

EXAFS Study of Disorder in SrTiO₃ Perovskite

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Abstract. Ti K-edge EXAFS spectra of SrTiO₃ at room temperature and at N₂ boiling point are measured to detect the Ti ion displacement above and below the antiferrodistortive phase transition occurring at $T_c = 105$ K. The data yield a definite value of the displacement, only slightly dependent on the temperature. The sensitive dependence of the amplitude of Ti-O-Ti focusing paths on the scattering angle is used to infer the correlation of Ti displacements. A preference to alternating displacements is indicated.

Keywords: Ti displacement in SrTiO₃ perovskite, displacive/order-disorder transition, Ti K-edge EXAFS

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INTRODUCTION

The cubic to tetragonal antiferrodistortive phase transition at 105 K in SrTiO₃ is associated with the condensation of a nonpolar soft mode at the Brillouin zone boundary [1]. The low-temperature phase with polar order is suppressed by zero-point quantum fluctuations of the soft mode [2], in contrast to BaTiO₃ where such a transition takes place at 410 K. Ferroelectric phase transitions in perovskites are generally considered to be classical examples of displacive soft mode type transitions. The transition type is confirmed by inelastic neutron scattering measurements. However, electron paramagnetic resonance measurements on doped crystals reveal a strong anharmonicity of the local potential of Ti ions, suggestive of an order-disorder transition, with Ti-ions hopping among the $\langle 111 \rangle$ off-center sites. The question is whether the potential in the cubic phase exhibits a minimum at the center of the oxygen cage or whether Ti ion is disordered between several off-center sites [Fig. 1]. Recent NMR studies performed in BaTiO₃, SrTiO₃, and SrTi₁₈O₃ [3,4] support the existence of dynamic disorder of the Ti ions in the cubic paraelectric phase. However, the ambiguity whether the observed tetragonal distortions are of the displacive type with static Ti displacements along the $\langle 100 \rangle$ directions or of the order-disorder type with biased averaging among the $\langle 111 \rangle$ displacements could not be resolved.

The question can be elucidated by EXAFS which, with its fast dynamics, represents a momentary snapshot of the ion positions. In an attempt to detect the distortions we measured Ti K-edge EXAFS spectra of SrTiO₃ at room temperature and at the temperature of liquid nitrogen, well below the temperature of the phase transition.

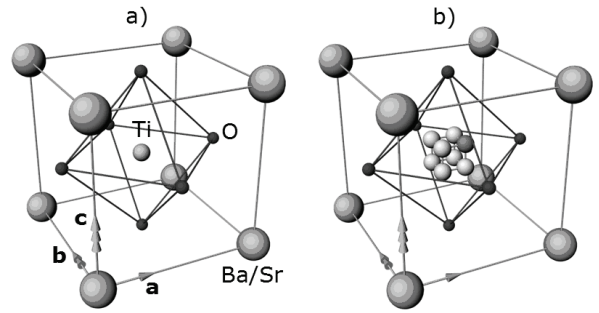


FIGURE 1. Possible titanium ion positions, compatible with the O_h symmetry in the paraelectric phase of SrTiO₃: a) static Ti at the ideal position in the center of the unit cell, b) Ti disordered among eight off-center displacements along the eight $\langle 111 \rangle$ directions. Ti shifts are shown greatly exaggerated.

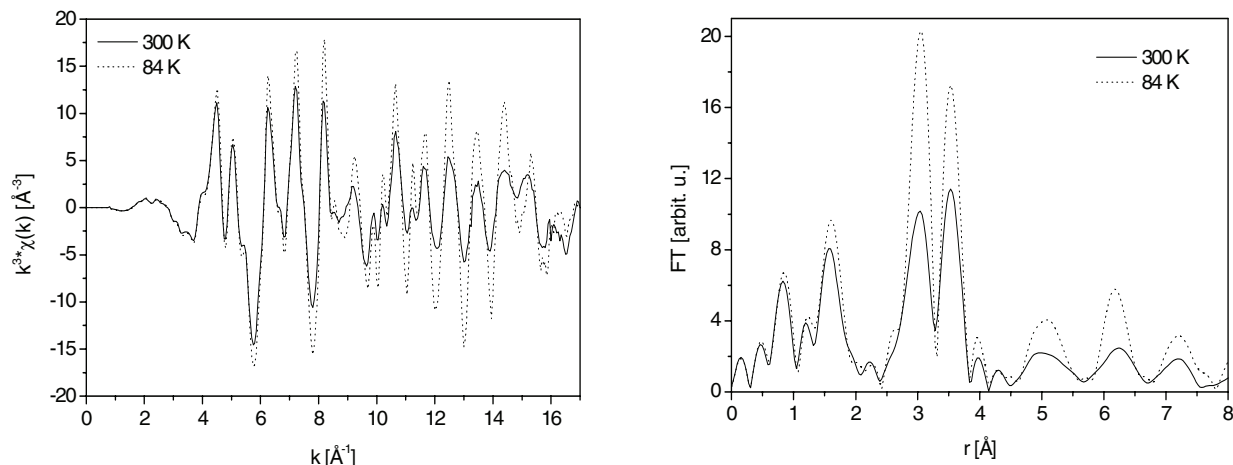


FIGURE 2. Ti K-edge EXAFS of SrTiO₃ at 300 K and 84 K in k-space (left), and its Fourier transform (right).

EXPERIMENT

Ti absorption spectra were measured at the XAFS (BL 11.1) beamline of ELETTRA, Trieste. The storage ring operated in multibunch mode at electron energy of 2.0 GeV and a current of about 300 mA. A double-crystal Si(111) monochromator with 0.8 eV resolution at the Ti K-edge (4966 eV) was used. A scanning interval [-250 eV .. 1600 eV] relative to the edge was adopted, with steps of 0.3 eV in the edge region and 2 eV outside. Several consecutive runs with integration time of 2 s per step were averaged to improve the signal-to-noise ratio. Precise energy calibration of the monochromator was maintained by interposed absorption scans on Ti metal foil.

As a sample, finely ground SrTiO₃ (3.1 mg/cm²) was mixed with boron nitride powder (16 mg/cm²) and pressed into self-supported pellets with the optimum absorption thickness of about 2 μm above the absorption edge. The sample was placed between ionization chambers, filled with gas mixtures of 200 mbar N₂/1800 mbar He and 1100 mbar N₂/900 mbar He.

RESULTS

The Ti K-edge spectra of SrTiO₃ at both temperature points extend to $k = 17 \text{ \AA}^{-1}$ without appreciable noise (Fig. 2). The first peak in the Fourier-transformed EXAFS signals, the fingerprint of the oxygen octahedron with a mean Ti-O distance of 1.95 Å, is expected to show the effect of the Ti displacement most directly. However, the strong second peak due to the eight Sr neighbors at the distance of 3.38 Å, with a clearly exposed low-R flank to enable precise shape modeling, offers another possibility. The third peak is due to Ti atoms in

adjacent unit cells at the distance of 3.90 Å, with strong contributions of focusing from the linear Ti-O-Ti paths. These contributions are conspicuously stronger in the room-temperature signal.

EXAFS analysis was performed with the IFEFFIT code [5]. The basic FEFF6 [6,7] model of the undistorted SrTiO₃ structure (cubic $Pm\bar{3}m$) [8] involved, within 4 Å, three single-scattering paths for the three nearest neighbor shells, and six multiple scattering paths. In the distorted-crystal model the central Ti atom was displaced in either the (001) or (111) directions, whereby the number of scattering paths is effectively tripled. An iterative relaxation to the best fit with the experimental data yielded displacement magnitudes of ~0.08 Å in both cases, with almost identical fits in the [1.3 Å .. 4 Å] interval. The value for the displacement was practically the same for both temperature points. Apparently, EXAFS signal does not, in the first order of perturbation, depend on the displacement vector, only on its magnitude.

The focusing properties of the Ti-O-Ti scattering paths are sensitively dependent on the Ti displacement. Our FEFF model only shifts the central Ti atom, while the other atoms remain at unshifted cubic positions. In the real crystal with all Ti atoms displaced, however, the focusing can be either stronger or weaker than in the model, depending on the correlation of Ti displacements. A variable factor F in the amplitude of the focusing paths is introduced in the model to account for the effect, in addition to standard variable *feffit* parameters. Of these, common values of the amplitude reduction factor and zero energy are used for data at both temperature points. Separate sets

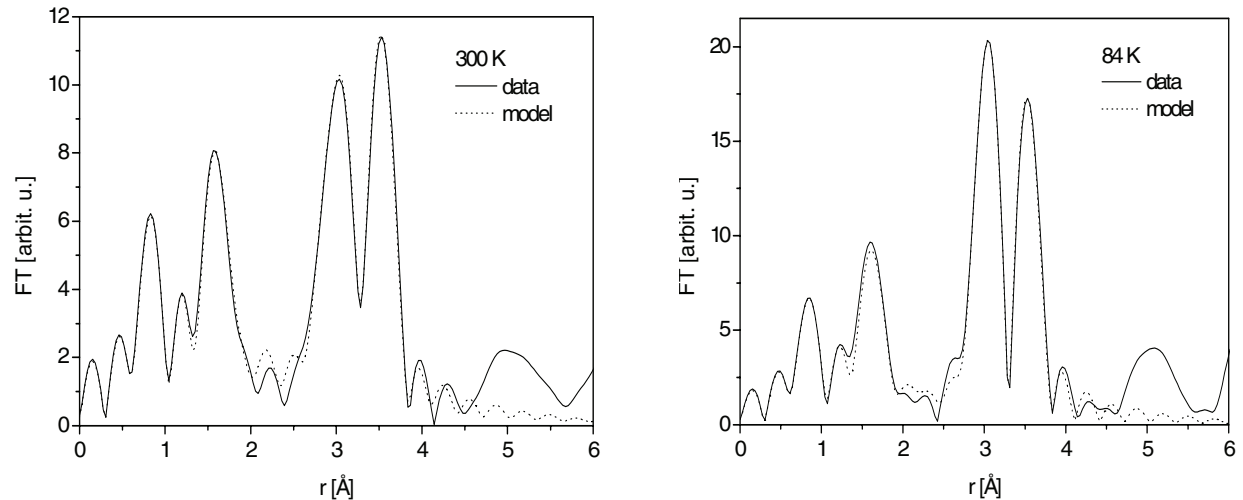


FIGURE 3. Best fit of Ti K-edge EXAFS using k -interval of $[5.5 \text{ \AA}^{-1} .. 15.5 \text{ \AA}^{-1}]$ and k^3 weight at room temperature (left) and at 84 K (right).

of parameters are employed for the single expansion coefficient for all paths, a small local correction to the Ti displacement, and three separate Debye-Waller widths for the three neighbor shells.

In the simultaneous fit of EXAFS signals of both temperature points, a nearly perfect fit (r -factor of 0.008) of the data up to and beyond $4.0 \text{ \AA}$ is obtained, using the k -interval of $[5.5 \text{ \AA}^{-1} .. 15.5 \text{ \AA}^{-1}]$ and exploiting the Artemis option of relaxation of background spline parameters [5] (Fig. 3). In spite of high correlation (0.95) with Ti displacement, Debye-Waller factors remain within reasonable limits, e.g. $0.0021(8) \text{ \AA}^2$ at 300 K and $0.0016(4) \text{ \AA}^2$ at 84 K for the first neighbor shell.

CONCLUSION

EXAFS cannot distinguish between different Ti displacement vectors, so the basic ambiguity remains. However, the magnitude of the Ti ion displacement is determined independently as $0.08(1) \text{ \AA}$ at 300 K, and $0.072(4) \text{ \AA}$ at 84 K, in accord with the NMR finding of displacements persisting above T_c . The obtained value of $1.13(10)$ for the focusing factor F points to a tendency of the alternating displacements in adjacent Ti ions.

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