Limitations on the extent of off-center displacements in TbMnO$_3$
from EXAFS measurements

F. Bridges,$^1$ C. Downs,$^1$ T. O’Brien,$^{1,2}$ Il-K Jeong,$^2$ and T. Kimura$^2$

$^1$Physics Department, University of California, Santa Cruz, California 95064, USA
$^2$Los Alamos National Laboratory, Los Alamos, NM 87545

(Dated: February 5, 2008)

Abstract

We present 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 0.005-0.01Å for all atoms which eliminates the possibility of moderate distortions (0.02Å) 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 6X10$^{-4}$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 6X10$^{-4}$ - 5X10$^{-3}$Å.

PACS numbers: 61.10.Ht,75.50.Cc,77.90.+k
I. INTRODUCTION

Multi-ferroics 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 co-exist at low T and large magnetoelectric effects are observed\cite{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 Neal 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 displacements 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\cite{1} suggest 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\cite{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 $P \sim 800 \mu $C/m$^2$. This value of $P$ corresponds to a dipole moment in each unit cell (volume $\sim 229$ Å$^3$) of approximately 0.01 eÅ (1 eÅ is a charge of 1 electron displaced 1 Å). Thus if there is one electron charge displaced along the $c$-axis, it is only displaced about 0.01Å. If the displaced atoms also have displacement components along the a- or b-axes (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 corresponding smaller or larger.

In this short paper we address the local ferroelectric distortions in TbMnO$_3$ and place upper limits on the magnitude of the atomic displacements from 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 PDF 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 (> 0.01Å) of any atoms if the transition is displacive.

II. EXPERIMENTAL DETAILS AND EXAFS 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\(_4\)O\(_7\) and Mn\(_2\)O\(_3\) were weighted to the prescribed ratios, mixed, and well ground. The mixture was heated at 1200 °C in air for 16 hours. After grinding, it was reheated at 1350 °C for 24 hours. 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 TbMnO3 was grown by the floating zone technique, as previously described. 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 (Run1) 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 (along the \( c \)-axis and perpendicular to the \( c \)-axis) were later collected at NSLS in fluorescence mode but the signal-to-noise was lower (in part due to small Bragg 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 we next averaged the data in three groups for each run: Group G1 - temperatures below \( T_c \) (27K), G2 - between the Neel temperature \( T_N \) (42K) and \( T_c \), and G3 - above \( T_N \), between 42 and 50K; the number of files averaged was generally
between 3 and 6. In Fig 1 we show the averaged Tb Fourier Transform (FT) data (L₃ edge) at low T < 27K, 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 10Å. On this plot several Tb-O peaks occur from 1.8-2.0Å, Tb-Mn peaks occur from 2.5-3.0Å, and the nearest Tb-Tb peaks occur near 3.5Å (note these are peak positions in the EXAFS spectra which have a shift from the actual bond length). Above about 3.5Å there is increasing overlap between Tb-O, Tb-Mn and Tb-Tb and the peaks cannot be assigned to specific pairs without a detailed fit.

In Fig 2 we show the corresponding averaged data from run 2 at low T (T < 27K) for the Mn K-edge. Here the Mn-O peaks occur near 1.5Å and the Mn-Tb peaks from 2.7-3Å; the first Mn-Mn peaks occur near 3.4 and 3.6Å. Again, above 3.5Å the peaks are a mixture of Mn-O, Mn-Tb and Mn-Mn 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 Tₑ, we have subtracted the averaged data G1 (below Tₑ) from the averaged data G2 (between Tₑ and Tₐ). In Fig. 3 we plot and compare this difference at the Tb L₃ edge for both experimental runs. The difference is very small for both cases and is ~ 1% of the magnitude of the original data - compare y-scales on Figs. 3 and 1. [Note that differences below r ~ 1.0Å 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 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 3Å - the Tb-Mn peaks, and near 2Å - 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
FIG. 1: Tb L₃-edge Fourier Transform data for TbMnO₃; k-range 3.5-12.8 Å⁻¹ with a Gaussian rounding of 0.3Å⁻¹. Solid line - Run 2, dotted line - Run 1. Top is from 0-5.5 Å, bottom from 5-10Å (note different y-scale). 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 envelops at the top and bottom are ± √I² + R² where I is the imaginary part of the FT.

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 Neel temperature Tₙ - if the magnetic
FIG. 2: The Mn K-edge r-space data for Run2; the data for run 1 are similar. The FT range is 4-12.5 Å\(^{-1}\) with a Gaussian rounding of 0.3Å\(^{-1}\).

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,\(^b\) 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 \(G_3-G_2\) (above and below \(T_N\)) for both edges and for both experimental runs; the calculations yield plots with slightly smaller amplitudes than in Figs. 3 or 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 neighbors atoms. In Fig. 5 we plot the theoretical difference for a displacement of the Tb atoms by 0.01Å relative to the rest of the unit cell. Here we have used \(\sigma^2 = 0.0025\)Å\(^2\) to include thermal broadening (zero-point-motion) effects. The difference data do not change much for increases in \(\sigma^2\) 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 0.01Å (likely < 0.005Å). For the Tb edge, a \(c\)-axis displacement of the O1 atoms would not
FIG. 3: The difference data G2-G1 at the Tb L₃-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 about 1-2% of the original data - Fig 2.

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 towards one
FIG. 5: The theoretical difference plots for a displacement of Tb by 0.01Å 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 Å) but comparable to the amplitude for r close to the Tb-O distances.

Tb atom and away from another; them 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 0.01Å O2 (rotation) displacement of this type was also tried and gave a similar magnitude in the difference calculation near 2.2Å as obtained by displacing the Tb relative to the unit cell; however the phase does not agree well with the experimental data suggesting a 0.01Å displacement is too large.

In Fig. 7 we plot the corresponding theoretical difference for a Mn atom displacement of 0.01Å relative to the rest of the unit cell; again we have used $\sigma^2 = 0.0025\AA^2$. Comparing this plot with Fig. 4 immediately shows that any displacements of Mn relative to Tb/O must also be much smaller than 0.01Å. For the Mn-O neighbors The main Mn-O peak is at 1.5Å; in the theoretical difference data for shifted Mn atoms, the amplitude is comparable to that in the experimental difference data - so a 0.01Å 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 considerable between the two runs suggesting a much smaller change of
FIG. 6: A sketch of the Mn-O2-Mn linkage viewed along the Mn-O-Mn chains (the x-axis in a pseudo-cubic 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 (Δθ in figure) generates both positive and negative a,b-axis displacements which would lead to zero polarization along the a- or b-axes.

Mn-O bonds than 0.01Å. Note, 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 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 the same amount, then the net dipole moment for the cell is $8 \times (2e) \times \delta r = 0.01 \epsilon \text{Å}$. This would infer a tiny displacement of $\delta r \sim 0.6 \times 10^{-3} \text{Å}$ 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 0.005Å 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
FIG. 7: The theoretical difference plots for a displacement of Mn by 0.01Å 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 2.8Å) but comparable to the amplitude for r close to the Tb-O distances.

charge for this O atom, the needed displacement must be at least $6 \times 10^{-4}$Å; these results constrain $\delta r - 6 \times 10^{-4}$Å $< \delta r < 5 \times 10^{-3}$Å. At this level one must also consider electronic contributions arising from changes in the distributions of charge on the various atoms.

Acknowledgments

The work at UCSC was partially supported by NSF grant DMR0301971. Work at Los Alamos was performed under the auspices of the US Department of Energy (DOE). The transmission EXAFS experiments were performed at Stanford Synchrotron Radiation laboratory (beamline 10-2), which is operated by the DOE, Division of Chemical Sciences, and by the NIH, Biomedical Resource Technology Program, Division of Research Resources. The polarized EXAFS were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory (beamline 19A), which was supported by the DOE, Office of Science,
1 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).
2 T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B 71, 224425 (2005).
3 N. Aliouane, D. N. Argyriou, J. Strempfer, I. Zegkinoglou, S. Landsgesell, and M.v. Zimmermann, Phys. Rev. B 73, 020102(R) (2006).