Local Structure of Magnetoresistive Oxides

Manganese-based magnetoresistive oxides are receiving increased attention be-cause they show promise in a wide variety of applications, particularly spin-based electronics, or "spintronics." The properties of magnetoresistive oxides depend sensitively on the structure of the MnO_6 octahedral building blocks that make up the crystal lattice. A deeper understanding of local structure—often studied using pair distribution function (PDF) analysis or x-ray absorption fine structure (XAFS)—is important because in many alloys it often differs from the average crystal structure probed by x-ray or neutron diffraction. Such diffraction studies have shown that in $LaMnO_3$, the four short and two long bonds of the MnO_6 octahedra exhibit a Jahn-Teller distortion that is removed by Sr doping ($La_{1-x}Sr_xMnO_3$). At an Sr composition of x ~0.175, no long-range Jahn-Teller distortion exists at room temperature in the average structure. Previous studies of the local MnO_6 structure used the PDF of $La_{1-x}Sr_xMnO_3$ (LMSO) as a function of x at 10K and near room temperature to show that the local MnO_6 structure does differ from the average structure. The lengths of both the short and long Mn-O bonds changed little until local distortion disappeared, possibly forming localized three-site polarons though additional work produced conflicting results.

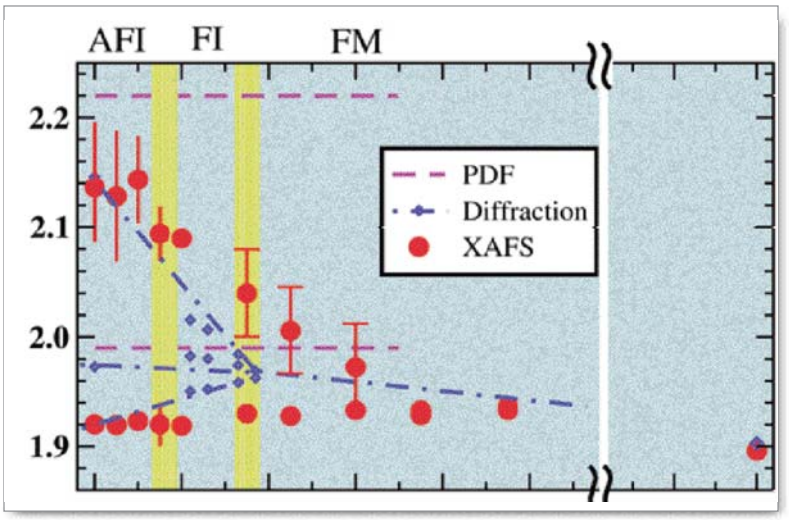

Fig. 1. Mn-O bond lengths as a function of x at 10K, Dots show low-temperature average structure from diffraction experiments. Hatched line is phase boundary: AFI (antiferromagnetic insulator), FI (ferromagnetic insulator), FM (ferromagnetic metal).

Using data collected at the MR-CAT 10-ID beamline at the APS, investigators from the University of Notre Dame and Argonne National Laboratory provided a more detailed picture of local structure by measuring Mn K-edge XAFS at T ≈ 10K and room temperature (290K) for various alloy compositions in the region x <0.475, thereby establishing the local MnO_6 structure as a function of x. They discovered some distortion in the metallic phase, where x varied between 0.175 and 0.3, but found the bond length-splitting to be substantially smaller than the PDF results and the local distortion of MnO_6 strongly correlated with the electronic phase diagram.

Samples for the Mn K-edge XAFS experiments were those previously used for La K-edge and Sr K-edge XAFS studies. The Mn K-edge XAFS spectra were measured at sample holder temperatures of T ≈ 10K and 290K in transmission mode at the MR-CAT beamline at the APS. Duplicate or triplicate measurement of each sample allowed a check on the repeatability and noise level of the spectra, and a Fourier transform was fit to a model built with theoretical scattering paths.

Several different fit methods were used to deal with parameter correlations among the Mn-O bond lengths, the Debye Waller Factor (DWF), and the population of short and long bonds. For example, the number of long bonds (N_L) and the DWF are strongly correlated. N_L was thus constrained according to four models among which N_L varied.

The first coordination shell carries six oxygen atoms with 8 La/Sr second neighbors and 6 third neighbors around Mn ions. A systematic edge-energy shift with Sr composition is consistent with the LSMO or other manganite systems, was observed. The long bond peak—a distinct feature for the $LaMnO_3$—appears in samples with low Sr doping and shifts with doping for x <0.175, nearly disappearing for x >0.175 (Fig. 1). The largest deviation from the PDF results exists in the low-x region (x <0.35). More detailed examination of these parameters shows either the absence of the bond at distances above 2.08 Å or a large length distribution, suggesting a maximum possible long bond length of about 2.08 Å, much shorter than that of $LaMnO_3$ (2.15 Å) or PDF results (2.22 Å). Room temperature results were similar to those at low temperature.

The finding that $LaMnO_3$ had three different bond lengths in average structure corroborates the previous PDF finding of three different bond lengths in local structure. The residual distortion found in the ferromagnetic metallic phase x >0.175 is less than the PDF results. The XAFS results suggest that the structure does change with doping. Taken together, the data allow a detailed view of the Mn-O bonds. m

See: T. Shibata[1], B.A. Bunker[1], and J.F. Mitchell[2], "Local distortion of MnO_6 clusters in the metallic phase of $La_{1-x}Sr_xMnO_3$," Phys. Rev. B **68**, 024103-024112 (2003).

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