Spectroscopic Detection of Double Exchange Magnetism Signatures in Mn L2,3 and O-vacancy Spectra in La1-xSrₓMnO₃ Alloys with x = 0.2

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1. Introduction

La₁₋ₓSrₓMnO₃ 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 d² 3d electron into a half-filled eg band. All Mn sites in the x = 0.2 alloy then have an equivalent d occupation corresponding to Mn³⁺. LaMnO₃ has a d⁴ electron occupancy in Mn³⁺ 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 L₂,3 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 La₁₋ₓSrₓMnO₃ films 20 nm thick have been deposited by reactive evaporation onto (La,Sr)(Al,Ta)O₃ (111) substrates with substrate alloy content matched to deposited film lattice constants. LaMnO₃ (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 0.2 and higher composition display metallic conductivity. x = 0.1 alloys are insulating, and alloys including the x = 0.2 alloy as well. Each spectrum displays nine triplet to triplet transitions with a spectral width of the Mn L₂,3 spectrum in the x = 0.2 alloy [4], and the x = 0.1 insulating films and the x = 0.2 film, provides the features between those derived from the L₃ and L₂ portions of the Mn L₂,3 spectrum. This correlation between the x = 0.2 alloy is consistent with an effective d³ Mn occupancy.

3. X-ray Spectra and Data Reduction

Figure 1 displays the Mn L₂,3 spectra for the alloy x = 0.2, La₀.₉Sr₀.₁MnO₃, at the I-M transition. This spectrum has the same number of features as in Fig. 1, 15 in the L₃ regime, and 12 in the L₂ 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. L₃ and L₂ 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 d³ 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 L₁ and L₂ portions of the Mn L₂,3 spectrum. This correlation has been addressed in Ref. 8 for nano-grain ZrO₂. The spectral width of the conduction band features, 13.3±0.2 eV, smaller than the spectral width of the Mn L₂,3 spectrum, 15.2±0.2 eV, similar to ZrO₂ comparisons in Ref. 8.

Figure 4 displays the Mn L₂,3 spectrum for the alloy x = 0.2 LaMnO₃ and the x = 0.2 alloy as well. Each spectrum displays nine triplet to triplet transitions with a spectral width of 2.5±0.1 eV equal to the Mn Δₐₙ 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 Δₐₙ. The Δₐₙ 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 LaMnO₃ in which Mn ions have the same Mn³⁺ formal charge state. In contrast, the O pre-edge
L2 12 3A1g 1A1g 3T1g 2T2g 1T1g 3A1g 3A1g 3T1g 2T2g 1T1g

2nd derivative absorption

Fig. 1. Second derivative Mn L2,3 spectrum for LaMnO3.

L3 15
L2 12

2nd derivative absorption

Fig. 2. Second derivative Mn L2,3 spectrum for La0.8Sr0.2MnO3.

LaMnO3: O K edge

ΔL2,3 = 13.3+/-0.2 eV

gap ~0.5 eV

L3 15
L2 12

2nd derivative absorption

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

double exchange mechanism, these four negative ion states are associated with two different charge states of Mn, Mn3+ and Mn4+, rather than their respective d5 occupancies.

4. Summary

The insulator to metal transition, accompanied by ferromagnetism, in La1-xSrMnO3 alloys for x = 0.2 is attributed to a double exchange mechanism. This electron delocalization 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 d5 electron occupancy, even though they have different formal charge states, Mn3+ and Mn4+. The Mn3+ ions in LaMnO3 have a d5 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 L2,3 spectrum from 15.2±0.2 eV in LaMnO3 to 16.0±0.2 eV in La0.8Sr0.2MnO3, and a doubling of the number of negative ion states in O K pre-edge O-vacancy energy regime.

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References