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LAYERED CMR MANGANITES: STRUCTURE, PROPERTIES, AND UNCONVENTIONAL MAGNETISM

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ABSTRACT

Neutron powder diffraction studies of the layered compounds $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Nd$), $RSr_2Mn_2O_7$ ($R = Pr, Nd$), and $La_{1.4}Sr_{1.6}Mn_2O_7$ show that the degree of distortion of the MnO_6 octahedra do not correlate with the appearance of a metal-insulator (MI) transition in these compounds. Instead, the in-plane Mn-O bond length appears to be a better indicator of the electronic behavior. Detailed bulk magnetization studies on single crystal $La_{1.2}Sr_{1.8}Mn_2O_7$ show that there are three magnetic regimes as a function of temperature: paramagnetic insulator, short-range ordered (SRO) ferrromagnet, and long-range ordered (LRO) ferromagnet. Scaling analysis indicates that a 2D finite-size XY model is an appropriate description of the magnetic state in the SRO regime.

INTRODUCTION

Current research in the mixed valent manganite perovskite materials has expanded to include the search for materials with other structure types exhibiting colossal magnetoresistance (CMR). Shimakawa, et al.¹ have reported CMR in a pyrochlore ($Tl_2Mn_2O_7$) synthesized at high pressure, and Cheong, et al.² have studied In substitution in this sytem. Moritomo, et al.³ have published a single crystal study of layered $La_{1.2}Sr_{1.8}Mn_2O_7$, the $n=2$ member of the Ruddlesden-Popper series $(La,Sr)_{n+1}Mn_nO_{3n+1}$. As shown in Fig. 1, this compound consists of double layers of MnO_6 octahedra separated by $(La,Sr)_2O_2$ layers. This material has coincident ferromagnetic (FM) and metal-insulator (MI) transitions at $T_C \sim 120$ K. Moritomo, et al. report a $\sim 20,000$ % MR (129 K, $H=7$ T) in this layered material and speculate on the role of reduced dimensionality in the electronic transport. This material is also significant due to its pronounced CMR in low field, $\sim 200\%$ at 129 K in 0.3 T.

We have synthesized a number of two-layer manganites ($R_{1.2}Sr_{1.8}Mn_2O_7$, $R = La, Pr, Nd$; $RSr_2Mn_2O_7$, $R = Pr, Nd$; and $La_{1.4}Sr_{1.6}Mn_2O_7$) to study the effect of doping and/or ionic size on the structural, magnetic, and electronic properties of this class of materials. Seshadri, et al.⁴ have published a study of the $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R=La,Pr,Nd$) series using x-ray powder diffraction and conclude that the smaller ionic size of the Pr and/or Nd results in an enhanced Jahn-Teller distortion of the MnO_6 octahedra in the double layers of $Pr_{1.2}Sr_{1.8}Mn_2O_7$ and $Nd_{1.2}Sr_{1.8}Mn_2O_7$. This increased distortion was presumed to suppress an MI transition observed in the $La_{1.2}Sr_{1.8}Mn_2O_7$ analog that coincides with the onset of long range FM order (LRO). This last compound was reported to have a much smaller distortion.

In contrast to the findings of Seshadri, et al., our neutron powder diffraction studies⁵ of these compounds show no correlation between the octahedral distortion and the suppression of the MI transition. Rather, our data suggest that perhaps the in-plane Mn-O bond is the metrical parameter sensitive to the electronic transition. We also demonstrate in the $La_{1.2}Sr_{1.8}Mn_2O_7$ compound the existence of an unusual magnetic state extending from T_C to near room temperature.⁶ Detailed magnetization measurements reveal that a short-range ordered (SRO) ferromagnetic (FM) state persists in this temperature regime. Furthermore, despite the absence of a long-range ordered state in the Pr and Nd analogs, these compounds also show evidence of this SRO state.

Fig. 1. Structure of $(\text{La,Sr})_3\text{Mn}_2\text{O}_7$

EXPERIMENTAL

Results reported below are for a single-crystal specimen of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ grown by the traveling-solvent floating-zone technique and polycrystalline samples of the remaining compounds. Details of the preparation of single crystal specimens of the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ have been published elsewhere.⁵ The remaining compounds were synthesized in polycrystalline form by routine solid state reaction of La_2O_3 (Johnson-Matthey, dried at 900 °C in flowing O_2), Pr_6O_{11} (Johnson-Matthey, as received), Nd_2O_3 (Johnson-Matthey, dried at 900 °C in flowing O_2), SrCO_3 (Johnson-Matthey, as-received), and MnO_2 (Johnson-Matthey, as received). Stoichiometric quantities of the starting materials were mixed and fired in three steps: (1) 900 °C for 12 hr in dynamic vacuum; (2) 1250 °C in flowing oxygen; and finally, (3) 1400 °C in flowing oxygen (with the exception of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ which was fired in 2% O_2 /balance Ar). Materials were reground between each firing cycle. For the final firing, pellets were cold-pressed at 20 kpsi. In each case, the final products were single-phase as judged by powder x-ray diffraction. Neutron powder neutron diffraction (NPD) was carried out at the SEPD at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS). NPD measurements were made either in the Earth's field or in an applied field of 0.6 T generated by permanent magnets.⁷ Diffraction measurements were made between 20 K and 300 K on a Displex refrigerator and between 300 K and 500 K in a radiation furnace. Magnetic and transport measurements were made in a Quantum Design PPMS system equipped with a 9 T superconducting solenoid. The trapped flux in the solenoid was monitored and field values adjusted accordingly. Magnetization measurements reported here on single crystal $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ utilize a field applied along the easy axis of the crystal, which is in the a-b plane.

Fig. 2 shows the temperature-dependent resistance of the series $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R=La,Pr,Nd$) normalized to the resistance at 300 K. In agreement with Seshadri, et al.,⁴ the Pr and Nd compounds are insulating throughout the temperature regime measured, while the La compound has an MI transition at $T_C \sim 120$ K, with the resistance dropping by a factor of 100 through the transition. Although the data are not shown, the compound $La_{1.4}Sr_{1.6}Mn_2O_7$ also has an MI transition near 120 K, while $NdSr_2Mn_2O_7$ and $PrSr_2Mn_2O_7$ are insulators with no transition observed between 20 K and 350 K.

Fig. 2. Normalized R vs. T for the series $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R=La,Pr,Nd$)

Results of room temperature neutron powder diffraction on the above series of compounds are presented in Table I, which focuses on the Mn-O bond lengths in the double layer of MnO_6 octahedra. The first two samples in Table I— $La_{1.2}Sr_{1.8}Mn_2O_7$ and $La_{1.4}Sr_{1.6}Mn_2O_7$ —exhibit an MI transition; the remaining samples do not. We note that there are some differences in the bond lengths reported here compared to those in reference 4, but neutron powder diffraction is expected to more precisely locate the oxygen atoms than the x-ray diffraction. We note first that the bond lengths in like-doped Pr and Nd compounds are quite similar; this is consistent with the similar ionic radii of these two trivalent ions. Increasing the Sr content in any member of these series results in a decrease of the apical Mn-O bonds—consistent with an oxidation of the Mn center—while the in-plane Mn-O bond remains essentially unchanged. In the last column of Table I, we present the octahedral distortion defined by Seshadri, et al.⁴ as the percent elongation of the apical (Mn-O(1) and Mn-O(2)) bond lengths compared to the in-plane (Mn-O(3)) bond length. If we look only at the $R_{1.2}Sr_{1.8}Mn_2O_7$ series, it would seem that this parameter separates those compounds with an MI transition from those without, as the $La_{1.2}Sr_{1.8}Mn_2O_7$ distortion (1.57%) is substantially less than that in the Pr or Nd analogs (3.07% and 3.30%, respectively). However, when the entire range of compounds is considered, this rule is seen to no longer hold true. Consider that $La_{1.4}Sr_{1.6}Mn_2O_7$ (with an MI transition) has a distortion of 2.74%, while $Pr_{1.0}Sr_{2.0}Mn_2O_7$ (an insulator at all T) is distorted by only 1.98%, and $Nd_{1.0}Sr_{2.0}Mn_2O_7$ by 2.31%. This fact, combined with the observation that the Mn-O(2) bond length in both insulators and compounds exhibiting an MI transition can be quite similar leads us to believe that the room temperature value of these parameters does not adequately predict the electronic behavior at low

temperature. On the other hand, the Mn-O(3) in-plane bond is considerably longer (1.937 Å) in the MI compounds than in the insulators (~1.925 Å). This bond length may be a more important parameter characterizing the electronic behavior of these materials. A larger sample population will be required to judge whether this rule will hold true in general for other compounds in this family.

Table I. Mn-O bond lengths in $(R,Sr)_3Mn_2O_7$ compounds at room temperature

	Mn-O(1) (Å)	Mn-O(2) (Å)	Mn-O(3) (Å)	Distortion (%)
$La_{1.2}Sr_{1.8}Mn_2O_7$	1.942	1.994	1.937	1.57
$La_{1.4}Sr_{1.6}Mn_2O_7$	1.953	2.030	1.937	2.74
$Pr_{1.2}Sr_{1.8}Mn_2O_7$	1.937	2.035	1.925	3.07
$Pr_{1.0}Sr_{2.0}Mn_2O_7$	1.927	2.003	1.926	1.98
$Nd_{1.2}Sr_{1.8}Mn_2O_7$	1.935	2.038	1.921	3.30
$Nd_{1.0}Sr_{2.0}Mn_2O_7$	1.927	2.010	1.923	2.31

Additional evidence that a large apical Mn-O bond length distortion is inconsistent with a metallic state is found in the temperature dependence of this parameter for the $La_{1.2}Sr_{1.8}Mn_2O_7$ sample. As can be seen in Fig. 3, the in-plane Mn-O(3) bond is essentially temperature independent, showing only a small anomaly at $T_C \sim 120$ K. Likewise, the Mn-O(1) apical bond shared between the layers (not shown) does not change with temperature.⁵ However, the Mn-O(2) apical bond *expands* by ~1% as the compound becomes metallic below T_C . This results in an increased octahedral distortion in the metallic state. This result is particularly interesting when compared to similar studies in the perovskite CMR family reported by Caignaert, et al.⁸ These researchers showed that the octahedral distortion coordinate in $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ became substantially reduced in the metallic regime. They attributed this reduced distortion to the delocalization of the $Mn^{3+} e_g$ electron, rendering the Mn sites Jahn-Teller inactive. In the layered compounds this does not seem to be the case; a large octahedral distortion is not inconsistent with an MI transition.

Fig. 3. Temperature dependence of Mn-O bonds of single crystal $La_{1.2}Sr_{1.8}Mn_2O_7$.

Fig. 4. Magnetization of single crystal $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$

We now present the results of magnetization measurements on single-crystal specimen of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Similar features are found in the $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, which shows a MI transition. The insulating compounds have a somewhat different magnetic behavior that will be discussed below. What is immediately apparent from Fig. 4 is that the magnetic behavior of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ falls into three regimes as a function of temperature. At low temperature (region I), in the metallic phase, a long-range, field-induced FM state is observed with Curie temperature $T_C \sim 120$ K. Neutron diffraction detects magnetic scattering in this regime.⁵ For $T > 287$ K (region II), the material is paramagnetic and insulating. Interestingly, for $T_C < T < 287$ K (region II), a weak FM state (with hysteresis) is observed. Neutron diffraction detects no magnetic scattering in this temperature regime,⁵ indicating that the FM correlations are short range. For $H = 15$ Oe, M scales as $(1-T/T^*)^\beta$, with $T^* = 287$ K and $\beta = 0.25 \pm 0.02$. This critical exponent is within experimental error of that predicted for the finite-size 2D XY model ($\beta = 3\pi^2/128 = 0.231$), suggesting that indeed the magnetic state in region II is of a short range nature.

Figure 5 shows the phase diagram of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ in the H - T plane. This diagram delineates three regions in this phase plane. At higher temperatures a fourth region, the paramagnetic insulating region, would appear on the phase diagram. Also shown on this diagram as dark circles are the results of *in situ* neutron powder diffraction measurements of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ in the Earth's field or in a field of 0.6 T. These points are the Curie temperatures in the respective fields. The $H = 0.6$ T point lies on the line determined by magnetization measurements, while the Earth's field measurement lies on an extrapolation of the line determined by these measurements. Together they yield a consistent picture of the magnetic behavior of this material from both bulk magnetization and structural measurements.

Fig. 5. Phase Diagram of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ in the H-T plane.

The insulating compounds $\text{R}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{RSr}_2\text{Mn}_2\text{O}_7$ ($\text{R} = \text{Pr}, \text{Nd}$) do not develop the LRO FM state, but there is evidence of a transition at higher temperature (near 300 K for each compound). The similarity to the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.4}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ materials suggests that these insulating compounds have an SRO state that never fully develops into the LRO FM state associated with the MI transition. Further detailed study of these compounds will be required to better understand the similarities and differences in the magnetic ordered states of the insulating and metallic compounds.

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