, in agreement with the conclusion of Müller and Berlinger. More recently [9], birefringence measurements on oxygen ^{16}O–^{18}O isotope-exchanged crystals of $SrTiO_3$ have shown evidence for a quantum ferroelectric transition near 21 K, the exact behaviour depending on the amount of isotope exchange. Although this latter work also covered the ferroelastic transition, the authors did not specifically analyse the birefringence data closely in this region beyond stating that their results agreed with those of Courtens.

In the present paper we revisit this transition using birefringence imaging techniques in order to ascertain the precise behaviour of the order parameter for the transition. We shall show that, at least in the crystal studied here, classical mean-field behaviour fits the transition in the case of birefringence.

The change of structure of strontium titanate at the transition has been documented widely, and we therefore only briefly describe the salient features here. This crystal, which belongs to the class of compounds known as perovskites, undergoes an improper ferroelastic cubic–tetragonal phase transition denoted by the ferroic species $m\bar{3}m\,F4/mmm$ [10]. The high-temperature phase is cubic and is characterized by oxygen octahedra corner-linked in all three directions with the Ti cations at the centres of the octahedra and the Sr ions at the centre of the space between the octahedra. In the notation of Glazer [11], the octahedral tilt system is denoted $a^0a^0a^0$, i.e. no octahedra are tilted. On cooling through the ferroelastic transition, the structure becomes tetragonal and the oxygen octahedra adopt the $a^0a^0c^-$ tilt system with the unit cell axes doubled. From lattice parameter measurements through the transition [12] it is found that on passing from the cubic to the tetragonal phase, the c_p-axis (we shall use the subscript p to denote the pseudocubic subcell) increases while the $a_p = b_p$-axes decrease. This can be explained from geometrical considerations by a combination of two contributions. First of all, the tilt of the octahedra alone[1], which is normally considered to represent the primary order parameter for the transition, causes a decrease in the a_p-parameter: if the in-plane Ti–O bond is considered to remain fixed, tilting of the octahedra about $[001]_p$ pulls the Ti atoms in the $(100)_p$ plane towards each other. The effect on the length of the a_p-axis is given by

$$a_p = a_0 \cos\theta \qquad (1)$$

where θ is the angle of tilt and a_0 is the length of the cubic high-temperature lattice parameter extrapolated to the temperature of interest. Thus the tilt alone causes the pseudocubic unit cell to become anisotropic, with a decrease in volume, and hence it introduces a 'tilt' strain term:

$$\varepsilon_\theta = \frac{a_p - a_0}{a_0} = \cos\theta - 1 \approx -\frac{1}{2}\theta^2 \qquad (2)$$

for small angles of tilt. The tilt alone does not affect the length of the c_p-axis.

Since birefringence is a measure of structural anisotropy through its relationship to strain, the tilt provides one contribution towards the observed birefringence. However, it is important to realize that the observed increase in c_p implies that at least the out-of-plane Ti–O bond length must in fact change to add a positive strain ε_c. Moreover, there is likely to be a corresponding lengthening of the in-plane Ti–O bond length, also in opposition to the tilt, leading to a strain ε_a. Indeed, such 'octahedral' strains have been found by Hayward and Salje. Both these octahedral strain terms will also add to the tilt strain to produce an overall spontaneous strain:

$$\varepsilon_s \approx -\frac{1}{2}\theta^2 + \varepsilon_c + \varepsilon_a. \qquad (3)$$

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[1] The Müller and Berlinger experiment is one of the few that measure this order parameter directly.

As the observed birefringence is proportional to this spontaneous strain, it therefore arises from a combination of all three strain terms together, *and is not due only to the effect of the primary order parameter,* θ.

Now it is possible that the tilt strain term could show a critical behaviour with temperature different to that of the octahedral strain terms, and this implies that we may not necessarily expect variation of birefringence with temperature to show the same critical exponent as that seen by Müller and Berlinger for the tilt angle, nor for it to behave simply. It is interesting therefore to test the temperature behaviour of the birefringence Δn to see if indeed it is governed by a simple power law:

$$\Delta n \propto \varepsilon_s \propto (T_0 - T)^{2\beta'} \tag{4}$$

where β' is a critical exponent.

2. Method

The sample was supported freely on an amorphous quartz plate within a high-precision temperature stage (Linkam TMSG600) combined with a modern version of the rotating-polarizer birefringence-imaging technique [13] (see www.metripol.com). In the temperature region of this study the hot stage is capable of maintaining a constant temperature to within 0.1 K, and to ramp the temperature at a rate of 0.1 K min^{-1}, making it possible to capture a high-quality dataset for every 0.05 K of change.

The Metripol system consists of a polarizing microscope equipped with a computer-controlled plane-polarizer capable of being rotated to fixed angles α from a reference position, a circular-polarizing analyser and a CCD camera. The intensity measured at any position within the captured image is given by the formula

$$I = \frac{I_0}{2} \left[1 + \sin(2\varphi - 2\alpha) \sin \delta \right] \tag{5}$$

where I_0 is the intensity of light passed through the sample and represents its transmittance. φ is the angle of an axis of the optical indicatrix of the specimen projected onto the image measured from a predetermined direction (we normally set this to be anticlockwise measured from the horizontal axis) and δ is the phase difference between the polarized light components and is given by

$$\delta = \frac{2\pi}{\lambda}(n_1 - n_2)t = Rt. \tag{6}$$

λ is the wavelength of the light, t is the thickness of the sample and $(n_1 - n_2)$ is the so-called planobirefringence (the birefringence measured as seen in projection down the microscope axis) of the sample. R is the retardance. By measuring several images with varying angle α it is possible to fit for each pixel position the quantities I_0, $|\sin \delta|$ and ϕ separately and then to plot images in false colour representing these three values. In this way, any spatial variations in the birefringence or orientation can readily be seen to very high sensitivity. A single-domain crystal of constant composition and thickness would appear to show a uniform colour in both the $|\sin \delta|$ and orientation images. One of the advantages of using an imaging method such as this is that it enables one to select the best region (i.e. a region free from obvious strain, domain boundaries or defects) of the sample for analysis, rather than using a whole image, as happens in most other methods of measuring birefringence. This technique has been successfully used in other phase transition studies both in the current imaging version [14, 15] and in its original single-beam version [16, 17].
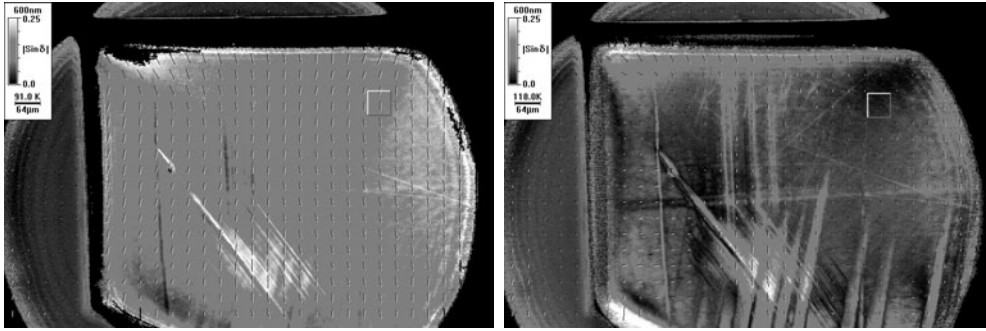
Figure 1. $|\sin \delta|$ images of the SrTiO$_3$ crystal at temperatures 91.0 and 118.0 K below and above the phase transition temperature of 104.3 K, respectively. The square marked in the two images indicates the region over which numerical values of the retardation and the background have been taken in each frame to create the graphs in figures 2–4. Azimuthal lines show the variation of the orientation of the slow axis within the sample. The variation in $|\sin \delta|$ and φ over the sample is mainly due to mechanical strain.

3. Experimental details

An almost strain-free crystal of SrTiO$_3$ was kindly provided by Professor K A Müller: the crystal was in the form of a rectangular bar, cut on the (110) plane with its long axis of about 2.5 mm parallel to [001] and width about 1.5 mm, and was polished to a thickness of 150 μm.

Two datasets were generated per minute, while the temperature was ramped down at a rate of 0.1 K min^{-1}. In order to reduce the random error, datasets were generated using 25 polarizer positions, and the numerical data were derived from the images by averaging over 1600 pixels in the apparently less mechanically strained right-hand side of the crystal. Figure 1 shows examples of $|\sin \delta|$ and orientation images above and below the phase transition temperature.

In spite of the careful selection of the crystal some internal strain persisted even at room temperature. The equation used to generate values of $|\sin \delta|$ was:

$$|\sin \delta| = |\sin \delta|_{\text{measured}} - |\sin \delta|_{\text{strain}} \tag{7}$$

where $|\sin \delta|_{\text{strain}}$ is the average of $|\sin \delta|$ measured between 118 and 106 K. From this, values of the phase shift δ, and hence the birefringence Δn, could be obtained. Figure 2 shows this plotted as a function of temperature.

The raw data presented in figure 2 indicate a very linear relationship in the temperature development of Δn (the variation in thickness over the temperature range is of the order of one part in 10^4 as calculated from the published lattice parameter measurements and so this can be ignored). A least-squares linear fit was performed on these measurements for temperatures lower than 104 K to establish the phase transition temperature (T_0) and the probability that there is actually a linear relationship between Δn and T. The fit gave the following temperature dependence:

$$\Delta n \times 10^5 = [-0.532(7)T + 5.55(8)] \tag{8}$$

with a transition temperature of 104.3 K for the selected strain-free region, although in some other regions where strain was not absent this increased to about 105.2 K. The standard error for the fit in the tetragonal phase of 1×10^{-6} and the correlation coefficient R^2 of 0.997(9) indicate a very good fit between the straight line and the data. The conclusion from this is that our sample seems to show a critical exponent of β' close to 0.5.
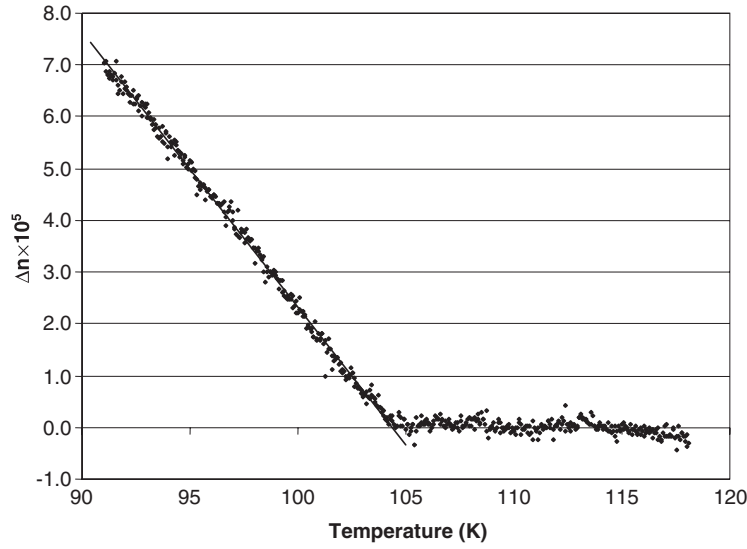
Figure 2. Birefringence as a function of temperature. The straight line is a fit to the observed data.

The position of the crystal within the field of view allowed for simultaneous background measurements. In order to investigate the data in closer detail, we sought to reduce the experimental noise by using a vector-based background compensation technique. The measured phase shift at a point in the sample can be represented by a vector in Euclidian space, with an amplitude δ and an inclination 2φ. The effective retardation can then be calculated according to:

$$\delta^* = \sqrt{[\delta_m \sin(2\varphi_m) - \delta_b \sin(2\varphi_b)]^2 + [\delta_m \cos(2\varphi_m) - \delta_b \cos(2\varphi_b)]^2} \qquad (9)$$

where $\delta_m = \sin^{-1}(|\sin \delta|_m)$ and φ_m are the phase shift and orientation angle measured in the sample, and $\delta_b = \sin^{-1}(|\sin \delta|_b)$ and φ_b are the phase shift and orientation angle measured as background values in the region outside the sample. Subtracting the background measured for each frame substantially reduced the noise in the data, but we found that this led to a significant temperature variation in the readings for the birefringence for $T > T_0$ (figure 3). This means that we could no longer use a constant compensating strain term, as in equation (7); instead we have compensated for the variation in the cubic phase by subtracting a second-order polynomial fitted to the data for $T > T_0$.

$$\delta = \delta^* - (AT^2 + BT + C) \qquad (10)$$

where A, B and C are values fitted for $T > 106$ K.

For the final values (figure 4) of Δn we calculated a standard error smaller than 5×10^{-7} and a correlation coefficient R^2 of 0.9998(9) for $T < 104$ K, making these birefringence measurements the most sensitive ever published for a crystal of SrTiO3, and again confirming the linear relationship already observed. This means that the overall exponent was close to 1/2 with an estimated transition temperature of 104.5(3).

To determine a more exact value for β' we recast equation (4):

$$\Delta n = At^{2\beta'} \Leftrightarrow \ln(\Delta n) = \ln(A) + 2\beta' \ln(t) \qquad (11)$$

where the reduced temperature $t = (T_0 - T)/T_0$.

In order not to be biased by assuming any initial fixed value for T_0 we generated a series of plots of $\ln(\Delta n)$ against $\ln(t)$, with T_0 varying from 104 to 105 K. We then fitted straight lines to our results. A linear least-squares regression gives for each T_0 a value for the
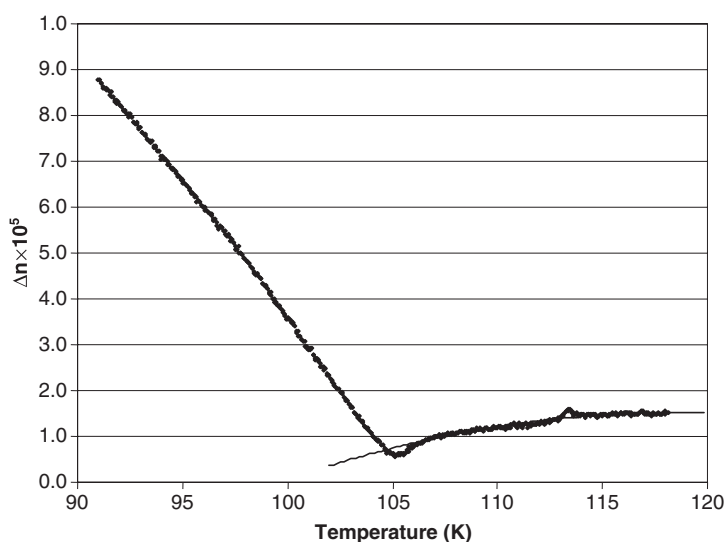
Figure 3. Birefringence as a function of temperature after, simultaneously measured, background subtraction to reduce experimental noise. Note that this results in an apparent curvature of residual birefringence in the cubic phase.
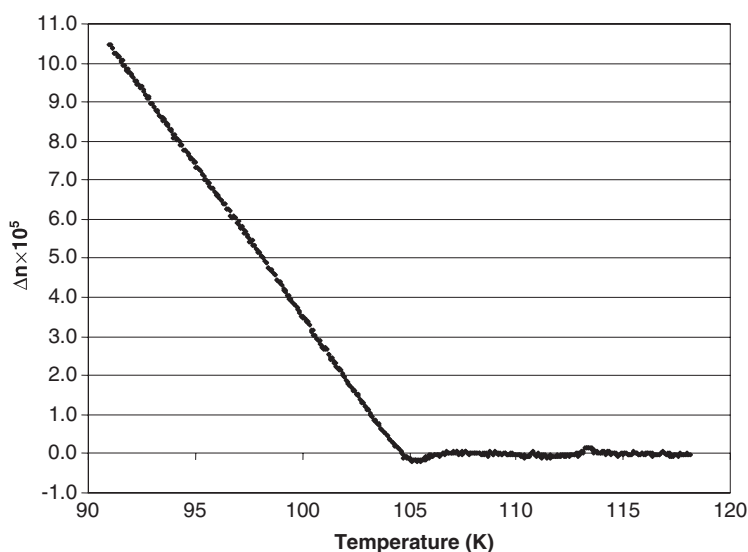

Figure 4. Birefringence corrected using simultaneous background correction followed by polynomial fit to the data in the cubic phase of figure 3.

slope of the graph ($2\beta'$), and a standard error on the slope (figure 5). Minimization of this standard error (and corresponding maximization of the R^2 value), led to $T_0 = 104.57(5)$ K and $\beta' = 0.5080(6)$. This value may be compared with that found by Courtens: $\beta' = 0.36(1)$.

It might be argued that one cannot assume that the birefringence above the phase transition is unrelated to the phase transition, in which case the use of equation (10) might be thought to be invalid. Using the values of the uncorrected Δn measurements (figure 3) as a basis for the full analysis of plotting $\ln(\Delta n)$ against $\ln(t)$, and repeating the linear regression (as in figure 5) we obtain $T_0 = 105.36(5)$ and $\beta' = 0.461(2)$. Thus the effect of not correcting for the residual birefringence above T_0 by using equation (10) is to reduce slightly the value of β' but increase greatly its standard deviation. Either way the conclusion still remains that the critical birefringence exponent is close to a value of 0.5.
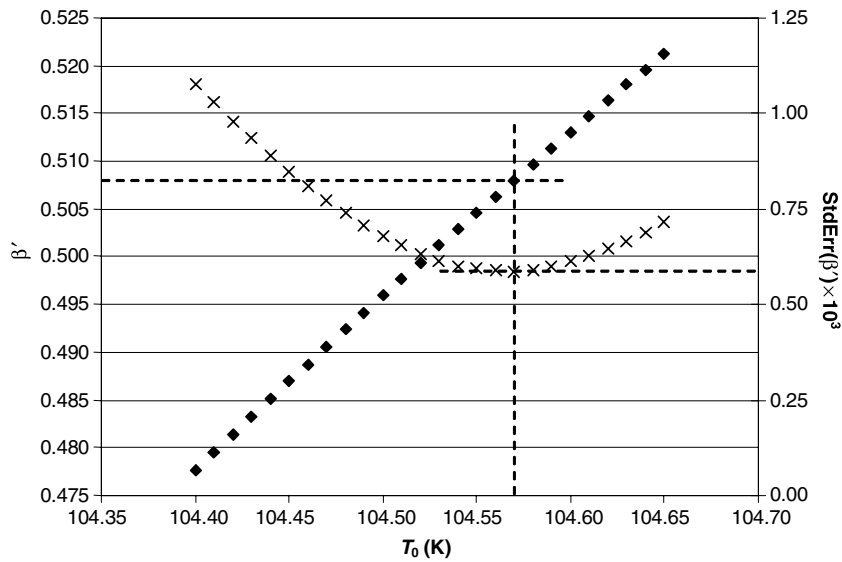
Figure 5. Calculation of β' ($\blacklozenge$), the error on β' ($\times$) and T_0.

Data averaged over the entire sample were also measured, but the resulting birefringence was measured to be roughly 70% of that measured for the pre-selected region. This is probably because averaging over the larger area is affected by the strain clearly visible in figure 1.

The earlier birefringence study of Courtens [8] reported the presence of a cusp in the measurements slightly above T_0, and interestingly enough we also observed something similar in our initial data analysis [18]. However, careful inspection of the strain in our sample at higher temperatures, led us to the conclusion that the observed cusp was the result of the presence of strain unrelated to the phase transition, as the region of the sample in which the cusp was found was visibly more strained than the region used for the data presented above. Because we use an imaging method, this has enabled us to select the best region of the crystal (approximately 60×60 μm^2) for analysis, whereas the method used by Courtens measured an average over a region $1/2$ mm^2.

It should be noted that our result is consistent, as is that of Courtens, with the prediction made by Gehring [19] that the birefringence exponent $2\beta' \sim 1.00$ should obey the relationship

$$2\beta' = 2 - \alpha - \phi > 2\beta \tag{12}$$

where α is the specific heat exponent, ϕ is the crossover exponent for Heisenberg to Ising behaviour and β is the critical exponent expected for the order parameter (0.33 ± 0.02 according to Müller and Berlinger [3]). This relationship is based upon the assumption that the order parameter in SrTiO₃ obeys Heisenberg critical behaviour in the first place. However, we must emphasize that as the birefringence in SrTiO₃ is not a measure of the effect of the order parameter (octahedral tilt angle) alone, such agreement may be coincidental only.

Perhaps more importantly, we should like to point out that such theories, as well as the interpretation of the original EPR measurements in terms of critical fluctuations, is of dubious applicability to SrTiO₃. Such treatments consider the order parameter to relate to spin-like quantities with relatively weak interactions between each other. However in SrTiO₃ what appears to have been overlooked is the fact that structurally the oxygen octahedra are physically attached to one another via shared oxygen atoms. Thus rotation of one octahedron must invariably give rise to rotation of all other octahedral within a plane perpendicular to the rotation axis (see [20]), otherwise it would be necessary to break chemical bonds. Such interactions

are therefore very long range and any critical region due to this would be extremely small. That leaves only the possibility of fluctuations in the rotation angle for octahedra between layers. One could in principle imagine short-range correlations between layers that grow as one approaches the phase transition to give the required critical behaviour, but the problem with this model is that one would expect to find in an x-ray or neutron scattering experiment extensive diffuse streaking close to the transition temperature (i.e. within the supposed critical regime) between the R and M points of the cubic Brillouin zone. To the best of our knowledge no such effect has been reported in $SrTiO_3$. The upshot of this is that we believe that the phase transition in this material is essentially of a mean-field nature.

Finally, we should comment on the difference found in temperature dependence of the birefringence between our work and that of Courtens. This may be explained if 'stacked' $90°$ domains (domains superimposed on one another) occurred in the crystal. Such domains would be more likely to affect measurements of thicker crystals (we note that the sample used by Courtens was $270\,\mu$m thick, almost double that used by us above). The effect of such domains leads to a reduction in the magnitude of the measured birefringence, as is indeed seen in comparing the two studies: for example, at 90 K Courtens obtained a value of Δn of about 70×10^{-6}, whereas we have 110×10^{-6}. It is worth noting here that in a recent study of another perovskite, $PbTiO_3$, we have measured birefringence in newly grown crystals that is as much as four times that reported in all earlier publications, including our own [21]. The importance of the effect of stacked domains of this sort on measurements of birefringence cannot be overemphasized.

Acknowledgments

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