Dynamic Fluctuations and Static Speckle in Critical X-Ray Scattering from $SrTiO_3$

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We report a study of critical x-ray scattering from $SrTiO_3$ near the antiferrodistortive structural phase transition at $T_C \approx 105$ K. A line shape analysis of the thermal diffuse scattering results in the most precise experimental determination to date of the critical exponent γ. The microscopic mechanism behind the anomalous ''central peak'' critical scattering component is clarified here by the first-ever observation of a static coherent diffraction pattern (speckle pattern) within the anomalous critical scattering of $SrTiO_3$. This observation allows us to directly attribute the origins of the central peak to Bragg diffraction from remnant static disorder above T_C.

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Historically, the antiferrodistortive structural phase transition in $SrTiO_3$ has been widely regarded as a prototype suitable for testing basic theories and concepts of phase transitions. For the most part, it is a second order displacive phase transition governed by the softening of a zone boundary phonon mode (R_{25}), describing an antirotation of the oxygen octahedra which results in a commensurate superlattice below $T_C \approx 105$ K [1–3]. Despite this apparent simplicity, several features of this system have generated continuing scientific interest. The correct theoretical prediction of the critical behavior of the system within the fluctuation-dominated Ginzburg interval has fostered development of sophisticated renormalization group techniques [4–6]. Within neutron scattering from the system, the observation of an anomalous $E = 0$ central peak has indicated unexpected slow or static dynamics above the phase transition [7,8]. Within x-ray scattering from the system, the observation of an anomalous central peak at the R-point in reciprocal space has indicated an unexpected second critical length scale [9–15]. This Letter addresses the origins and precise criticality of the x-ray critical scattering central peak component. We present here a unified synchrotron x-ray study of both the critical phonon softening and anomalous critical scattering in $SrTiO_3$ over a wide temperature range from room temperature to the structural phase transition.

Previous neutron experiments have characterized the constituent R_{25} phonon frequency softening, but have been unable to study critical softening behavior near the transition due to the phonon branch merging with a quasielastic central peak, and are limited to a sparse data set above the transition [3,7,8]. With the advent of third-generation synchrotron sources such as the Advanced Photon Source, studies of lattice dynamics through x-ray thermal diffuse scattering (TDS) have recently been made possible [16,17]. Results of our TDS analysis agree well with the predictions of mean-field theory and available experimental data [3,8,9] over a wide temperature range and confirm renormalization group predictions of critical behavior in the near-transition region [5,6,18].

The central peak critical scattering component has been previously observed in x-ray data at temperatures well above T_C and has been the subject of much debate [9–15]. This feature has generated continuing scientific interest as it could represent a second critical length scale of the system, in principle violating the scaling hypothesis central to many modern theories of phase transitions [19]. The precise microscopic mechanism has been historically unclear, but the phenomenon is thought to be related to either the high density of dislocations and defects [11,20], or a spontaneous strain gradient [13–15] in the near-surface region relative to the bulk. Our first-ever observation of a coherent speckle pattern within the central peak critical scattering sheds new light on the nature and dynamics of this anomalous feature. Speckle analysis leads us directly to the following assertions regarding the central peak: (i) it is caused by Bragg diffraction from a remnant disordered state above T_C, (ii) this disorder is static on all observed time scales and reproducible under thermal cycling, (iii) the length scale of this disorder is comparable with observed defect density, and (iv) the criticality of this component is separate from the bulk phase transition.

The TDS experiment was performed at the undulator beamline of sector 33 (XOR/UNI), and the coherent diffraction images were taken at sector 8 (XOR) at the Advanced Photon Source, Argonne National Laboratory. A commercially available single crystal of $SrTiO_3$ was mounted on the copper cold finger of a closed-cycle He Displex for cooling. The sample assembly was enclosed in a vacuum shroud equipped with a hemispherical Be dome for the x-ray measurements. The temperatures reported below were the readings from a Si diode attached to the copper cold finger. The temperature was stable to within 0.1 K, and we estimate the absolute variance to be no more

than 0.5 K—this temperature was maintained with the circulating Displex turned off when collecting the coherent diffraction images. Incident radiation was set at 13.4 keV for the TDS experiment and 8 keV for the coherent diffraction experiment.

Line scans collected along the *M*-*R*-*M* line in reciprocal space are shown in Fig. 1(a). The TDS intensity near the *R*-point increases upon cooling to the transition temperature, and the line shape narrows, indicating a frequency drop of the lowest-lying phonon mode. At about 30 K above the transition temperature, a sharper central component is detected above the broader TDS component. This central component was fit with a Lorentzian-squared line shape (Fig. 1(a); gray line) following previous work [9]. It is important to note that this component is well separated from the TDS component in both width and intensity, and so the two are well distinguished within this analysis. Below 104 K, the central component greatly picks up in intensity (inset to Fig. 1(b)), and the width reduces to the nominal instrument resolution. This indicates that a true superlattice peak has emerged and that a static lattice distortion has occurred within the bulk of the crystal. A fit with the expected order parameter dependence (solid line, inset to Fig. 1(b)) suggests that the transition temperature is $T_C \approx 104 \pm 0.2$ K, in agreement with the abrupt shift in behavior of the TDS component intensity (gray line, Fig. 1(b)). The phonon frequency softening extracted from the TDS line shape analysis described below is shown in Fig. 1(c), and agrees well with available neutron data (solid circles) [7].

The TDS lineshape in Fig. 1(a) (solid line) is a theoretical fit to the data given by

$$I(\mathbf{q}) \propto \sum_{j=1}^{15} \frac{|F_j(\mathbf{q})|^2}{\omega_j(\mathbf{k})} \coth\left(\frac{\hbar\omega_j(\mathbf{k})}{2k_BT}\right), \quad (1)$$

where the phonon structure factor F and the phonon frequency ω are summed over all modes. This TDS analysis method has the advantage of explicitly accounting for temperature-dependent higher-order phonon effects at all temperatures above the transition, and is discussed in greater detail elsewhere [16,17]. Near the transition, the TDS line shape is functionally equivalent to a Lorentzian—which is the expected Ornstein-Zernicke form for the susceptibility of the soft-mode lattice in reciprocal space [9,19].

The critical behavior of the soft-mode TDS component versus reduced temperature, $t = (T - T_C)/T_C$, is shown on a logarithmic-logarithmic scale in Figs. 2(a) and 2(b). As expected from a scaling theory of phase transitions, both the width σ and intensity I of the TDS critical scattering follow a power law dependency on reduced temperature (where $I_{\mathrm{TDS}} \approx t^{-\gamma}$ and $\sigma_{\mathrm{TDS}} \approx t^{\nu}$, given by straight lines on the log-log scale) [19]. At temperatures far from the phase transition, the intensity is in principle governed by a mean-field prediction for continuous phase transitions ($\gamma = 1$). However, at temperatures near the phase transition, fluctuations begin to dominate, and these predictions are no longer valid. Within this non-mean-field

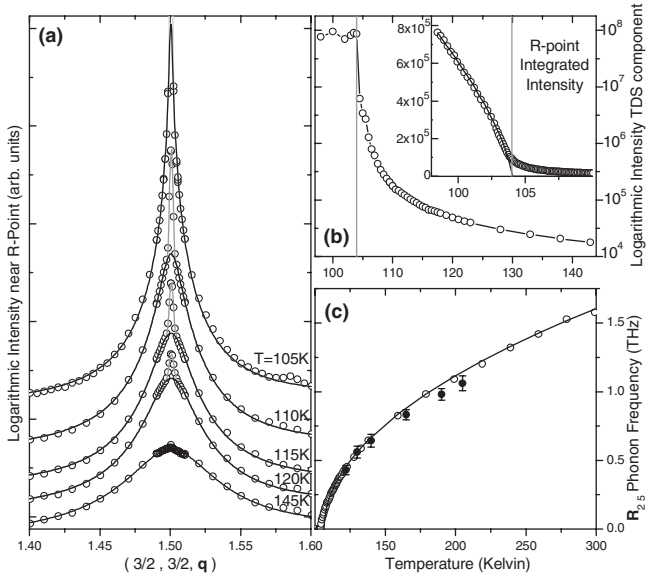

FIG. 1. Fig. 1(a). Intensity of critical x-ray scattering from $SrTiO_3$ as a function of temperature near the *R*-point; the solid lines are a two-component fit to the data discussed in the text. The TDS component intensity is shown in Fig. 1(b), with the *R*-point integrated intensity inset. Fig. 1(c) shows the resulting phonon frequency of the lowest-lying zone boundary phonon mode; the solid circles are available neutron data points [7].

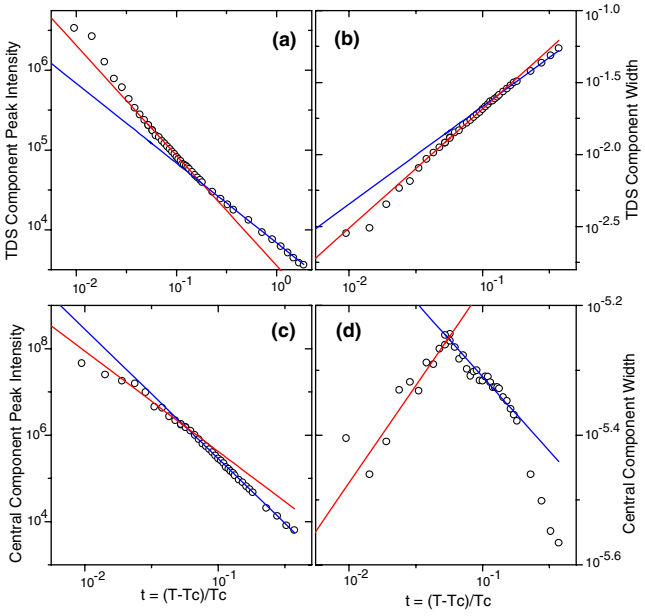

FIG. 2 (color online). Log-log plots of the temperature dependence of critical scattering from $SrTiO_3$. Figures 2(a) and 2(b) show the criticality of the TDS line shape component peak intensity and width as a function of temperature, while Figs. 2(c) and 2(d) show the respective peak intensity and width of the central component. Power law dependencies of these parameters appear as straight lines on this scale.

interval, the critical properties of the system are predicted by renormalization group techniques to be $\gamma = 1.386 \pm 0.004$ [18] for the expected universality class of a Heisenberg antiferromagnet [5]. Following Fig. 2(a), we see that there are indeed two distinct regions of soft-mode critical scattering that indicate a transition from mean-field to non-mean-field behavior, agreeing with previous estimates of the Ginzburg criterion for this system ($T_{\text{Ginzburg}} \approx T_C + 10$ K) [21,22]. The exponents resulting from a power law analysis of the experimental parameters are summarized in Table I and agree within error to theoretical prediction and previous experimental observation. The error bars of all data points in Fig. 2 are on the order of the shown circle size. However, as the horizontal scale depends sensitively on the value of T_C, the majority of our estimated error is due to the precision with which we established T_C above.

The images in Fig. 3 show coherent diffraction images (speckle patterns) taken at the diffraction condition of the central peak. The sample was illuminated with a coherent x-ray beam of size 15 μm $\times$ 15 μm, and the resulting diffraction pattern was captured on a direct illumination CCD camera positioned 1.6 m away from the sample with 22 μm $\times$ 22 μm pixels. The three image panels show data taken at three temperatures near the bulk transition temperature ($T_C - 0.5$ K, $T_C + 0.25$ K, and $T_C + 0.75$ K, corresponding to Figs. 3(a)–3(c), respectively). Following Fig. 3(d), we see that the integrated intensity of the peak increases smoothly and monotonically as we cool the sample through the bulk phase transition. However, the coherent diffraction images at the central peak diffraction condition change dramatically from a broad, complicated speckle pattern immediately above T_C (Figs. 3(b) and 3(c)), to a single speckle at temperatures immediately below T_C (Fig. 3(a)). All patterns were static in time (data were taken for up to 10 min in integrated length) and reproducible under thermal cycling. The patterns above T_C were unique to physical regions on the sample. As will be discussed further below, the above observations all indicate that the origin of the central component is a static, heterogeneous structure of the low temperature phase above T_C.

Our observation of static speckle patterns under a coherent illumination of the central peak scattering condition above T_C calls for a careful interpretation. In general, a coherent interference pattern of scattered x-rays requires that two things be present: (i) a scattering mechanism that preserves phase over the time scales observed and (ii) a disorder mechanism responsible for a broadening in the scattering. In our case, we should note that the scattering mechanism cannot be diffuse scattering from fast dynamic fluctuations, such as TDS or classical critical fluctuations, as their speckle patterns are lost when averaged over long times, much longer than any intrinsic correlation time. Since we measure scattering at the low-T superlattice position, some fraction of the illuminated volume must have the low-T crystal structure above T_C.

Phase contrast patterns within Bragg diffraction are typically found in crystalline systems that possess a high degree of intrinsic disorder, which results in regions of differing lattice constants within an illuminated volume [23]. Extrinsic disorder, such as surface roughness or pathological strain states, may also cause diffractive speckle. However, we can rule out any such contrast mechanism unrelated to the order parameter, as it would persist below T_C and so cannot account for the single peak observed in Fig. 3(a). The sharpness of this peak indicates that the crystal in the scattering volume has completely transformed to the new structure below T_C, so we can attribute the speckle above T_C to a simple static mixture of high and low temperature structures. As this phase contrast, at fixed temperature, does not vary in time, and is repeatable under thermal cycling, the low-T regions are presumably pinned to defects or other inhomogeneities within the scattering volume. It is the local random strain field associated with these defects that likely affects the order parameter, caus-

TABLE I. Observed criticality of TDS component and central component. Numbers in parentheses are theoretical values.

Line shape component	Critical exponent γ		Critical exponent ν
TDS—away from T_C	1.0 ± 0.05	(1.000)	0.68 ± 0.05
TDS—near T_C	1.38 ± 0.05	(1.386)	0.83 ± 0.05
Central—away from T_C	3.05 ± 0.05		-0.30 ± 0.05
Central—near T_C	2.60 ± 0.05		0.23 ± 0.05

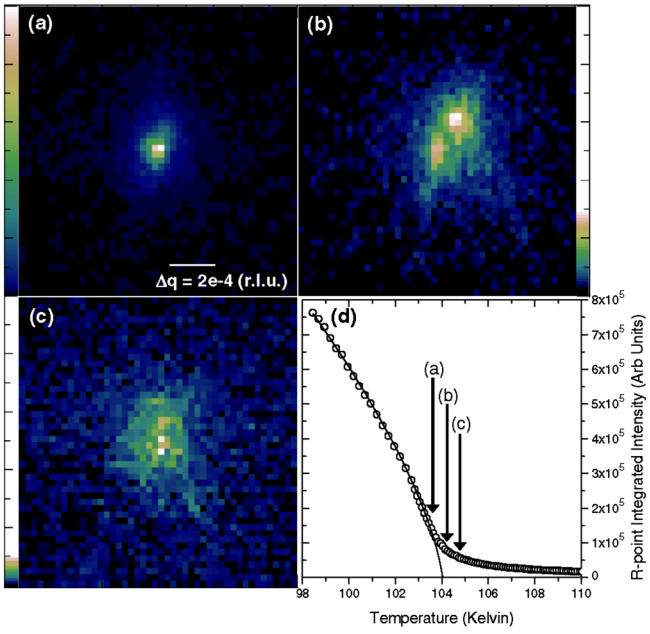

FIG. 3 (color online). Coherent diffraction patterns at the anomalous central peak critical scattering condition. All images are shown on a linear scale; the relative per-pixel intensity color scale is given on the side of each figure for comparison. Temperatures are marked for reference to the bulk phase transition temperature in Fig. 3(d).

ing a static persistence of the low-T phase [19,20]. Analyzing the width of the speckle observed in Fig. 3(b) compared to the width of the single speckle in Fig. 3(a), we estimate the average correlation length between pinned low-T regions is approximately $\xi_\ell \approx 2.7$ μm. This is a reasonable volume fraction as it indicates a local defect density of $\approx 2 \times 10^7$ cm^{-2}, comparable with previous estimates of the defect density in $SrTiO_3$ [20]. We should note that the x-ray attenuation length at this energy is ~ 15 μm, indicating that we are sampling a substantially near-surface scattering volume. However, recently proposed mechanisms for the central peak phenomenon involving a spontaneous near-surface strain gradient or ''skin effect'' [12,13,24,25], that are in principle unrelated to defects, cannot explain our data, as a smoothly varying strain field would not cause a speckle pattern.

The quasicritical behavior of the central peak is shown on the bottom panels of Fig. 2. From our coherent diffraction results, we expect that this scattering arises from highly localized regions, and so the results of a power law analysis, fundamentally based on a scaling hypothesis, are not expected to be physically meaningful. The resulting exponents in Table I do not, in fact, agree with any calculated universality class, and the ''critical interval'' of the central component disagrees with the criticality of the bulk phase transition by ~ 5 K, further indicating that local, nonscaleable physics governs these parameters. What actually causes the observed quasicriticality of the central peak component (observed in Figs. 2(c) and 2(d)) is the topic of ongoing experiment and theoretical work. At this time, we hypothesize that the behavior of the central peak width away from T_C is governed by the formation of precursor clusters, while the near-T_C behavior is dominated by the relative growth of these precursor regions. This quasicriticality is expected to be related to the exact distribution of defects and so highly dependent on sample and surface preparation, as has been previously observed [9,12].

In summary, we have presented a study of critical x-ray scattering phenomena related to the 105 K antiferrodistortive phase transition in $SrTiO_3$. Analysis of the x-ray thermal diffuse scattering line shape allows us to establish mean-field and critical behavior of the dynamic lattice fluctuations of the system with a high degree of precision. The first-ever observation of coherent diffraction patterns within x-ray critical scattering above T_C directly confirms the origin of the anomalous central peak feature as a simple static mixture of high and low temperature structures pinned to defects within the scattering volume. This method of complementing synchrotron x-ray TDS analysis with time-resolved observation of coherent speckle holds great potential in elucidating static and dynamic fluctuations in a wide range of critical systems of interest to materials studies.

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