Observations of a Very Large Critical Length Scale in $SrTiO_3$

R. J. Nelmes, P. E. Hatton, and H. Vass
Department of Physics, University of Edinburgh, Edinburgh EH9 3JZ, Scotland

(Received 30 October 1987)

High-resolution x-ray scattering measurements have revealed a second critical length scale at the cubic-to-tetragonal transition in $SrTiO_3$, corresponding to very large correlation lengths of the order of 2500 Å at T_c+1 K. The correlation length becomes substantially larger still after the sample temperature has been cycled once through T_c, a novel memory effect in large-length-scale critical behavior of this kind. We discuss the interpretation of these observations in terms of the effect of extended defects close to a weakly first-order transition.

PACS numbers: 64.70.−p

We report observations of a second, and very large, critical length scale at the structural phase transition in $SrTiO_3$, and a novel and unexpected memory effect in this behavior. The second critical length scale can be interpreted as evidence that the transition is intrinsically first order in character.

The critical fluctuations associated with the cubic-to-tetragonal transition at $T_c \simeq 105$ K in the perovskite $SrTiO_3$ are known to display two distinct time scales near T_c.[1] One is determined by the dynamics of the R-point soft mode; the other—the "central peak"— is much slower and is believed to be due to the presence of defects.[2] Recently, high-resolution x-ray scattering measurements have shown that the critical fluctuations also exhibit two distinct *length* scales at the equivalent transition (at $T_c \simeq$ 190 K) in the isomorphous compounds $RbCaF_3$ [3,4] and $KMnF_3$ [5]: Just above T_c the x-ray scattering at the R point has a sharp component superimposed on the broad peak from the intrinsic critical fluctuations, and the width of the sharp component narrows continuously to the instrumental resolution as $T \rightarrow T_c$. It has long been known that $SrTiO_3$ also has a sharp component in the R-point x-ray scattering above T_c, but high-resolution studies—most recently and comprehensively performed by Andrews[6]— have always found the width of the component to be resolution limited and independent of temperature.

The width and position of the sharp component in $RbCaF_3$ and $KMnF_3$ correspond to scattering from large clusters, $\simeq 500$ Å across (cluster sizes given for $RbCaF_3$ and $KMnF_3$ in this paper differ from previously published values following a more rigorous recalculation of their magnitudes) at T_c+1 K, with a tetragonally distorted structure.[3-5] The tetragonal distortion was detected as a small, temperature-independent displacement of the sharp component from the exact R point, by just the amount of the discontinuous change in the reciprocal-lattice dimensions at the (slight) first-order transitions in these two materials. This feature, and the T dependence of the width of the scattering, have been interpreted[3-5] in terms of the qualitative predictions by Imry and Wortis[7] of the effect of defects on first-order transitions. Close to such a transition, in this picture, there will be fluctuations between the high- and low-temperature phases mediated by the strain energy around the defects. The spatial extent of the fluctuations will then vary inversely with the difference in free energy between the phases, and so diverge as $T \rightarrow T_c$.

We have now found critical behavior of this kind in $SrTiO_3$. Almost certainly, this has eluded previous diffraction studies because the clusters are considerably larger than $RbCaF_3$ and $KMnF_3$ (being $\simeq 2500$ Å across at T_c+1 K) and become substantially larger still after cycling of the temperature through T_c even once. The sheer size of the clusters is remarkable, even in the virgin sample, and the memory effect after passage through T_c is a new feature in critical behavior of this kind.

The sample used was cut from the same colorless boule as was Andrew's sample.[6] The boule was grown by the Verneuil (frame fusion) method and was obtained from the Titanium Division of the National Lead Company in about 1960. Although the boule had been cycled through T_c previously, it had been maintained at room temperature for about 20 yr. A single-crystal (100) plate approximately $10 \times 10 \times 3$ mm^3 was cut from the boule, polished, and deeply etched by repeated agitation in dry H_3PO_4 at 280 °C for 1-h intervals. This procedure removed all surface damage and produced an x-ray rocking curve width of only 0.008(1)° (FWHM). This is significantly less than the width of 0.020° reported by Andrews,[6] and very similar to the values obtained for the samples used in the $RbCaF_3$ (Refs. 3 and 4) and $KMnF_3$ (Ref. 5) experiments.

The sample was mounted in a strain-free manner in a closed-cycle cryostat and orientated with the face normal, [011], and a cubic [110] direction in the (horizontal) scattering plane of our triple-axis x-ray diffractometer.[8] The temperature stability of the cryostat was ±0.01 K. Measurements were made in reflection geometry with Cu $K\alpha_1$ x rays from a rotating-anode source, with Si(111) monochromator and analyzer crys-

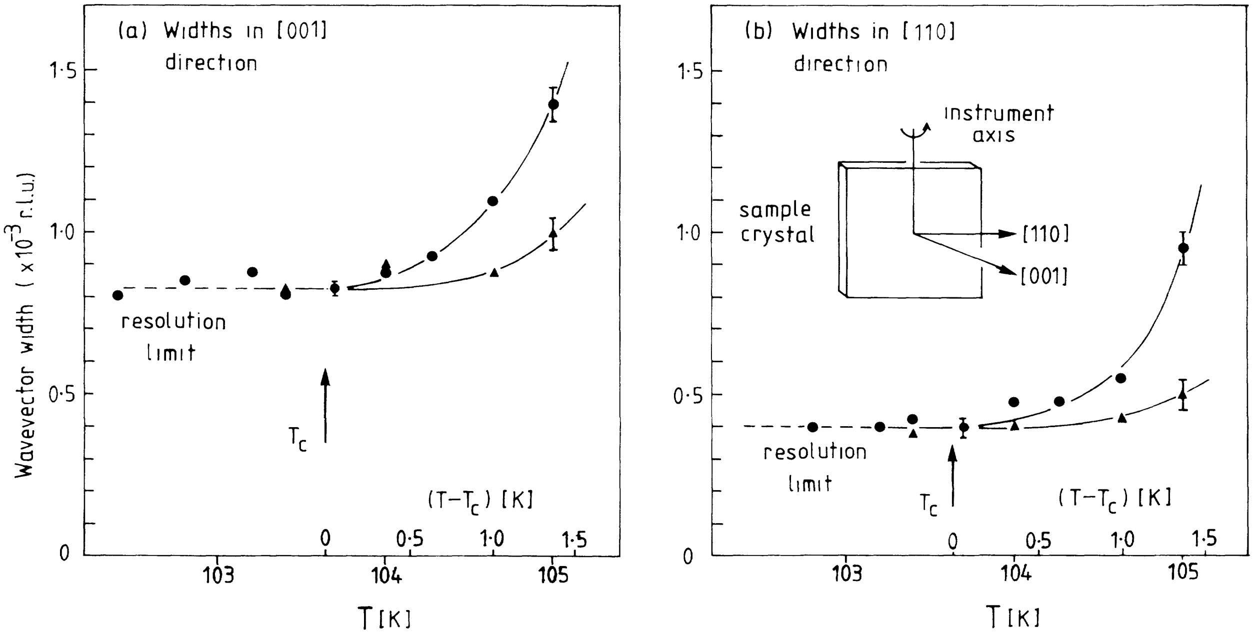

FIG. 1. The temperature dependence of the wave-vector widths for the sharp component of the critical scattering at the (0.5,0.5,2.5) R point (a) perpendicular and (b) parallel to the crystal surface. The filled circles are the FWHM, in reciprocal-lattice units, measured with decreasing temperature for a virgin sample. The triangles are the FWHM measured after the sample had been cooled through T_c and then warmed to room temperature. The solid lines are guides to the eye. Inset in (b): Orientation of the sample on the instrument.

tals. The instrumental resolution in the scattering plane varies as a function of wave-vector transfer[9] but is typically 5×10^{-4} Å^{-1}. Perpendicular to the scattering plane, the resolution was limited by a simple slit to approximately 2×10^{-2} Å^{-1}. Under these conditions *only* the sharp component is detected: The broad component becomes simply part of the general background. Our measurements therefore probe only the long-correlation-length scales. Details of the behavior of the shorter correlation length in $SrTiO_3$ are given by Andrews.[6]

The transition temperature of etched samples cut from the same boule had been determined previously as 103.65 ± 0.1 K,[6] with use of the same cryostat and temperature controller. The temperature of our sample was slowly reduced to 106 K, taking care that there were no excursions down to or below T_c. Then the position, integrated intensity, and wave-vector width of the R-point scattering were measured at a series of temperatures, stepping towards T_c, by performance of grid scans of the regions of reciprocal space around (0.5,0.5,2.5) and around the three cubic-phase Bragg reflections (0,0,2), (0,0,3), and (1,1,3); these three Bragg reflections were used to define and check a cubic reference frame. The sample was maintained for at last 36 h at each of the temperatures where measurements were made.

The filled circles in Fig. 1 show the results obtained for the wave-vector width. In contrast to the measurements of Andrews,[6] we find that the width is *not* resolution limited above T_c. The additional, noninstrumental width is isotropic—the same within error along [110] and [001], as found also in $RbCaF_3$ (Refs. 3 and 4) and $KMnF_3$ (Ref. 5)—and decreases continuously to zero at T_c, corresponding to a divergence in the correlation length of the features giving rise to the scattering. The change in width with temperature can be seen clearly in Fig. 2(a), which shows the measured scan profiles along [110] through the R point at $T_c+1.4$ K and just above T_c.

A simple deconvolution of the instrumental resolution yields an estimate of 1100 ± 80 Å for the correlation length at $T_c+1.4$ K, along both [110] and [001], rising to 2400 ± 400 Å at T_c+1 K. These are *very* large sizes, and considerably greater than was found in $RbCaF_3$ (Refs. 3 and 4) and $KMnF_3$ (Ref. 5) ($\simeq500$ Å at T_c+1 K). The difference becomes greater still if the comparison is made in terms of the reduced temperature, $(T-T_c)/T_c$.

The results obtained for the T dependence of the integrated intensity of the scattering reveal that, within error, the intensity varies in proportion to the correlation length. This observation is discussed further below. Unlike $RbCaF_3$ (Refs. 3 and 4) and $KMnF_3$,[5] the *position* of the scattering remained exactly at the R point for all temperatures above T_c, within the resolution of our measurements ($\pm2\times10^{-5}$ reciprocal-lattice units). This is consistent with any discontinuity in the lattice parame-

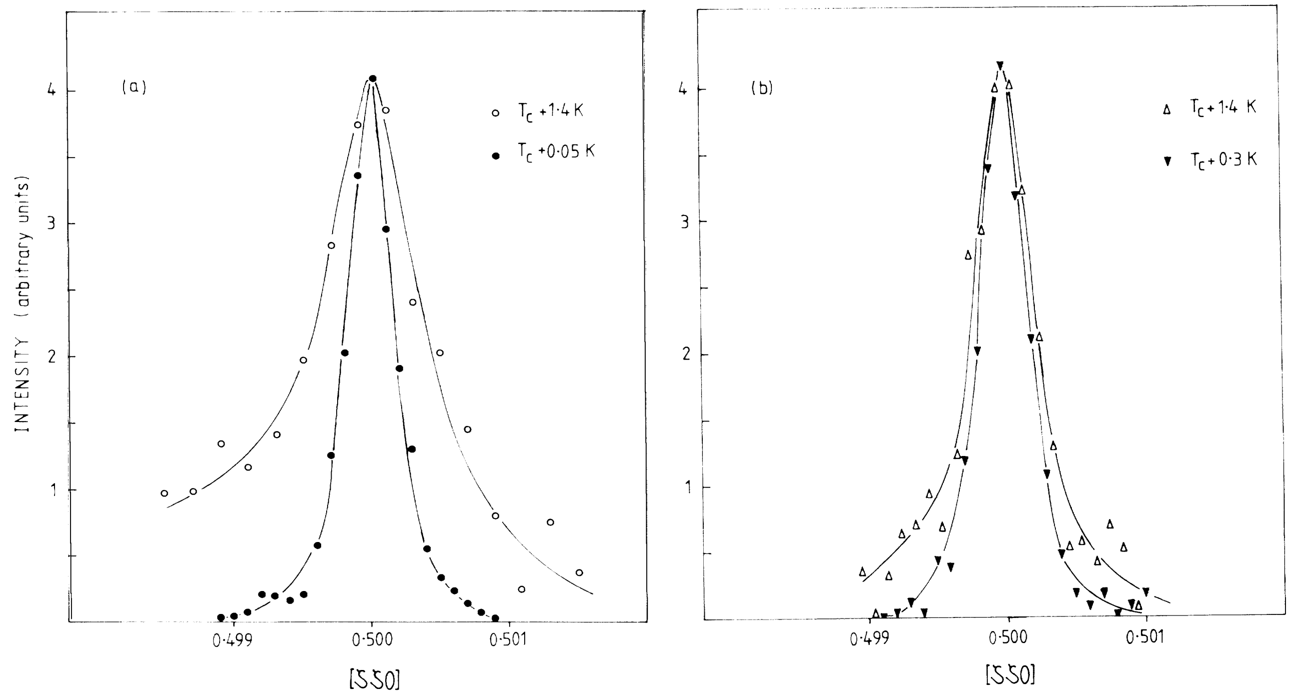

FIG. 2. The intensity observed in [$\zeta\zeta 0$] scans through the sharp component of the critical scattering at the (0.5,0.5,2.5) R point, measured at $T_c+1.4$ K and just above T_c and normalized to the same peak intensity (a) for the virgin sample and (b) after the sample had been cooled through T_c and then warmed to room temperature. The solid lines are guides to the eye.

ters at T_c being less than 10^{-6} Å in SrTiO$_3$,[10] compared with $\simeq 10^{-3}$ Å in RbCaF$_3$[11] and KMnF$_3$.[5]

Below T_c, the R-point scattering is a Bragg reflection, and its width remained constant at the resolution limit (Fig. 1). Measurements were made down to T_c-10 K; then the sample was warmed up to room temperature and the whole experiment was repeated. As before, the temperature was carefully reduced to $\simeq 106$ K and then stepped towards T_c, maintaining the sample for several hours at each of the temperatures where measurements were made. The behavior of the position and integrated intensity of the R-point scattering was unaltered, but the wave-vector width was considerably less, as shown by the triangles in Fig. 1. (Because the scattering was sharper, the time spent at each temperature was less than in the first run: The sample was maintained for 14 h at $T_c+1.4$ K, and for 4 h at temperatures closer to T_c.) The width still exhibits critical behavior, decreasing to the resolution limit in the vicinity of T_c (Fig. 1); the decrease is very small, but the measured scan profiles in Fig. 2(b) confirm that it is significant. The additional width above T_c remains isotropic, corresponding to an increased correlation length of $\simeq 3600\pm 1200$ Å along both [110] and [001] at $T_c+1.4$ K. The same result was obtained, within error, on our heating back to $T_c+1.4$ K after cycling through T_c the second time: There was no evidence of the width either increasing towards its initial value or decreasing further. In this final measurement, the sample was maintained at $T_c+1.4$ K for over 30 h.

We ascribe the observed R-point scattering above T_c to the presence of large clusters of the tetragonal phase embedded within the cubic matrix. The form of the temperature dependence of the larger correlation length is similar for all three perovskites studied so far, and is indicative of a common origin. The tetragonal nature of the clusters was clearly demonstrated in both RbCaF$_3$ (Refs. 3 and 4) and KMnF$_3$ (Ref. 5) by the offset position of the scattering, and the corresponding abrupt jump into registry at T_c by the cubic-phase Bragg reflections.[3-5] As explained, we believe the lack of any measurable offset in SrTiO$_3$ is simply a reflection of the extremely small tetragonal strain stabilized at T_c in this case. The tetragonal clusters are interpreted (see above) as spatial fluctuations occurring close to a first-order phase transition through the effect of strain energy around extended defects such as dislocations, and the cluster size will then be larger (at a given reduced temperature) the smaller the free-energy difference between the phases. The large but finite correlation length above T_c in SrTiO$_3$ is thus indicative of a small first-order character in the transition, at least in the virgin sample.

This conclusion is in accord with recent evidence from ultrasonic attenuation and velocity measurements,[12] and probably from EPR studies too,[13] that a weakly first-order transition can be detected in unstressed, well-annealed SrTiO$_3$. However, some other aspects of the observed behavior are less readily assimilated. First, it is surprising that the system can support critical fluctuations on a length scale well in excess of 10^3 Å as much as 1 K above T_c—a reduced temperature, $(T-T_c)/T_c$, of $\simeq 0.01$. Secondly, there is the memory effect. Such behavior might plausibly be explained—within the proposed interpretation of the large-length-scale fluctuations—on the basis that unstressed (and, so, first-order) $SrTiO_3$ is close to a tricritical point and small stresses will make the transition continuous.[12,13] The introduction of residual stresses after passing through T_c could have this effect, and a more nearly continuous transition would be predicted to give rise to the larger clusters observed. But a memory effect, of whatever cause, associated with a very weakly first-order transition, is not expected to survive heating to room temperature (more than 150 K above T_c); moreover, the sample was maintained for over 30 h at $T_c+1.4$ K in the making of the second set of measurements. Thirdly, the variation of the integrated intensity in proportion to the correlation length indicates that the large-length-scale clusters, despite their size, cannot be regarded as simply regions of nearly uniform tetragonal distortion which just grow larger as $T \rightarrow T_c$. The behavior is more consistent with the varying distortion profile expected around isolated point defects, and the corresponding Lorentzian-squared form of the scattering.[14,15] As yet, it is far from clear why critical behavior on a much larger length scale, and around extended defects, should exhibit this similarity. Such features underline the need for a more detailed understanding of the large critical length-scale behavior.

Finally, we stress that we believe all the observed effects to be characteristic of the bulk, rather than the surface.[3-5] This is strongly suggested by the very close similarity of the size *and* temperature dependence of the correlation lengths parallel (along [110]) and perpendicular (along [001]) to the surface (Fig. 1). Also, the surface was deeply etched, as in the preparation of the $RbCaF_3$ sample,[3] and in one of those samples the sharp component in the R-point scattering was entirely absent.[3] Previously published results for $SrTiO_3$ showing resolution-limited R-point scattering persisting well above T_c are, we believe, attributable to surface damage following cutting and polishing with no,[16] or insufficient, etching.

We have benefitted from several helpful discussions with A. D. Bruce and R. A. Cowley. Financial support was provided by the Science and Engineering Research Council (United Kingdom).

---

[1] T. Riste, E. J. Samuelsen, K. Otnes, and J. Feder, Solid State Commun. **9**, 1455 (1971).

[2] A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor and Francis, London, 1981).

[3] T. W. Ryan, R. J. Nelmes, R. A. Cowley, and A. Gibaud, Phys. Rev. Lett. **56**, 2704 (1986).

[4] A. Gibaud, T. W. Ryan, and R. J. Nelmes, J. Phys. C **20**, 3833 (1987).

[5] U. J. Nicholls and R. A. Cowley, J. Phys. C **20**, 3417 (1987).

[6] S. R. Andrews, J. Phys. C **19**, 3721 (1986).

[7] Y. Imry and M. Wortis, Phys. Rev. B **19**, 3580 (1979).

[8] T. W. Ryan, Ph.D. thesis, Edinburgh University, 1986 (unpublished).

[9] R. A. Cowley, Acta Crystallogr. Sect. A **43**, 825 (1987).

[10] M. Sato, Y. Soejima, N. Ohama, A. Okazaki, H. J. Scheel, and K. A. Müller, Phase Transitions **5**, 207 (1985).

[11] C. Ridou, M. Rousseau, and A. Freund, J. Phys. (Paris), Lett. **38**, L359 (1977).

[12] J. O. Fossum and K. Fossheim. J. Phys. C **18**, 5549 (1985).

[13] K. A. Müller and W. Berlinger, Z. Phys. B **46**, 81 (1982); and the discussion in Ref. 12.

[14] B. I. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).

[15] A. Gibaud, R. A. Cowley, and P. W. Mitchell, J. Phys. C **20**, 3849 (1987).

[16] C. N. W. Darlington and D. A. O'Connor, J. Phys. C **9**, 3561 (1976).