# Spectroscopic Detection of Double Exchange Magnetism Signatures in Mn L<sub>2,3</sub> and O-vacancy Spectra in La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> Alloys with x = 0.2

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## 1. Introduction

La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> alloys display insulator to metal (I-M) and ferromagnetic transitions at the x = 0.2 composition [1]. These transitions satisfy criteria for a double exchange mechanism for ferromagnetism associated with changes in mixed valence Mn 3d-states. This derives from delocalization of a d-electron contributing to a metallic conductivity.[1-3] This transition involves transfer of one d<sup>4</sup> 3d electron into a half-filed eg band. All Mn sites in the x = 0.2 alloy then have an equivalent d<sup>3</sup> occupation corresponding to Mn<sup>4+</sup>. LaMnO<sub>3</sub> has a d<sup>4</sup> electron occupancy in Mn<sup>3+</sup> sites. These differences in Mn d-state occupancy are the basis for spectroscopic detection of the double exchange mechanism as (i) an increase of the width of the Mn L<sub>2,3</sub> spectrum in the x = 0.2 alloy [4], and (ii) a doubling of the number of O-vacancy negative ion states [5].

# 2. Experimental Methods

Epitaxial La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> films 20 nm thick have been deposited by reactive evaporation onto (La,Sr)(Al,Ta)O<sub>3</sub> (111) substrates with substrate alloy content matched to deposited film lattice constants. LaMnO<sub>3</sub> (x = 0.0), and the x = 0.1 alloys are insulating, and alloys including the x = 0.2 and higher composition display metallic conductivity. The resistivity dropped by 2 orders of magnitude between the x = 0.0 and 0.1 insulating films and the x = 0.2 film, and by 3 orders of magnitude in films with higher Sr content extending to x = 0.6.

# 3. X-ray Spectra and Data Reduction

Figure 1 displays the 2nd derivative Mn  $L_{2,3}$  spectrum for LaMnO<sub>3</sub>. The Mn  $L_{2,3}$  transition for trivalent  $Mn^{3+}$  is from an occupied Mn d<sup>4</sup> state and Mn spin-orbit split 2p core states, and represented using charge transfer multiplet (CTM) theory [3,4] by  $2p^{6}3d^{4}$  to  $2p^{5}3d^{5}$ , equivalently from a <sup>5</sup>D<sub>4</sub> term to a <sup>7</sup>P<sub>4</sub> term. Based on Table 4.8 in Ref. 6, there are nine triply degenerate <sup>5</sup>D<sub>4</sub> to <sup>7</sup>P<sub>4</sub> terms that apply. Five in the L<sub>3</sub> regime with <sup>5</sup>F symmetry and J = 1 to 5, and four in the L<sub>2</sub> regime with <sup>5</sup>P symmetry and J = 1 to 4. After the three-fold degeneracy is removed by final state effects in the intermediate strength ligand field, 15 features are predicted in the L<sub>3</sub> regime, and 12 in the L<sub>2</sub> regime [6].

The 2nd derivative Mn  $L_{2,3}$  spectrum for LaMnO<sub>3</sub> in Fig. 1 contains the predicted 27 features, each marked with arrows. The total spectral width is 15.2±0.2 eV with spectral widths in the L<sub>3</sub> and L<sub>2</sub> regimes equal to, ~7.8 eV and ~6.4 eV, and with a 1.0 eV gap in between. The total width with is significantly larger than the ligand field splitting,  $\Delta_{LF} = 2.5\pm0.2$  eV,[1] and the spin-orbit splitting of the Mn

2p states,  $\Delta_{\text{SPIN ORBIT}} \sim 11.2 \pm 0.2 \text{ eV}$  [1]. It is not possible to extract the  $\Delta_{\text{LF}}$  from this spectrum. Instead the ligand field splitting is obtained from the spectral width of O-vacancy transitions in O K pre-edge spectra in Fig. 4  $\Delta_{\text{LF}}$  is determined from spectral widths of singlet and triplet terms in Tanabe-Sugano plots, but excluding negative ion states [7].

Figure 2 displays the Mn  $L_{2,3}$  spectra for the alloy x = 0.2, La  $_{0.8}$ Sr  $_{0.2}$ MnO<sub>3</sub>, at the I-M transition. This spectrum has the same number of features as in Fig. 1, 15 in the L<sub>3</sub> regime, and 12 in the L<sub>2</sub> regime. Similar spectra, not shown, are obtained for other compositions within the metallic regime. The total spectral width in Fig. 2 is increased by 1 eV from 15.2 eV to 16.2 eV with respect to Fig. 1, L<sub>3</sub> and L<sub>2</sub> spectral widths are increased to ~8.2 eV, and ~7.6 eV, respectively. Based on charge transfer associated with the double exchange mechanism the increased spectral width in the x = 0.2 alloy is consistent with an effective d<sup>3</sup> Mn occupancy.

Figure 3 is a plot of the 2nd derivative O K edge spectrum in the spectral regime at the conduction band regime between ~529 eV and 545 eV. An energy of 537.5 eV divides the features between those derived from the  $L_3$  and  $L_2$  portions of the Mn  $L_{2,3}$  spectrum. This correlation between has been addressed in Ref. 8 for nano-grain ZrO<sub>2</sub>. The spectral width of the conduction band features,  $13.3\pm0.2$  eV, smaller than the spectral width of the Mn  $L_{2,3}$  spectrum,  $15.2\pm0.2$  eV, similar to ZrO<sub>2</sub> comparisons in Ref. 8.

Figure 4 displays the O K pre-edge spectrum for the x = 0 LaMnO<sub>3</sub> alloy, and the x = 0.2 alloy as well. Each spectrum displays nine triplet to triplet transitions with a spectral width of  $2.5\pm0.1$  eV equal to the Mn  $\Delta_{LF}$  in an intermediate strength ligand field. This follows directly from the Tanabe-Sugano diagrams for d-state multiplet transitions. Next, starting at the lowest eV singlet feature at ~525 to 526 eV, the first five singlet features, extending to about ~ 528.5 eV and below the negative ion states have transition energies have a spectral width also equal to the Mn  $\Delta_{LF}$ . The  $\Delta_{LF}$  values reflect the average properties of the Mn 3d orbitals directed into the vacated O-atom site, and are not formal charge state dependent [5].

Finally, the terms labeled as negative ion states at X-ray energies >529 eV are Mn charge state specific, rather than averages over Mn 3d states bordering on the vacancy [5]. Two negative ion states are expected from Tanabe-Sugano diagrams in which all Mn atoms are equivalent [7]. This is what is observed for LaMnO<sub>3</sub> in which Mn ions have the same Mn<sup>3+</sup> formal charge state. In contrast, the O pre-edge



Fig. 3. Second derivative O K edge spectrum for LaMnO3.

for the x = 0.2 alloy has four negative ion states, or equivalently two pair of negative ion states. Consistent with the



double exchange mechanism, these four negative ion states are associated with two different charge states of Mn,  $Mn^{3+}$  and  $Mn^{4+}$ , rather than their respective d<sup>3</sup> occupancies.

#### 4. Summary

The insulator to metal transition, accompanied by ferromagnetism, in  $La_{1-x}Sr_xMnO_3$  alloys for x = 0.2 is attributed to a double exchange mechanism. This electron delocallization pathway to ferromagnetism is associated with a metallic hopping conductivity that requires all of Mn sites in the x = 0.2 alloy have an equivalent d<sup>3</sup> electron occupancy, even though they have different formal charge states,  $Mn^{3+}$  and  $Mn^{4+}$ . The  $Mn^{3+}$  ions in  $LaMnO_3$  have a d<sup>4</sup> occupancy. This difference between the x = 0.0 and 0.2 formal charge states results in two different distinguishing spectroscopic signatures. These are an increase of the spectral width in the Mn  $L_{2,3}$  spectrum from  $15.2\pm0.2$  eV in  $LaMnO_3$  to  $16.0\pm0.2$  eV in  $La_{0.8}Sr_{0.2}MnO_3$ , and a doubling of the number of negative ion states in O K pre-edge O-vacancy energy regime.

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