# Origin of the critical scattering on two length scales in $SrTiO_3$: A high-energy synchrotron-radiation diffraction study

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High-$q$-resolution diffraction experiments performed with 100 keV synchrotron radiation on the identical $SrTiO_3$ crystal used in neutron and x-ray-scattering experiments before, unambiguously show that the bulk critical scattering above $T_c = 99.5$ K does not exhibit a sharp component, which had been found in recent x-ray-diffraction experiments. The observed temperature dependence of the inverse correlation length is in excellent agreement with the neutron data. However, scattering on two length scales was observed in a near-surface volume element of the same crystal.

$SrTiO_3$ has been proven as one of the most instructive model systems to discuss phonon-driven structural phase transitions because it shows both a zone-center soft mode, whose energy does not go to zero at finite temperatures,[1] and a zone-boundary ($R$-point) phonon instability whose energy does go to zero as the temperature approaches $T_c$ from above.[2] It also exhibits an elastic central component associated with the zone-boundary phonons,[3,4] the intensity of this so-called central peak diverges at $T_c$. The nature of the central peak is still under discussion. Some theories state it is dynamical in origin due to anharmonic processes,[5] which contradicts the nowadays well-established elastic nature of the central peak. It is more likely that the central peak is due to defects in the sample.[6] More recently a sharp quasi-Bragg peak has been discovered by means of x-ray-diffraction experiments in $SrTiO_3$,[7-9] as well as in other perovskites and the question has been raised, if the sharp quasi-Bragg peak observed by x-ray diffraction on top of the broad critical scattering peak at the $R$ point several degrees above $T_c$ is related to the central peak.

The $q$-space resolution achieved in x-ray-diffraction is in general by orders of magnitude better than in neutron scattering, however phonon scattering cannot be separated from elastic scattering in most cases. Thermal neutrons probe bulk properties, whereas x-ray-diffraction data are related to near-surface regions of some 10 $\mu$m thickness. This motivated an investigation of the critical scattering of $SrTiO_3$ with a triple-crystal diffractometer for high-energy synchrotron radiation,[10] where bulk properties of large samples of even strongly absorbing materials can be probed with two orders of magnitude higher $q$-space resolution than achieved in common neutron-diffraction experiments.[11]

In the one-phonon approximation the critical scattering above $T_c$ is well described by an anisotropic Lorentzian distribution.[7] The quasi-Bragg peak has an isotropic Lorentzian squared shape[8] in $q$ space. For $KMnF_3$ (Ref. 12) and $RbCaF_3$ (Ref. 13) it was shown that it is part of the low-temperature tetragonal phase of the crystal. In neutron-scattering experiments Hastings, Shapiro, and Frazer[14] observed, that the central peak depends on defects and the suggestion was made, that the quasi-Bragg peak may also be related to defects. However, Cox and Cussen[15] showed that the intensity of the quasi-Bragg peak does not depend on the defect concentration. Recently Shirane, *et al.*[16] performed neutron-scattering experiments on their highly perfect, top seeded grown $SrTiO_3$ single crystal with a $q$ resolution sufficient to observe the quasi-Bragg peak. However, no quasi-Bragg peak was found, whereas a preliminary x-ray experiment performed on the same sample indicates the presence of the quasi-Bragg peak only.[9]

The temperature dependence of the inverse correlation length of $SrTiO_3$ for 1/2(311) and scans along [011] is summarized in Fig. 1. $\kappa_c$ represents the inverse correlation length related to the central peak, which is determined directly by means of neutron scattering from high-resolution constant energy scans. The temperature dependence of the inverse correlation lengths $\kappa_0$ and $\kappa_\infty$ were calculated from constant $q$ scans.[4] $\kappa_\infty$ denotes the inverse correlation length of the soft-phonon peak, while $\kappa_0$ is the total inverse correlation length containing both the central peak and the softening phonon peaks. $\kappa_0$ corresponds to the half-width at half maximum (HWHM) of the critical scattering expected for energy integrating x-ray-diffraction experiments. In addition the neutron data are compared with the inverse correlation lengths $\kappa_{L1}$ and $\kappa_{L2}$ of the broad and the sharp component measured by means of x-ray diffraction.[8,9] Obviously the central peak is different in nature from the quasi-Bragg peak observed in high-$q$-resolution x-ray experiments.

Because the sharp quasi-Bragg peak has been observed by x-ray diffraction on the highly perfect top seeded $SrTiO_3$ crystal but not in neutron-scattering experiments probing the bulk of the same sample, it has been pro-

 

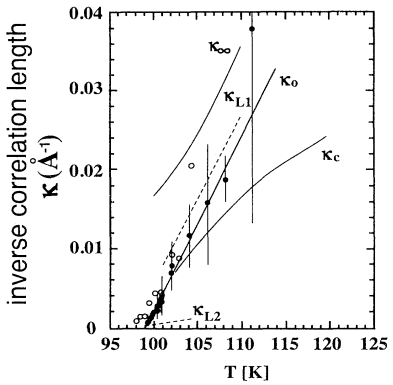


FIG. 1. The solid lines represent the temperature dependence of the inverse correlation lengths of $SrTiO_3$ for scans along [011] reproduced from Ref. 16. $\kappa_c$ is related to the central peak, $\kappa_\infty$ to the soft phonon peak, while $\kappa_0$ represents the total inverse correlation length containing both, the central peak and the softening phonon peaks. $\kappa_{L1}$ and $\kappa_{L2}$ are the inverse correlation lengths of broad and sharp component in x-ray experiments (Ref. 8), respectively. The full circles represent the inverse correlation length determined from scans in the center of the crystal using 100 keV synchrotron radiation. The open circles are determined from scans in the corner of the crystal.

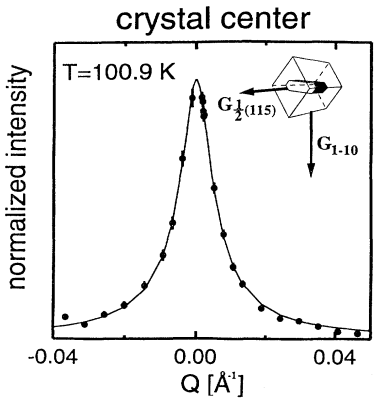


FIG. 2. Scan parallel to [011] at the 1/2(115) $R$-point reflection 1.5 K above $T_c$ (photon energy 100 keV). The solid line is a Lorentzian convoluted with the resolution. The inverse correlation length $\kappa_0$ determined by the fit is equal to $4\times10^{-3}$ $Å^{-1}$. The inset shows the orientation of the sample together with the illuminated volume.

posed that the origin of the sharp quasi-Bragg peak is related to the near-surface region of the crystal. This suggestion is supported by recent neutron-diffraction studies on the magnetic phase transition in Tb,[17] where a sharp component has been located in a 0.3 mm thick near-surface region of the crystal.

In order to solve the discrepancy between x-ray and neutron-diffraction data for $SrTiO_3$ a high-$q$-space diffraction experiment has been performed at the BW5-wiggler beam line at HASYLAB with the new triple-crystal diffractometer[10] for high-energy synchrotron radiation. The sample is again the highly perfect top seeded crystal used in the neutron[4,16] and the most recent x-ray-scattering experiments.[9] The beam was collimated to a size of $2\times2$ mm$^2$ by 3 mm thick tungsten slits. The FWHM of the mosaic distribution of the crystal was determined at the $SrTiO_3$ 400 main reflection in the [01$\bar{1}$] zone to $\leq1.5$ arcsec in an almost dispersion-free double-crystal scan using 150 keV photons and a perfect Si 440 monochromator. The mosaicity is homogeneous over the whole crystal. For 100 keV photons the absorption coefficient of $SrTiO_3$ has been measured to $\mu=2.3$ cm$^{-1}$.

The sample was mounted in a strain-free manner in an He-bath cryostat. The temperature stability was better than 0.05 K. The transition temperature in the center of the crystal was determined from the temperature dependence of the integrated reflecting power at the 1/2(511) superlattice reflection and the intensity overshoot of the 511 main Bragg peak. The results of these independent measurements provided a critical temperature of $T_c=(99.7\pm0.2)$ K. This value is in good agreement with earlier neutron[16] and $\gamma$-ray-diffraction data.[18]

Imperfect Si 311 crystals with a mosaicity of $\approx2.5$ arcsec were used as monochromator and analyzer in the synchrotron-radiation measurements of the critical scattering at the $R$ point. With this choice $\lambda/2$ is sufficiently well suppressed. The photon energy was fixed at 100 keV and again the [01$\bar{1}$] zone was selected. The Bragg angle for 1/2(511) at 100 keV is 2.38°. The $q$-space resolution in the scattering plane at the $R$ point has been determined from the peak shape measured 10 K below $T_c$. In terms of HWHM it is $1\times10^{-3}$ $Å^{-1}$ for scans parallel to [100] and $5.6\times10^{-5}$ $Å^{-1}$ for scans parallel to [011]. Perpendicular to the scattering plane the resolution function is of triangular shape with a HWHM=0.044 $Å^{-1}$. In Table I the resolution of the

TABLE I. Comparison of the resolution width (HWHM in $Å^{-1}$) obtained in common x-ray, neutron, and the present high-energy x-ray-diffraction experiments in the [01$\bar{1}$] zone.

| | Scan direction | | |
|---|---|---|---|
| | [011] | [100] | Vertical to the scattering plane |
| x-ray $E\approx10$ keV (Ref. 8) | 0.000 6 | 0.0009 | 0.035 |
| Neutrons $E=4.4$ meV (Ref. 16) | 0.001 5 | 0.002 | 0.025 |
| High-energy photons $E=100$ keV | | | |
| Crystal center, low resolution | 0.000 056 | 0.001 | 0.044 |
| Crystal corner, low resolution | 0.000 84 | 0.001 | 0.044 |
| Crystal corner, high resolution | 0.000 14 | 0.0003 | 0.044 |

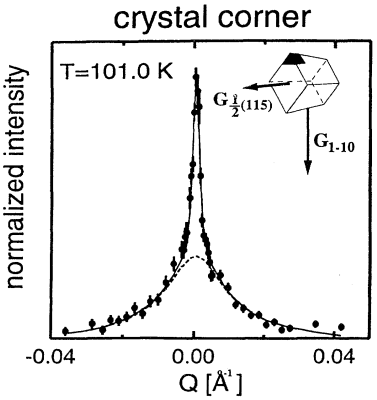


FIG. 3. [011] scan at 1/2(511) at $T=101$ K (photon energy 100 keV). The solid line is the result of a fit of a Lorentzian plus a Lorentzian squared convoluted with the resolution to the experimental data. The inset shows the orientation of the sample together with the illuminated volume.

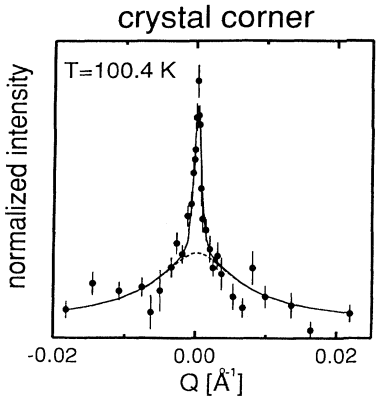


FIG. 4. Same as Fig. 3 with six times better transverse resolution, $T=100.4$ K.

100 keV synchrotron-radiation experiment is compared with the resolution of the recent neutron[16] and an earlier x-ray experiment.[8]

Scans were performed in the [011] direction because of the better $q$-space resolution. Figure 2 shows a scan measured 1.5 K above $T_c$ together with the best fit of a Lorentzian of HWHM$=4\times10^{-3}$ Å$^{-1}$ convoluted with the three-dimensional resolution, the procedure has been described by Andrews.[7] The goodness of fit was 1.3. Obviously no sharp component on top of the broad response function is observed. The crystal volume eluminated by the incident beam is located in the center of the crystal as indicated in the inset of Fig. 2. Figure 1 shows the measured inverse correlation length as full circles. The agreement between neutron data and the high-energy synchrotron-radiation data measured with a $q$-space resolution 27 times better than that of the neutron experiments and ten times better than the resolution achieved using x rays with energies of the order of 10 keV is excellent.

Recent measurements in Tb (Ref. 17) located the sharp component in a 0.3 mm thick near-surface layer of the crystal. Therefore the critical scattering of $SrTiO_3$ was measured in a corner of the crystal, where the fraction of the near-surface region in the irradiated volume element is larger. If one assumes the value of the thickness of such a region to be 0.3 mm, the relation between surface to bulk volume is approximately 0.45 in the corner and 0.075 in the center of the crystal. Indeed, a sharp component on top of the critical scattering has been observed. Figure 3 shows a scan parallel [011] at 101 K, the probed volume element is indicated in the inset. The solid line is a fit of a Lorentzian plus a Lorentzian squared convoluted with the three-dimensional resolution function, which, for scans parallel to [011] was by a factor of 15 broader than in the center of the crystal. However, the width of the main 400 reflection in the corner is the same as in the center of the crystal. In Fig. 1 the temperature dependence of the inverse correlation length of the broad component measured in the crystal corner is shown as open circles.

The HWHM of the sharp component is resolution limited in this setup. Therefore high-resolution measurements were performed using perfect silicon crystals as monochromator and analyzer. The resolution parallel to [100] and parallel [011] was determined to be $3\times10^{-4}$ Å$^{-1}$ and $1.4\times10^{-4}$ Å$^{-1}$, respectively. Because of the long measuring times only one scan was performed at 100.4 K (Fig. 4). The sampling time for each data point was 20 min. The value of the HWHM$=3.07\times10^{-4}$ Å$^{-1}$ of the Lorentzian squared component is in good agreement with the value observed by McMorrow *et al.*[8]

A systematic study of the occurrence of the two length scales in the critical scattering in the near-surface region of $SrTiO_3$ will be performed with the undulator beam line at the PETRA storage ring at DESY, which will be available in summer 1995. At phonon energies around 100 keV the brightness of this beam will be at least by three orders of magnitude higher than presently available at DORIS III. Using perfect silicon crystals as monochromator and analyzer high $q$-space resolution experiments with sufficiently high intensity will become possible. In addition the vertical size of the beam cross section can be reduced to approximately 10 $\mu$m, so that thin slices at variable distance from the sample surface can be investigated.

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