

Diffuse X-ray Scattering from Persistent Local Displacements in Perovskite Ferroelectrics

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Introduction

Despite extensive studies of the ABO_3 perovskite ferroelectrics, the origin of the diffuse x-ray scattering sheets in the paraelectric cubic phases of $BaTiO_3$ and $KNbO_3$ is still a matter of debate [1, 2]. In the previously prevailing displacive model introduced by Cochran [3], the diffuse sheets are explained by the formation of linear chains of correlated vibrational displacements caused by the soft mode [4]. In the alternative order-disorder model, the diffuse sheets are explained by the formation of linear chains of correlated local displacements that persist in the paraelectric phase [1, 5]. In the latter model, the ferroelectric distortions are still present in the paraelectric phase, and the proper order parameter is determined by the average of the persistent local displacements.

The existence of local ferroelectric distortions in the paraelectric phases has been demonstrated by x-ray absorption fine structure measurements of the local structure of $PbTiO_3$ [6], $BaTiO_3$ [7] and $KNbO_3$ [8]. These measurements have shown that the persistent local displacements in $PbTiO_3$ are along the tetragonal [100] directions (the six-site model), in contrast to the case of $BaTiO_3$ and $KNbO_3$, where the displacements are along the rhombohedral [111] directions (the eight-site model). Molecular dynamics simulations of paraelectric $KNbO_3$ reveal local polar distortions with short-range chainlike correlations, present far above the transition temperature [9].

In order to address the long-standing controversy of the origin of the diffuse sheets, we investigated, for the first time, the diffuse x-ray scattering from the single-crystal $PbTiO_3$ as a function of temperature. If the soft mode is the cause of the diffuse sheets, since the soft mode is similar in all three perovskites, we would expect to find similar diffuse sheets in $PbTiO_3$. On the other hand, if the chainlike ordering of the local displacements in the eight-site systems is the cause of the diffuse sheets, then we would expect to find something different in the diffuse scattering from cubic $PbTiO_3$. Indeed, this is what we found.

Methods and Materials

The $PbTiO_3$ crystals were grown from stoichiometric melts, which is described in more detail elsewhere [10]. All x-ray measurements were made at the PNC-CAT bending magnet beamline 20-BM at the APS. The incident beam (12 keV) was focused in the vertical direction to approximately 50 μ m by using an elliptically bent mirror, which also rejected higher harmonics. The incident and fluorescent signals were monitored by ionization chambers, and the scattered signal was measured by an Oxford NaI detector. The x-ray scattering measurements were made by running SPEC and using a kappa four-circle Huber goniometer.

For temperature control of the samples, we constructed a small furnace that could be mounted onto the goniometer head (Huber 1003). Heating is achieved by means of a single cartridge heater inserted into a copper plate on which the sample is placed. The sample is surrounded by an aluminum radiation shield, and this assembly is contained in an evacuated aluminum vacuum shroud (pressure of ~ 10 mTorr). Kapton® window slots allow access to the sample over a large solid angle. Sample temperatures as high as 850K have been reached, with control within a few degrees.

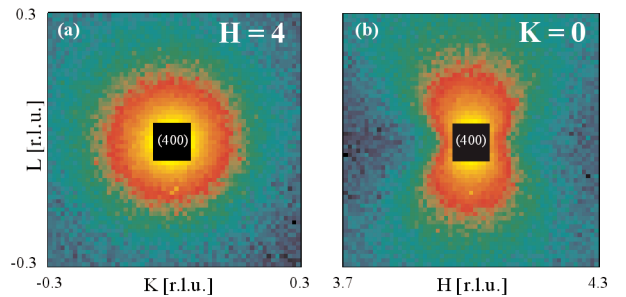


FIG. 1. Diffuse scattering profiles around the (400) reflection from cubic $PbTiO_3$ in the (a) KL plane and (b) HL plane, plotted on a logarithmic intensity scale. The black regions at the center avoid the much more intense vicinity of the Bragg point. The sample temperature was 793K.

Results

Figure 1 shows the diffuse scattering measured around the (400) Bragg reflection from PbTiO_3 at a temperature of $\text{TC} + 30\text{K} = 793\text{K}$. The integration time was 1 per point, with a step size of 0.05 r.l.u. The total scan time was about 4 h. The slight asymmetry in the data seen in the KL plane is due to the self-absorption effect, which was corrected for in subsequent analyses.

The diffuse profiles are well-characterized by first- and second-order thermal diffuse scattering (TDS) calculations in the continuum theory. The first order TDS per unit cell is described by the expression [11]:

$$I_1(\vec{q}) = |F_{hkl}|^2 \frac{k_B T}{m} \frac{|\vec{q}|^2}{|\vec{g}|^2} \sum_j \frac{\cos^2 \alpha_{ij}}{v_{ij}^2}$$

where the summation is over the three different modes of the acoustical phonon modes. F_{hkl} is the structure scattering amplitude that includes the Debye-Waller factor, k_B is Boltzmann's constant, T is the absolute temperature, m is the mass of the unit cell, \vec{q} is the photon wave vector, \vec{g} is the phonon wave vector, v is the velocity of the thermal wave, and Δ is the angle between the thermal displacements and the photon wave vector. The measurements in the immediate vicinity of the Bragg reflections are consistent with TDS calculations using the elastic moduli $C_{11} = 234$ GPa, $C_{44} = 62$ GPa, and $C_{12} = 150$ GPa. However, phonon dispersion in cubic PbTiO_3 is significant and must be accounted for.

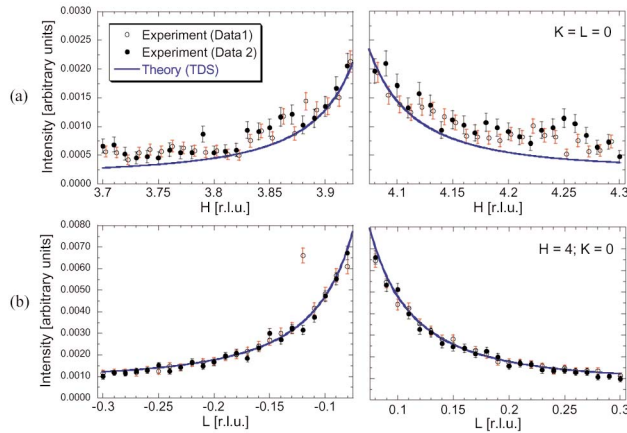


FIG. 2. Comparison between theory and experiment (a) along the H-direction at $K = L = 0$ and (b) along the L-direction at $H = 4$ and $L = 0$. The theory includes first- and second-order TDS from using the measured phonon dispersion of the TA and LA modes by inelastic neutron scattering [12]. The diffuse scattering is well characterized by TDS, with no discernible anisotropic structure in the diffuse scattering from the local displacements.

The phonon dispersion in cubic PbTiO_3 has been measured only along the [100] direction by inelastic neutron scattering [12]. Figure 2 shows the comparison between the experiment and the calculation of TDS from using the phonon dispersion of the TA and LA phonon modes along these directions. The calculation includes first- and second-order TDS contributions and has been corrected for self-absorption from the sample, Compton scattering, and instrumental broadening.

The agreement between the theory and the experiment is quite good, with evidence of a weak, broad, featureless background that is not accounted for by theory. The absence of any contributions from diffuse sheets is clear. The diffuse sheets in BaTiO_3 and KNbO_3 are present along all principal axis directions except those passing through the origin. So if there were diffuse sheets, we would see additional diffuse intensity along the L-direction but not along the H-direction. The fact that diffuse sheets are not observed is consistent with the unique orientation of the displacements in PbTiO_3 .

Discussion

We have presented the first diffuse x-ray scattering measurements from paraelectric PbTiO_3 . We find an absence of diffuse sheets in cubic PbTiO_3 , in stark contrast to the diffuse sheets that are observed in BaTiO_3 and KNbO_3 . A quantitative analysis of the thermal diffuse scattering indicates that the soft mode contribution is negligible in all three perovskites and that the difference in the diffuse scattering from PbTiO_3 is due to the different disordering of the local structure. This is in agreement with the finding that local distortions in the perovskite ferroelectrics persist above the phase transition but lose their long-range correlation.

The absence of diffuse sheets in PbTiO_3 is consistent with the unique type of local distortions in this system. In BaTiO_3 and KNbO_3 , the local distortions have rhombohedral symmetry and are in the [111] directions, whereas in PbTiO_3 , the local distortions have tetragonal symmetry and are in the [100] directions. In the former case, it is possible to form linearly correlated chains of the displacements along the [100] directions while preserving the cubic symmetry of the lattice. In the latter case of PbTiO_3 , it is impossible to form linearly correlated chains along these directions without destroying the cubic symmetry of the lattice. The competition between strain and entropy therefore favors a short correlation length of tetragonal unit cells randomly oriented along the cubic axes. This work constitutes the Ph.D. thesis of B.D. Chapman. A more detailed report on the work is currently being prepared for publication.

The results of this study are consistent with the vibronic theory of ferroelectricity in the perovskites.

According to this theory, the local ferroelectric distortions in the lattice cause a mixing of the high-symmetry ground electronic state with the excited states, lowering the energy [13]. Recent theoretical work has extended the vibronic theory from the local atomic picture to the band picture and has quantitatively shown how spontaneous, off-center, local displacements can couple to the soft mode, leading to both the displacive-type and order-disorder-type features in PbTiO_3 and KNbO_3 [14]. This theory shows that although the long-range Coulomb interactions may soften the lattice creating the soft mode, they do not produce the instability assumed by the displacive model.

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