PHYSICAL REVIEW B VOLUME 57, NUMBER 17 1 MAY 1998-I

Effect of lanthanide ions on the magnetotransport properties in layered $Sr_{1.6}R_{1.4}Mn_2O_7$ (R = La, Pr, Nd, Gd)

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(Received 4 September 1997; revised manuscript received 15 December 1997)

The magnetoresistances (MR's) and magnetic properties of layered manganese oxides, $Sr_{1.6}R_{1.4}Mn_2O_7$ (R = La, Pr, Nd, Gd; R-327), have been investigated. The La-, Pr-, and Nd-substituted compounds show metal insulator transitions below 150 K, whereas isostructural Gd-327 compound is semiconducting and paramagnetic. For La-327, the transition temperature corresponds well to the onset of ferromagnetic ordering and the MR ratio is fairly large compared with perovskite-type $AMnO_3$ oxides. The Pr and Nd analogs show negative MR's, but both compounds display other anomalous transitions to semiconductors below 50 K. Neither material shows a transition to a ferromagnetic state below 350 K. The observation of colossal magnetoresistance in the absence of bulk ferromagnetism suggests that the double-exchange interaction alone is not sufficient to explain the resistivity of R-327 near T_c. [S0163-1829(98)04217-9]

INTRODUCTION

Recent interests in ternary manganese oxides with a perovskite structure are largely due to the colossal magnetoresistance (CMR) found in these materials.[1] Several studies on doped $La_{1-x}M_xMnO_3$ (M = Ca, Sr, Ba) materials revealed that the mixed-valence state of Mn ions (Mn^{3+} and Mn^{4+}) was responsible for the occurrence of CMR transitions.[2] This behavior has been understood by the double-exchange model in which carrier hopping between $Mn^{3+}(t_{2g}^3 e_g^1)$ and $Mn^{4+}(t_{2g}^3)$ depends on the relative alignment of ionic local magnetic moments.[3] Recent reports on the complicated field dependence of the resistivity in $AMnO_3$-type oxides and the absence of a mixed-valence state in $Tl_2Mn_2O_7$ with a pyrochlore structure, however, suggest that additional theories are required to understand the basic mechanism of CMR.[4,5] In order to resolve this discrepancy, other models such as polaron effects that are accompanied by strong electron-phonon interactions have been reported.[6]

Many works on CMR materials thus far have been focused on $AMnO_3$-type perovskite oxides that have simple three-dimensional structures. The tolerance factor, namely, lattice effects, has been known to be a crucial element in determining magnetotransport properties in $AMnO_3$ oxides.[7] In view of the sensitivity of MR properties to the structure, our present study on $Sr_{1.6}R_{1.4}Mn_2O_7$ (R = La, Pr, Nd, Gd; denoted as R-327) might provide another idea to elucidate fundamental understanding of the CMR property because it has a two-dimensionally layered structure. The structure of R-327 is considered as the $n=2$ member of the Ruddlesden-Popper series $A_{n+1}B_nO_{3n+1}$ in which two perovskite blocks composed by two-dimensional layers of BO_6 corner-sharing octahedra are separated by rocksalt AO layers. In order to investigate the effect of lanthanide ions, we fixed the formal oxidation state of Mn ions as $Mn^{3.3+}$. In view of the results found in $AMnO_3$-type oxides, this doping ratio for R-327 seems to be optimal to exhibit the CMR characteristics.[8] An important finding in this work is that the CMR properties of the layered R-327 compounds are largely affected by the nature of lanthanide ions. In this paper we report magnetic and magnetotransport properties of R-327.

EXPERIMENTS

Polycrystalline samples of $Sr_{1.6}R_{1.4}Mn_2O_7$ (R-327) were prepared from stoichiometric mixtures of $SrCO_3$, Mn_2O_3, and corresponding lanthanide oxides that were completely dried prior to use. The samples were reacted at about 1400–1500 °C in air with several intermediate grindings until pure phases were formed. Phase purity was confirmed by using a Rigaku RAD x-ray-powder diffractometer equipped with Cu-$K\alpha$ radiation. Rietveld refinement was performed with the RIETAN program. The magnetic susceptibility was measured by a superconducting quantum interference device magnetometer (Quantum Design). The measurements were taken in both zero-field-cooled (ZFC) and field-cooled (FC) conditions under applied fields of 5000 G. Magnetoresistance was measured in an applied field of up to 6 T using a standard four-probe method.

RESULTS AND DISCUSSION

To obtain single phases of R-327, reaction temperatures were very carefully controlled due to the facile conversion to other perovskite-related $(Sr,R)_2MnO_4$ and $(Sr,R)MnO_3$ compounds. Every sintering step of the reactions was thus monitored by x-ray-powder diffraction. Although all the reactions were performed in air, starting lanthanide oxides were dried completely and weighed in the dry box because the content of lanthanide is important in determining the oxidation state of Mn ions. Optimal sintering temperatures are

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TABLE I. Lattice parameters and sintering temperatures of $Sr_{1.6}R_{1.4}Mn_2O_7$ (R=La, Pr, Nd, Gd).

Compound	a (Å)	c (Å)	Temperature (°C)
La-327	3.8686(6)	20.238(4)	1500
Pr-327	3.8558(5)	20.197(3)	1400
Nd-327	3.8495(6)	20.214(4)	1500
Gd-327	3.8164(9)	20.059(6)	1400

illustrated in Table I. Figure 1 displays powder x-ray-diffraction patterns for R-327. All the peaks are well indexed by the space group of $I4/mmm$. The calculated lattice parameters of R-327 are also shown in Table I, which correspond well to the expected values for the typical $R_3Mn_2O_7$ structure.[9] As anticipated from contractions by $4f$ electrons in lanthanide ions, lattice parameters are slightly reduced with increasing the atomic number.

The top panel of Fig. 2 displays the temperature dependence of magnetic susceptibilities for $Sr_{1.6}La_{1.4}Mn_2O_7$ (La-327) collected at a field of 5000 G, where the ferromagnetic ordering occurs at about 105 K. The saturation magnetic moment at 10 K is about $3.29\mu_B$ per Mn site, which is close to the expected moment value $(3.7\mu_B)$ of a $Mn^{3.3+}$ ion. A metal-insulator (MI) transition occurred near the onset of ferromagnetism. Under magnetic fields, the resistivities of La-327 are enormously decreased as shown in the bottom panel of Fig. 2. The MR ratio defined as $(\rho_0-\rho_H)/\rho_H$ is about 1000% at 105 K and 6 T, which is roughly two orders of magnitude higher than that of the three-dimensional $La_{1-x}Sr_xMnO_3$.[10] This remarkable MR effect in polycrystalline La-327 might be associated with the interplane tunneling of spin-polarized electrons, which was introduced by Kimura *et al.* to explain magnetoresistance data in a single crystal of $Sr_{2-2x}La_{1+2x}Mn_2O_7$ $(x=0.3)$.[11] They claimed that field-induced coherent motion of electron spins between planes mostly contributed to the large MR effect. Our MR data of polycrystalline samples render similar results as observed in their c-axis-oriented single crystal, suggesting that granular properties directly reflect intrinsic bulk properties.

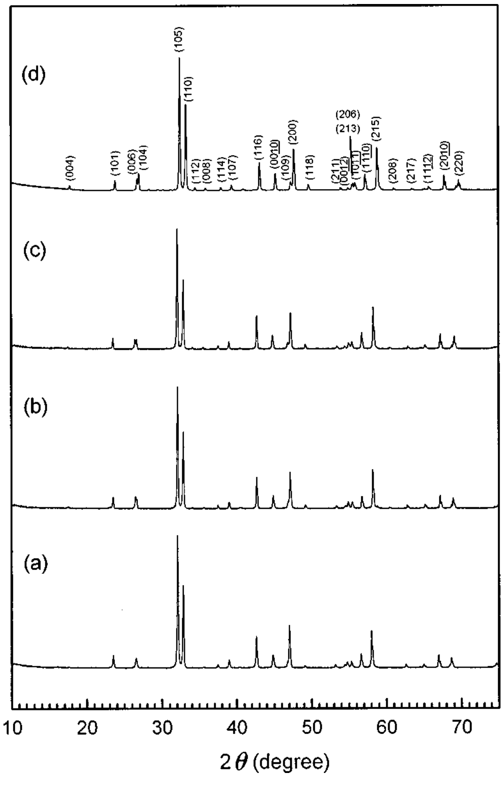

FIG. 1. X-ray powder-diffraction patterns of $Sr_{1.6}R_{1.4}Mn_2O_7$: (a) La-327, (b) Pr-327, (c) Nd-327, (d) Gd-327.

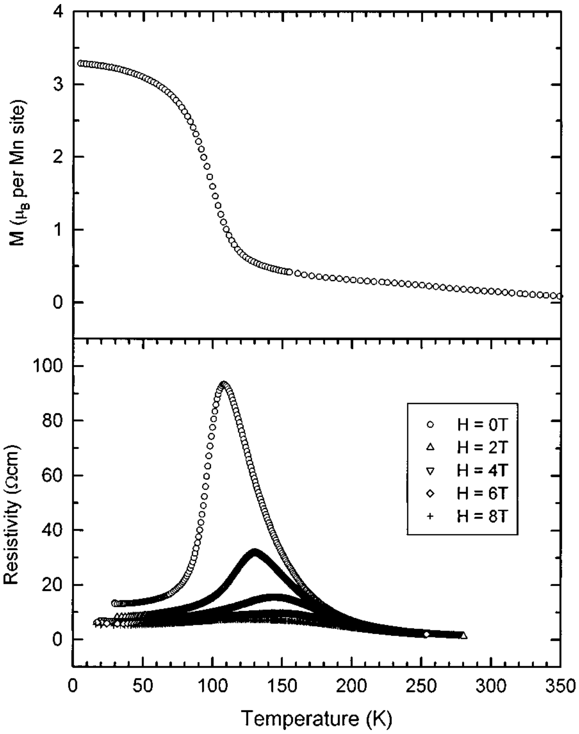

FIG. 2. Top panel displays temperature dependence of magnetic susceptibility for $Sr_{1.6}La_{1.4}Mn_2O_7$. Temperature dependence of the resistivity in $Sr_{1.6}La_{1.4}Mn_2O_7$ for different values of the magnetic field is shown in bottom panel.

In contrast to the magnetic data of a La-327 compound, magnetization measurements on $Sr_{1.6}Pr_{1.4}Mn_2O_7$ (Pr-327) do not show any sign of complete ferromagnetic order down to 5 K as illustrated in the top panel of Fig. 3. Saturation magnetization is equal to about $1.0\mu_B$ per Mn site at about 30 K, which is quite small compared with an expected value. In the absence of bulk ferromagnetism, however, this compound undergoes a MI transition at 95 K and displays CMR behavior as shown in the bottom panel of Fig. 3. The observation of CMR in Pr-327 is thus not readily explained by the double-exchange model and distinguishes this compound from La-327 where a MI transition is accompanied by the appearance of ferromagnetic order. The ZFC and FC magnetizations increase monotonously with decreasing temperature below 320 K and then split below about 40 K. The divergence of magnetization in the low-temperature region implies the presence of a nonhomogeneous state in which ferromagnetic clusters and disordered state co-exist. A similar result on a perovskite $(La,Tb)_{2/3}Ca_{1/3}MnO_3$ oxide was reported by De Teresa *et al.* where the compound has two regions with different magnetotransport properties.[12] An interesting observation in the $\rho(H)$ vs T curve for Pr-327 is that the anomalous transition to the insulating state also occurred at about 40 K. The increase of resistivity below 40 K

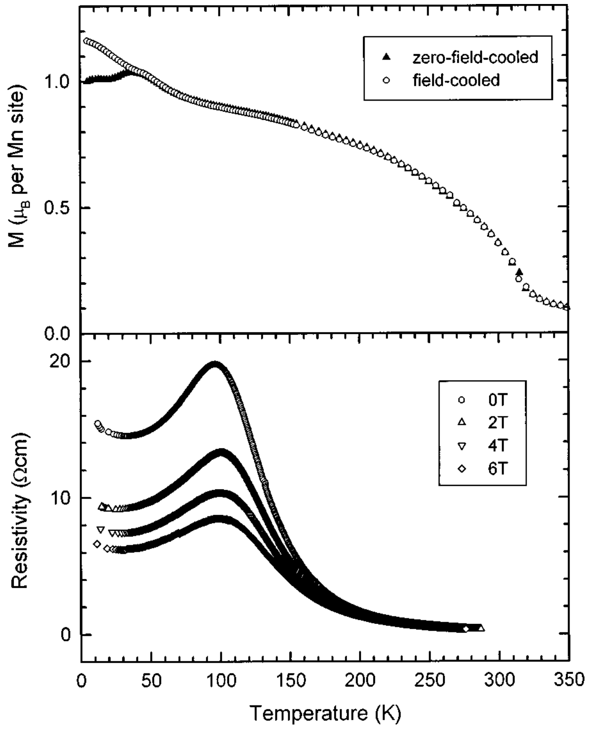

FIG. 3. The field-cooled and zero-field-cooled magnetization (top panel) measured at an applied field of 0.5 T and temperature dependence of the resistivity for different values of the magnetic field in $Sr_{1.6}Pr_{1.4}Mn_2O_7$ (bottom panel).

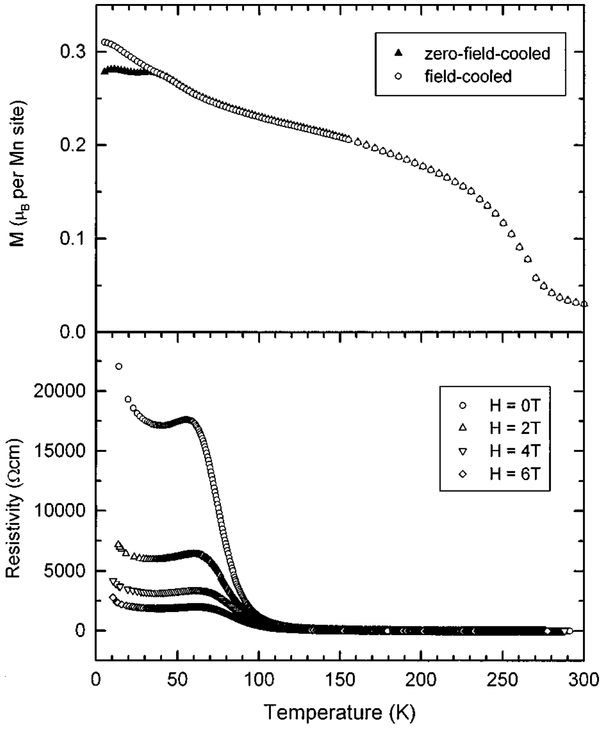

FIG. 5. The field-cooled and zero-field-cooled magnetization of $Sr_{1.6}Nd_{1.4}Mn_2O_7$ measured in a field of 0.5 T as a function of temperature is shown in the top panel. The bottom panel displays temperature variance of the resistivity for different values of magnetic field.

seems to be associated with the magnetically frustrated spins in the low-temperature region. The $M(H)$ curve at 10 K is shown in Fig. 4, which would support this explanation. The hysteresis effect is apparent in this temperature region and the hysteresis loop suggests a tendency of superparamagnetism or the development of ferromagnetic clusters as observed in $Sr_{2-x}Nd_{1+x}Mn_2O_7$ ($x=0.0,0.1$) by Battle *et al.*[13] The MR ratio of Pr-327 is about 134% at 95 K and 6 T, which is smaller than that of La-327. This reduced MR ratio appears to be related to the magnetic interaction between Pr and Mn ions.

The Nd analog, $Sr_{1.6}Nd_{1.4}Mn_2O_7$ (Nd-327), provides similar magnetic behaviors and MR characteristics as observed in Pr-327. The top panel of Fig. 5 displays the temperature dependence of magnetization for Nd-327, indicating that the magnetic frustration exists below 30 K. The calculated magnetic moment at low temperature is about a moment of $0.27\mu_B$ per Mn site, which is much smaller than what would be expected from the fully saturated moment of an Mn ion. One plausible explanation of the reduction of magnetization is a gradual canting of the moments due to lattice distortion caused by small size of a Nd^{3+} ion. As shown in the bottom panel of Fig. 5, the MI transition occurs at 55 K, but this

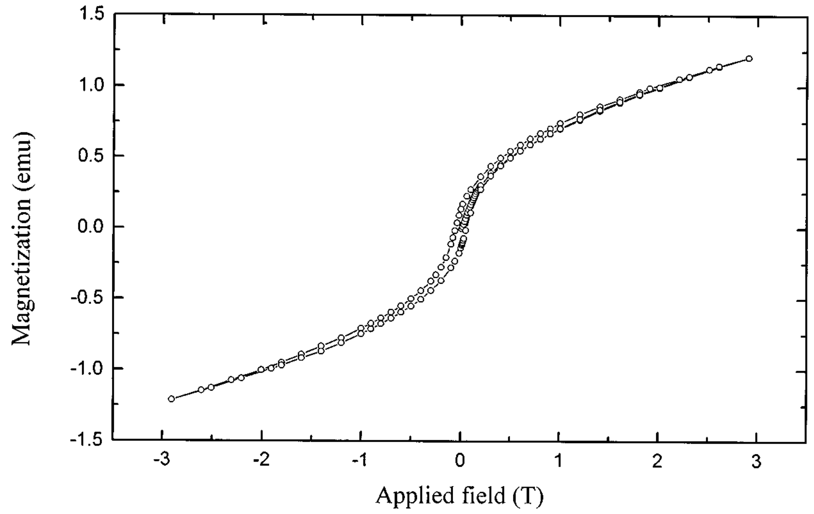

FIG. 4. Magnetization of $Sr_{1.6}Pr_{1.4}Mn_2O_7$ at 10 K as a function of magnetic field.

TABLE II. Radii and magnetic moments of selected lanthanide ions (R^{3+}).

Property	La	Pr	Nd	Gd
Radius (Å)[a]	1.356	1.319	1.303	1.247
Magnetic moment (μ_B)[b]	0.00	3.58	3.62	7.94

[a] Shannon's radii of the nine-coordinated R^{3+} ions (Ref. 15).

[b] Calculated from $g[J(J+1)]^{1/2}$.

metallic state suddenly changes to the insulating state at 30 K that corresponds to the onset of the magnetic frustration. This complex behavior of the temperature-dependent resistivity might also be related to a nonhomogeneous state in the low-temperature region. A metallic transition at 55 K might be associated with the ferromagnetic clusters and another transition to the insulating state below 30 K is ascribed to the magnetically frustrated spin-glass state. Neutron-diffraction studies on Nd-327 revealed no indication of long-range magnetic ordering down to 12 K while La-327 showed ferromagnetic peaks below 100 K, supporting a spin-glass state in Nd-327.[14] These results are in agreement with our magnetic data. An interesting outcome in the $\rho(H)$ vs T curve for Nd-327 is that the maximum MR ratio at 6 T is about 780%, which is close to that of La-327. This also suggests that ferromagnetism is not a prerequisite to lowering the resistivity near T_c in CMR manganese oxides.

In order to assess the effect of the lanthanide ions in R-327 further, we made $Sr_{1.6}Gd_{1.4}Mn_2O_7$ (Gd-327) by substitution of the Sr^{2+} ion site with the Gd^{3+} ion. As anticipated from a large magnetic moment and a small ionic radius of Gd^{3+} ion that are illustrated in Table II,[15] a new Gd-327 compound provides a remarkable contrast with other R-327 (R=La, Pr, Nd) analogs where resistivity maxima are all observed in the absence of magnetic fields and negative MR effects are also found near the MI transition temperatures. The temperature-dependent resistivity of Gd-327 shown in the bottom of Fig. 6, however, is typical of a semiconductor. The magnetic susceptibility of Gd-327 shown in the top panel of Fig. 6 displays a paramagnetic behavior, which follows a Curie-Weiss law with a calculated magnetic moment of $13.07\mu_B$. The magnetic data reveal no evidence of any ferromagnetic order over a wide temperature range. The paramagnetic insulating state of Gd-327 is primarily due to large structural distortion on the basis of the Rietveld profile analyses on R-327.[14] One axial Mn-O bond close to the rock-salt site is elongated and the other axial bond exhibits no appreciable change, while the equatorial Mn-O bonds are shortened, indicating a Jahn-Teller distortion.[16]

The data described for the four isostructural R-327 compounds above suggest that their physical properties are quite sensitive to the nature of lanthanide ions. It is thus interesting to see how CMR's in R-327 are affected by the sizes and magnetic moments of lanthanide ions. The MI transitions were observed only for the compounds having large cations, such as La^{3+}, Pr^{3+}, and Nd^{3+}. This is somewhat coincidental with the phase diagram of $R_{0.7}M_{0.3}MnO_3$ where the perovskite compounds exist as ferromagnetic metallic states by increasing the ionic radius of lanthanide ions and display insulating states when tolerance factors are low.[7] The large lanthanide ions are large enough to fully occupy the interstitial site in the MnO_6 octahedra so that the Mn-O-Mn bond angle is close to 180°. This will reduce the lattice distortion of the MnO_6 octahedra. As in the case of layered R-327 compounds, the overlaps between the Mn $3d$ orbital and the O $2p$ orbital are also expected to be a crucial element in exhibiting electronic conduction. This orbital interaction is obviously very sensitive to bond lengths and angles of Mn-O-Mn that result from the variations of the size of lanthanide ions. Substitution of smaller ions like Gd^{3+} induces tilting or rotation of the MnO_6 octahedra due to the size mismatch, resulting in the deviation from the ideal bond angle and length. The lattice distortions could thus lead to the loss of metallic conductivity. Another factor that causes the absence of a metallic transition in Gd-327 might be the large magnetic moment in the Gd^{3+} ion. In Gd-327, the magnetic moment of the Gd^{3+} ion is large enough to interfere with the ordering of the ferromagnetic spins on the Mn ions, which makes the spin states disordered and in turn leads to the paramagnetic insulator.

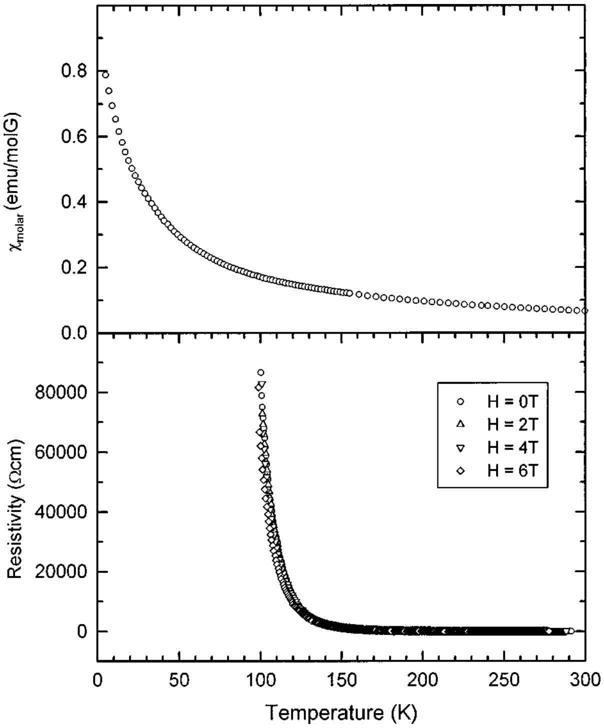

FIG. 6. Temperature dependence of magnetic susceptibility at a field of 0.5 T (top panel) and temperature variance of the resistivity for different values of magnetic field for $Sr_{1.6}Gd_{1.4}Mn_2O_7$ (bottom panel).

In summary, we have found that the magnetotransport properties in the layered $Sr_{1.6}R_{1.4}Mn_2O_7$ (R=La, Pr, Nd, Gd; R-327) change drastically with the nature of R^{3+} ions. Both sizes and magnetic moments of lanthanide ions are important in displaying CMR in R-327. It is difficult to quantitatively analyze which factor dominates for CMR in R-327 at this stage. Our preliminary studies of $Sr_{1.6-x}M_xLa_{1.4}Mn_2O_7$ (M=Ba and Ca) suggest that the lattice size, especially the length of the c axis, is crucial in showing the MI transition and CMR.[17] The observation of CMR in the absence of ferromagnetism clearly demonstrates that the double-exchange interaction alone cannot explain the magnetotransport properties in R-327. The complicated CMR behavior of R-327 emphasizes the need for more detailed studies on the relationship between structure and magnetism.

ACKNOWLEDGMENTS

We are grateful to Nam K. Cho for his assistance. We also thank the Korea Science and Engineering Foundation (KOSEF) and the Ministry of Science and Technology (MOST) for financial support.

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