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Abstract

We report powder neutron diffraction results on the crystal and magnetic structures of the bilayer Ruddlesden-Popper phase $\text{Sr}_3\text{Mn}_2\text{O}_{7-\delta}$ ($\delta=0.0, 0.45$) and correlate these structures with their magnetic and transport properties. The $\delta=0.45$ compound contains a large number of oxygen vacancies that are disordered in the MnO_2 planes. As a result of this disordered vacancy structure, $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ is a nonmagnetic insulator. $\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ ($\delta=0$) is an antiferromagnetic insulator whose magnetic structure is related to that of the SrMnO_3 perovskite. Comparison of this end-member compound to its doped congeners in the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series highlights the extreme sensitivity of magnetic structure to dopant concentration in these layered materials.

I. Introduction

Mixed-valent oxides of Mn^{3+} and Mn^{4+} have received substantial attention in recent years because of their strong coupling among lattice, spin, and charge degrees of freedom leading to colossal magnetoresistance (CMR).¹⁻⁶ While the three-dimensional perovskites (e.g., $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) have the longest history of study, layered materials of the formula $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ have gained importance because of their inherent anisotropy and its consequences for studying low-dimensional physics.^{5,7-11} Importantly, these layered materials have also been shown to have substantially better low-field magnetoresistance than their perovskite relatives.⁹

Both ceramic and single crystal samples of the layered solid solution $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ have been reported for $0.3 \leq x \leq 0.5$, although ceramic samples at the $x=0.5$ composition are known to phase separate.⁸ Unlike the perovskites, where end-member (i.e., LaMnO_3 , SrMnO_3) compositions have been studied in detail, the magnetic and transport characteristics of such undoped compounds have not been investigated in the layered systems. In this report, we describe the synthesis and full structural and magnetic characterization of one such end-member, $\text{Sr}_3\text{Mn}_2\text{O}_{7-\delta}$ ($\delta=0.45, 1.0$).¹² Both of these compounds provide a valuable reference point for studying the doped bilayer manganites $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($0.3 \leq x \leq 0.5$). The highly oxygen-deficient $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ formally contains Mn^{3+} and Mn^{4+} in a ratio 45:55, but is “doped” in a fashion considerably different than the La-substituted materials. The result is a mixed-valent compound abounding with O vacancies and whose differing coordination polyhedra localize the e_g electrons and preclude magnetic order. The magnetic structure of the end-member compounds is compared with that of the doped ($0.3 \leq x \leq 0.5$) compounds to show the rich variation of magnetic interactions with composition.

II. Experimental

The synthesis of the double-layer Ruddlesden-Popper (R-P) phase $\text{Sr}_3\text{Mn}_2\text{O}_7$ was first reported by Mizutani, *et al.*¹³, who stabilized the compound at $T > 1650^\circ\text{C}$. The compound is metastable below this temperature and must be cooled rapidly to below 1000°C to prevent decomposition. Mizutani, *et al.* slow cooled their sample from 1000°C to room temperature and indexed their powder x-ray pattern on a tetragonal cell with lattice parameters given in the first column of Table I. No further characterization of this compound has been reported in the literature.

We synthesized $\text{Sr}_3\text{Mn}_2\text{O}_7$ by firing a stoichiometric mixture of SrCO_3 and MnO_2 at 1650°C for 12 hrs. Unlike Mizutani's sample, our pelletized sample was quenched directly from synthesis temperature into a container of dry ice to preserve the high temperature structure. A portion of as-made material was rapidly heated to 400°C on a thermogravimetric analysis (TGA) balance, held until no further weight gain was observed, then quickly cooled to room temperature. The observed weight gain indicated that a substantial quantity of oxygen was absorbed by the sample. Independent measure of the oxygen content was obtained by iodometric titration. Samples suitable for neutron diffraction (3-5 g) were prepared by annealing quenched samples for six hours at 400°C in an oxygen atmosphere.

Crystalline samples of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($0.32 \leq x \leq 0.4$) were prepared by the floating-zone method. Description of the synthesis conditions has been reported elsewhere.⁵ The center of the resulting crystalline boules were cut to yield 2-3 gram samples that were pulverized for neutron powder diffraction.

Time-of-flight (TOF) neutron powder diffraction was performed as a function of temperature on the Special Environment Powder Diffractometer (SEPD) at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS). An additional room temperature powder diffraction pattern of the $\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ sample was recorded on the high resolution diffractometer D2B (Ge (335), $\lambda = 1.594 \text{ \AA}$) at the Institut Laue-Langevin (Grenoble) as an independent check on the TOF data. All TOF and constant wavelength data were analyzed with the Rietveld program FullProf.¹⁴

III. Results and Discussion

Powder x-ray diffraction of the as-made sample revealed a single-phase material that was qualitatively the same as that reported by Mizutani. However, the drastically different synthesis procedure resulted in a rather different compound containing a substantial concentration of oxygen vacancies. As shown in Table I, full profile Rietveld analysis of the powder neutron data revealed a considerably larger unit cell volume than that reported by Mizutani. This larger cell volume can be understood by considering a substantial concentration of Mn^{3+} in what was intended to be a nominally Mn^{4+} compound, $\text{Sr}_3\text{Mn}_2\text{O}_7$. The only plausible way of generating a Mn^{3+} concentration in $\text{Sr}_3\text{Mn}_2\text{O}_7$ is by the formation of oxygen vacancies. Thermogravimetric analysis corroborates this inference: Within three hours at 400 °C in pure O_2 the weight gain has saturated, testifying to the high affinity of the as-made material for oxygen. Assuming that the endpoint compound is stoichiometric (i.e. $\text{Sr}_3\text{Mn}_2\text{O}_{7-\delta}$, $\delta=0$), then the as-made material can be formulated as $\text{Sr}_3\text{Mn}_2\text{O}_{6.56}$, i.e., $\delta=0.44$. Iodometric titration confirmed these results, yielding values of $\delta=0.45\pm0.01$ and $\delta=0.02\pm0.01$ for the as-made and O_2 -annealed samples, respectively. We believe that Mizutani's slow-cooling procedure (*vide supra*) resulted in oxygen uptake, yielding the stoichiometric $\delta=0.0$ compound.

Neutron diffraction experiments on the $\delta=0.45$ compound revealed an unusual defect structure. As shown in Table I, the refined oxygen occupation is consistent with the TGA and iodometric titration results presented earlier, $\delta=0.45(2)$. We note that the neutron diffraction patterns of double-layer $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ in the temperature range $20 \text{ K} \leq T \leq 300 \text{ K}$ show no superlattice reflections associated with either vacancy, ordering or antiferromagnetism. Interestingly, the Rietveld refinements unambiguously locate all of the O vacancies in the MnO_2 planes. Oxygen deficient R-P phases with $n=2$ and $n=3$ more commonly have vacancies shared between the MO_2 layers, as found in $\text{Sr}_3\text{V}_2\text{O}_{7.8}$,¹⁵ $\text{Sr}_4\text{V}_3\text{O}_{10.8}$,^{16,17} $\text{Sr}_3\text{Fe}_2\text{O}_{7.8}$,¹⁸ $\text{Sr}_3\text{Co}_2\text{O}_{6.06}$,¹⁹ $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$,²⁰ and the mixed transition metal compound $\text{Sr}_2\text{LaCuRuO}_{7.8}$.²¹ However, an arrangement of in-plane oxygen defects has been reported by Leonwicz, et al. in the single-layer R-P manganite $\text{Ca}_2\text{MnO}_{3.5}$.²² This defective K_2NiF_4 -type compound contains exclusively Mn^{3+} and forms an ordered defect structure of corner-sharing MnO_5 square pyramids

Despite the fact that neutron diffraction gives no information regarding the local defect structure, it is reasonable to infer that in $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ the Mn sites will have two distinct coordination polyhedra: octahedral and square pyramidal, as shown by Fig. 1a. By analogy to $\text{Ca}_2\text{MnO}_{3.5}$, we may associate the octahedral sites with Mn^{4+} and the square pyramidal sites with Mn^{3+} . The formal oxidation state of Mn in $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ is 3.55, indicating that there are approximately equal numbers of these octahedra and square pyramids. Apparently there is no long-range correlation among these coordination polyhedra either within or between the bilayers.

The highly defective structure can explain the transport and magnetic behavior of $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$. Four-probe resistance measurements on a sintered pellet revealed a highly resistive compound with $dp/dT < 0$ between 12 K and room temperature. Since the defect structure of $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ is disordered, details of the individual Mn-O bond lengths cannot

be determined by diffraction methods. However, we can infer an approximate model from the aforementioned compound $\text{Ca}_2\text{MnO}_{3.5}$. In this ordered defect compound, the five Mn-O bond lengths are: 1.80 Å, 1.93 Å, 1.94 Å (x 2), and 1.96 Å. If this geometry is representative of that found in $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$, then the extreme distortion can be associated with localization of the e_g electron on the Mn^{3+} site. In particular, the largest distortion (shortest bond length) lies in what would nominally be the conduction planes of the doped $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ R-P compounds. As shown by neutron diffraction, $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ has no long-range magnetic order above 20 K. The double-exchange ferromagnetism associated with the CMR manganites^{23,24} is not expected when the e_g electron is localized. Furthermore, the disordered array of Mn^{3+} and Mn^{4+} sites apparently frustrates antiferromagnetic superexchange interactions as well.

The fully oxygenated $\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ compound ($\delta=0$) has intact MnO_2 sheets and contains only Mn^{4+}O_6 octahedra, as shown in Fig. 1b. As expected, this material is an antiferromagnetic insulator whose magnetic structure bears strong resemblance to its congener, the $\text{SrMnO}_{3.0}$ perovskite. Fig. 2a shows the results of full profile Rietveld refinements of TOF neutron powder diffraction data taken on a sample of $\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$. Selected results of the refinement—including corroboration of the oxygen content—are collected in Table I. The 8 K diffraction pattern shows reflections that can be indexed on a $2a_0 \times 2a_0 \times c_0$ supercell, where a_0 and c_0 are the unit cell dimensions of the paramagnetic phase. The Néel temperature, as determined by the appearance of superlattice reflections, is $T_N = 160$ K. The refined magnetic structure is shown schematically in Fig. 2b; it consists of an array of Mn moments aligned parallel to the c -axis. The refined moment on Mn at 8 K is $2.31(7) \mu_B$. Each spin is oriented antiparallel to each of its five neighboring spins, analogous to the G-type antiferromagnetism observed in the perovskite $\text{SrMnO}_{3.0}$ ($T_N = 260$ K).²⁵ The single-layer compound $\beta\text{-Sr}_2\text{MnO}_4$ has a similar spin arrangement in its antiferromagnetic phase ($T_N = 170$ K),²⁶ indicating that the exchange interactions in all

of these undoped R-P phases are similar. The trend in Néel temperatures— $T_N(n=2) \approx T_N(n=1) \ll T_N(n=\infty)$ —indicates that the ordering temperature is determined by interplane magnetic interactions. Like cubic SrMnO_3 and $\beta\text{-Sr}_2\text{MnO}_4$, $\text{Sr}_3\text{Mn}_2\text{O}_7$ is an insulator due to exchange splitting of the occupied t_{2g} orbitals.

Figure 3 shows a schematic of the low-temperature (20 K) magnetic structures of compounds in the series $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ as determined by neutron powder diffraction of pulverized single-crystal samples (The $x=0.5$ result is from a polycrystalline sample whose magnetic structure has been reported by Battle, et al.⁸) Without exception all of these doped compounds have ferromagnetically (FM) coupled MnO_2 sheets. However, how the sheets couple within (*intrabilayer*) and between bilayers (*interbilayer*) is highly concentration dependent. For high doping ($x=0.5$), the Mn moment lies in the a - b plane and the intrabilayer coupling is antiferromagnetic (AF), while the interbilayer coupling is FM. With decreasing x , the moment remains in the plane, but both intra- and interbilayer coupling becomes FM ($x=0.4$). This magnetic structure is stable through $x=0.33$. For $x=0.32$, the coupling is again FM both within and between the bilayers, but the moment has rotated 90° and is now parallel to the c -axis. Finally, at $x=0.3$ the moment remains parallel to c , but the interbilayer coupling has become AF.²⁷⁻²⁹ As can be seen, a rich variation of magnetic structures appear over this concentration range, showing that the competing ferromagnetic and antiferromagnetic interactions are delicately balanced and highly sensitive to doping concentration. An understanding of how this balance of magnetic interactions (FM vs. AFM) and spin orientation (a - b plane vs. c -axis) depends on structure and/or orbital ordering remains for further study.

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Table I. Crystal Structure Data from Neutron Powder Diffraction^a

	$\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ (300 K) ^b	$\text{Sr}_3\text{Mn}_2\text{O}_{7.8}$ (300 K, quenched)	$\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ (300 K, O ₂ annealed)	$\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$ (8 K, O ₂ annealed) ^c
a (Å)	3.801(1) ^d	3.82812(3)	3.79972(5)	3.78936(4)
c (Å)	20.06(1)	20.1042(3)	20.0959(4)	20.0638(4)
δ	-----	0.45(2)	0.00 ^e	0.00 ^e
μ(μ _B /Mn)	-----	-----	-----	2.31(7)

^aEntries in this table are from TOF data taken on SEPD. ^bData from Ref. 13. ^cRefined in magnetic supercell; parameters refer to crystallographic subcell. See text for details.

^dNumbers in parentheses are esd's. ^eFixed at full O stoichiometry based on refinement of constant wavelength data measured on D2B.

Figure Captions

Figure 1. (a) Schematic drawing of a single MnO_2 plane of $\text{Sr}_3\text{Mn}_2\text{O}_{6.55}$ showing oxygen vacancies and the different coordination polyhedra for Mn^{3+} and Mn^{4+} . (b) Schematic drawing of a stoichiometric MnO_2 plane found in $\text{Sr}_3\text{Mn}_2\text{O}_{7.0}$.

Figure 2. (a) Results of Rietveld refinement of neutron powder data on $\text{Sr}_3\text{Mn}_2\text{O}_7$ taken at 298 K (top) and 8 K (bottom). (+): Observed; (—): calculated. Difference curves are shown at the bottom of each panel. Vertical lines mark positions of (top to bottom) fundamental reflections for double-layer material, magnetic reflections (bottom panel only), and SrMnO_3 impurity phase. (b) Magnetic unit cell of $\text{Sr}_3\text{Mn}_2\text{O}_7$ at 8 K. Only Mn sites are shown for clarity.

Figure 3. Doping dependence of the 20 K magnetic structure of the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series as determined by neutron powder diffraction.

(a)

(b)