

Limitations on the extent of off-center displacements in TbMnO_3 from EXAFS measurements

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We present extended x-ray-absorption fine structure (EXAFS) data at the Mn K and Tb L_3 edges that provide upper limits on the possible displacements of any atoms in TbMnO_3 . The displacements must be less than 0.005–0.01 Å for all atoms, which eliminates the possibility of moderate distortions (0.02 Å) with a small c -axis component, but for which the displacements in the ab plane average to zero. Assuming the polarization arises from a displacement of the O2 atoms along the c axis, the measured polarization then leads to an O2 displacement that is at least 6×10^{-4} Å, well below our experimental limit. Thus, a combination of the EXAFS and the measured electrical polarization indicate that the atomic displacements likely lie in the range 6×10^{-4} – 5×10^{-3} Å.

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I. INTRODUCTION

Multiferroics have been an area of intense investigation in recent years. In such systems, two or more orderings occur; in the case of TbMnO_3 , which we discuss here, both antiferromagnetism and ferroelectricity coexist at low T , and large magnetoelectric effects are observed.^{1,2} For ferroelectricity to occur, inversion symmetry must be broken, and there should be displacements of some of the atoms in each unit cell to form an electric dipole moment per cell; such a transition is called a displacive transition. Alternatively, inversion symmetry might already be broken locally with some atoms displaced slightly off-center—perhaps at the Néel temperature T_N . Then at temperatures above the ferroelectric transition temperature T_c , the off-center displacement orientation is random, no net polarization occurs, and, on average, the center of positive charge is not displaced relative to the center of negative charge. For such systems, the ferroelectric transition is called an order-disorder transition; here, there is no change in the magnitude of the local disorder at the nearest neighbor level, only an ordering of the off-center displacement directions to form a net dipole moment.

To date, the distortions that lead to ferroelectricity have not been identified in TbMnO_3 although Kimura *et al.*¹ suggested that it is likely the O atoms that are displaced. Some studies suggest that there is a variation in the buckling of the Mn-O-Mn linkage that is correlated with the antiferromagnetic coupling.³ In that model, there will be O displacements in different directions—only when the antiferromagnetic order becomes commensurate with the lattice does it lead to a net displacement along some axis and to ferroelectricity.

The net magnitude of the displacement must be small based on the measured c -axis ferroelectric polarization,¹ $P \sim 800 \mu\text{C}/\text{m}^2$. This value of P corresponds to a dipole moment in each unit cell (volume $\sim 229 \text{ \AA}^3$) of approximately $0.01 e\text{ \AA}$ ($1 e\text{ \AA}$ is a charge of one electron displaced 1 Å). Thus, if there is one electron charge displaced along the c axis, it is only displaced by about 0.01 Å. If the displaced atoms also have displacement components along the a or b axis (which average to zero), the total local displacements can be much larger. Similarly, if the charge of the displaced atom is larger than e or only a fraction of a charge, the

displacement will be correspondingly smaller or larger.

In this Brief Report, we address the local ferroelectric distortions in TbMnO_3 and place upper limits on the magnitude of the atomic displacements from extended x-ray-absorption fine structure (EXAFS) measurements. If there are moderately large displacements of some atoms but only a small net component along the c axis, it will produce a series of long and short bond lengths which will broaden the pair distribution functions and show up as an amplitude change in the transmission EXAFS. We will show using difference data that the changes in local distortions are very small and this rules out significant displacements ($>0.01 \text{ \AA}$) of any atoms if the transition is displacive.

II. EXPERIMENTAL DETAILS AND EXTENDED X-RAY-ABSORPTION FINE STRUCTURE DATA

A powdered sample and a small single crystal of TbMnO_3 were provided by Kimura. The powdered sample of TbMnO_3 was prepared by the solid state reaction. Powders of Tb_4O_7 and Mn_2O_3 were weighed to the prescribed ratios, mixed, and well ground. The mixture was heated at 1200 °C in air for 16 h. After grinding, it was reheated at 1350 °C for 24 h. A measurement of the powder x-ray diffraction revealed that the resultant powder is of single phase with the $Pbnm$ orthorhombic structure at room temperature. A single crystal of TbMnO_3 was grown by the floating zone technique, as previously described.² The crystal was oriented using Laue x-ray diffraction and patterns, and cut into thin plates with the widest faces perpendicular to the crystallographic principal axes.

EXAFS data were collected in 2005 (run 1) at the Mn K and Tb L_3 edges for a powdered sample in transmission mode on Beamline 10-2 at SSRL using a Si 111 monochromator in focused mode; the slit height was 0.7 mm and the energy resolution was about 2 eV. For these data, changes in the spectra with T were very small as T increased through the ferroelectric transition temperature T_c . Some polarized EXAFS data (along the c axis and perpendicular to the c axis) were later collected at NSLS in fluorescence mode, but the signal-to-noise ratio was lower (in part due to small Bragg

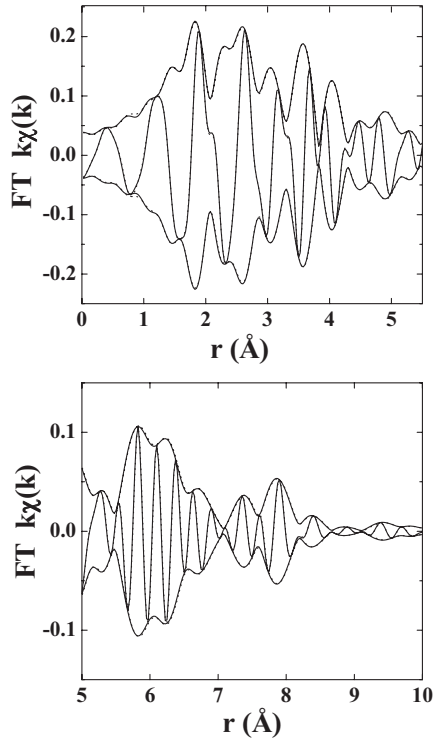


FIG. 1. Tb L_3 -edge Fourier transform data for TbMnO_3 ; k range, 3.5–12.8 \AA^{-1} with a Gaussian rounding of 0.3 \AA^{-1} . Solid line, run 2; dotted line, run 1. Top is from 0 to 5.5 \AA ; bottom from 5 to 10 \AA (note different y scales). Even for the higher range in r , the data overlap so well that it is difficult to see both lines. This shows the high reproducibility of the data. The fast oscillation in this figure and in subsequent r -space plots is the real part of the FT, R , while the envelopes at the top and bottom are $\pm\sqrt{I^2+R^2}$, where I is the imaginary part of the FT.

peaks from the sample) and limits on changes in amplitude were poorer than for the powder transmission data. To improve the transmission data and check reproducibility, a second transmission data set was collected at SSRL in 2006 (run 2) on Beamline 10-2 using the same monochromator. Again, there was no obvious change in the EXAFS plots as T increased through T_c . Note that the powder data are sensitive to displacements in all directions.

To improve the signal-to-noise ratio, we next averaged the data in three groups for each run: Group G1, temperatures below T_c (27 K); G2, between the Néel temperature T_N (42 K) and T_c ; and G3, above T_N , between 42 and 50 K. The number of files averaged was generally between 3 and 6. In Fig. 1, we show the averaged Tb Fourier transform (FT) data (L_3 edge) at low $T < 27$ K, collected in runs 1 and 2. In this figure, the reproducibility of the data is so good that the difference between the two data sets is not visible all the way to 10 \AA . On this plot, several Tb-O peaks occur from 1.8 to 2.0 \AA , Tb-Mn peaks occur from 2.5 to 3.0 \AA , and the nearest Tb-Tb peaks occur near 3.5 \AA (note these are peak positions in the EXAFS spectra which have a shift from the actual bond length). Above about 3.5 \AA , there is increasing overlap between Tb-O, Tb-Mn, and Tb-Tb peaks, and the peaks cannot be assigned to specific pairs without a detailed fit.

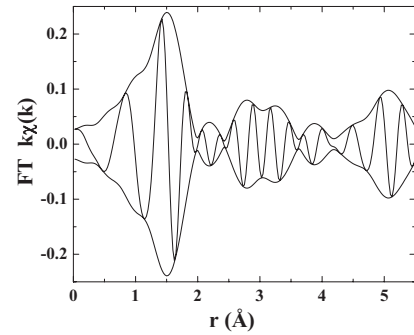


FIG. 2. The Mn K -edge r -space data for run 2; the data for run 1 are similar. The FT range is 4–12.5 \AA^{-1} with a Gaussian rounding of 0.3 \AA^{-1} .

In Fig. 2, we show the corresponding averaged data from run 2 at low T ($T < 27$ K) for the Mn K edge. Here, the Mn-O peaks occur near 1.5 \AA and the Mn-Tb peaks from 2.7 to 3 \AA ; the first Mn-Mn peaks occur near 3.4 and 3.6 \AA . Again, above 3.5 \AA , the peaks are a mixture of Mn-O, Mn-Tb, and Mn-Mn peaks, and not easily assigned to specific atom pairs.

III. ANALYSIS

To explore the magnitude of any ferroelectrically induced local structure changes as the temperature increases through T_c , we have subtracted the averaged data G1 (below T_c) from the averaged data G2 (between T_c and T_N). In Fig. 3, we plot and compare this difference at the Tb L_3 edge for both experimental runs. The difference is very small for both cases and is $\sim 1\%$ of the magnitude of the original data—compare y scales in Figs. 1 and 3. (Note that differences below $r \sim 1.0$ \AA are not real as this is where small errors in determining the background show up.) The small magnitude of the difference shows the high reproducibility of the data and

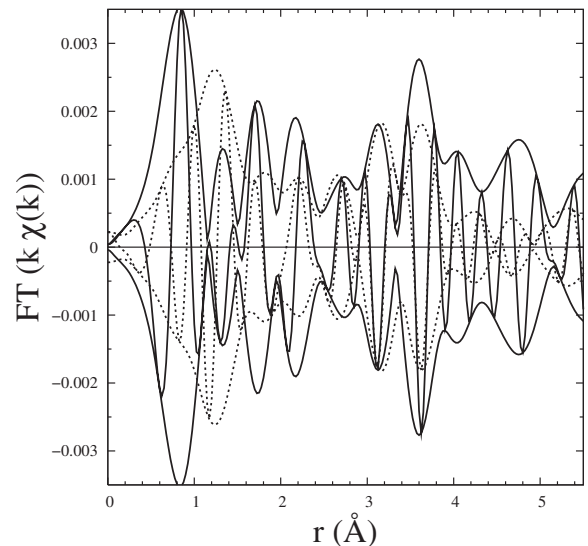


FIG. 3. The difference data G2-G1 at the Tb L_3 edge. Solid line, run 1; dotted lines, run 2. The difference for both runs is about 1% of the magnitude shown in Fig. 1.

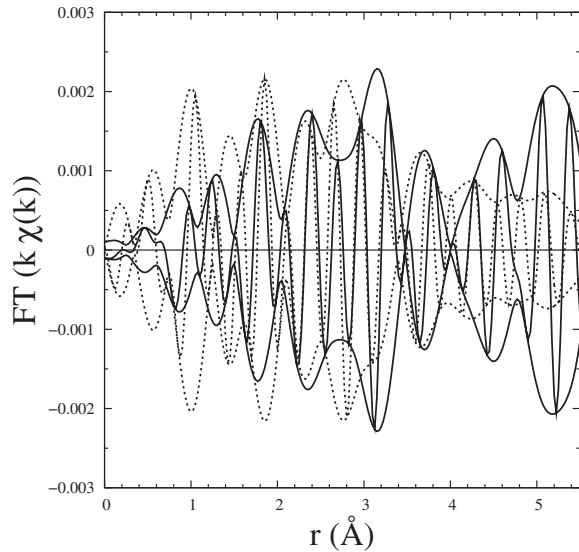


FIG. 4. The difference data G2-G1 at the Mn K edge. Solid line, run 1; dotted lines, run 2. Here, the difference is slightly smaller than for Tb, but, again, by about 1%–2% of the original data (Fig. 2).

indicates that displacements of Mn or O relative to a Tb atom are very small. A further requirement for a real distortion is that the phase of the real part R of the Fourier transform difference data for the two experimental runs must be the same—over much of the r range, they are not. Only in a few places does the phase for the two runs agree (near 3 Å, the Tb-Mn peaks, and near 1.9 Å, the Tb-O peaks). These would be the only places where the difference data might suggest a real lattice distortion.

A similar result is obtained for the Mn K -edge difference data plotted in Fig. 4. Again, the difference is comparable for both runs and is about 1%–2% of the magnitude of the original data, indicating at most very tiny changes in the local distortions about the Mn atom as the sample becomes ferroelectric. Again, the phase of the real part R of the transform varies for the two runs—only near 3 Å, the Mn-Tb peaks, does the phase suggest a possible real effect. For both edges, the difference is near the reproducibility level, and smaller differences would be difficult to obtain. From a consideration of the phases, there may be a small change in the Tb-Mn, Mn-Tb distances or in the Tb-O distances.

Another comparison can be made across the Néel temperature T_N —if the magnetic coupling causes a distortion of the Mn-O-Mn buckling angle that depends on whether the Mn spins locally are parallel or antiparallel, similar to that proposed by Aliouane *et al.* when a field is applied along the b axis,³ a small off-center O distortion might then first appear at T_N but be randomly oriented for $T > T_c$; however, it would produce longer and shorter bonds and show up in the EXAFS data at T_N . In that case, there would be no change in the local distortions across T_c (same numbers of long and short bonds); instead, there would be an ordering of the off-center displacements. To look for changes in the local distortions at T_N , we calculated difference data G3-G2 (above and below T_N) for both edges and for both experimental runs; the calculations yield plots with slightly smaller amplitudes than in

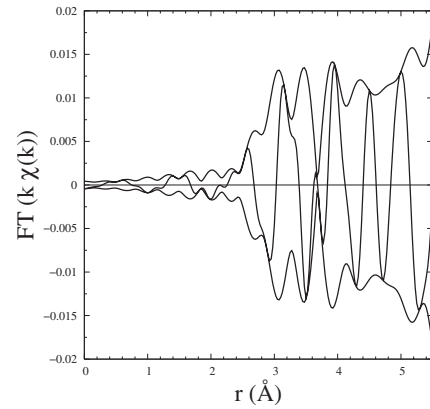


FIG. 5. The theoretical difference plots for a displacement of Tb by 0.01 Å along the c axis relative to the rest of the unit cell. The difference is much larger than observed experimentally for the metal-metal atom pairs (above 2.8 Å) but comparable to the amplitude for r close to the Tb-O distances.

Figs. 3 and 4, and are not plotted. These results show no evidence for a significant distortion appearing at T_N .

The above plots show that across T_c there is very little change in the EXAFS spectra. To place limits on the possible distortions, we need to calculate how much the spectra should change for various small displacements of different neighbor atoms. In Fig. 5, we plot the theoretical difference for a displacement of the Tb atoms by 0.01 Å relative to the rest of the unit cell. Here, we have used $\sigma^2 = 0.0025 \text{ \AA}^2$ to include thermal broadening (zero-point motion) effects. The difference data do not change much for increases in σ^2 for this edge or for the Mn edge discussed below. Comparing this plot with Fig. 3 immediately gives the result that any displacements of Tb relative to Mn/O must be much smaller than 0.01 Å (likely $< 0.005 \text{ \AA}$). For the Tb edge, a c -axis displacement of the O1 atoms would not change the Tb-O1 bond length significantly. However, unlike the Mn K -edge data discussed below, the Tb-O2 distribution is sensitive to displacements of Tb along the c axis relative to the unit cell, or conversely, c -axis displacements of the O2 in the unit cell. In addition, it should be noted that the Mn-O2-Mn linkage is not in the ab plane but lies in a plane that is roughly 55° from the c axis. If this plane rotates slightly, the O2 moves toward one Tb atom and away from another; then the projection in the ab plane produces a buckling of the (in-plane) Mn-O-Mn group that increases or decreases depending on the sign of the rotation angle $\delta\theta$ (see Fig. 6). Such rotations (equal numbers of $\pm\delta\theta$) would not have any net polarization along the a and b axes, but would produce a net O2 displacement along the c axis. A 0.01 Å O2 (rotation) displacement of this type was also tried and gave a similar magnitude in the difference calculation near 2.2 Å, obtained by displacing the Tb relative to the unit cell; however, the phase does not agree well with the experimental data, suggesting a 0.01 Å displacement is too large.

In Fig. 7, we plot the corresponding theoretical difference for a Mn atom displacement of 0.01 Å relative to the rest of the unit cell; again, we have used $\sigma^2 = 0.0025 \text{ \AA}^2$. Comparing this plot with Fig. 4 immediately shows that any displacements of Mn relative to Tb/O must also be much smaller

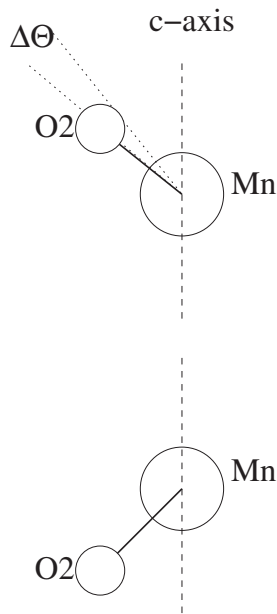


FIG. 6. A sketch of the Mn-O2-Mn linkage viewed along the Mn-O-Mn chains (the x axis in a pseudocubic perovskite unit cell); the second Mn atom is behind the first one. The O2 atoms are displaced above or below the xy plane such that the angle between the c axis and the plane containing the Mn-O-Mn linkage is about 55° . A rotation of the plane of the Mn-O2-Mn linkage that produces a positive c -axis displacement ($\Delta\theta$ in figure) generates both positive and negative a, b -axis displacements which would lead to zero polarization along the a or b axis.

than 0.01 \AA . For the Mn-O neighbors, the main Mn-O peak is at 1.5 \AA . In the theoretical difference data for shifted Mn atoms, the amplitude is comparable to that in the experimental difference data, so a 0.01 \AA displacement of O relative to Mn is not ruled out from the magnitude of the Mn K -edge difference results. However, the shape and phase differ considerably between the two runs, suggesting a much smaller change of Mn-O bonds than 0.01 \AA . Note that for Mn-O, only the O1 atoms along the c axis produce a significant change for a c -axis displacement of Mn; the Mn-O distances for O2 atoms (which are roughly in the ab plane) change little for a c -axis displacement of Mn.

Finally, we return to the magnitude of the dipole moment per unit cell inferred from the polarization and consider that it is caused by a c -axis displacement of only the O2 atoms. In the unit cell, there are four formula units, which means eight O2 atoms (charge -2) per cell. If all are displaced by the same amount, then the net dipole moment for the cell is $8 \times (2e) \times \delta r = 0.01 e \text{ \AA}$. This would infer a tiny displacement

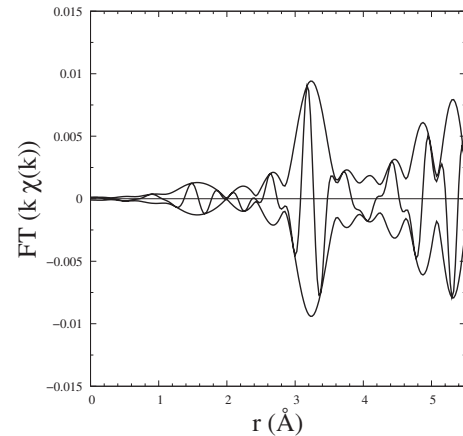


FIG. 7. The theoretical difference plots for a displacement of Mn by 0.01 \AA along the c axis, relative to the rest of the unit cell. The difference is much larger than observed experimentally for the metal-metal atoms pairs (above 2.8 \AA), but comparable to the amplitude for r close to the Tb-O distances.

of $\delta r \sim 0.6 \times 10^{-3} \text{ \AA}$, which is well below the limits obtained from the above measurements. If not all the O2 atoms are displaced or the effective charge on the O2 ion is less than 2, then the displacement will be correspondingly larger. A similar estimate is obtained by displacing the metal atoms along the c axis, relative to the O atoms.

In summary, we show from difference EXAFS data that displacements of atoms must be at or below 0.005 \AA , which rules out larger displacements which have a and b components that average to zero. Assuming only O2 atom displacements along the c axis and a full, $-2e$ charge for this O atom, the needed displacement must be at least $6 \times 10^{-4} \text{ \AA}$; these results constrain $\delta r - 6 \times 10^{-4} \text{ \AA} < \delta r < 5 \times 10^{-3} \text{ \AA}$. At this level, one must also consider electronic contributions arising from changes in the distributions of charge on the various atoms.

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