Magnetic Properties of Quasi-Two-Dimensional $La_{1-x}Sr_{1+x}MnO_4$ and the Evolution of Itinerant Electron Ferromagnetism in the $SrO \cdot (La_{1-x}Sr_xMnO_3)_n$ System*,†

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Quasi-two-dimensional oxides of the $La_{1-x}Sr_{1+x}MnO_4$ system, possessing the K_2NiF_4 structure, show no evidence for ferromagnetic ordering in contrast to the corresponding three-dimensional $La_{1-x}Sr_xMnO_3$ perovskites. Instead, there is an increasing tendency toward antiferromagnetic ordering with increasing x in $La_{1-x}Sr_{1+x}MnO_4$. Furthermore, these oxides are relatively high-resistivity materials over the entire compositional range. Substitution of Ba for Sr in $La_{0.5}Sr_{1.5}MnO_4$ decreases the ferromagnetic interaction. Increasing the number of perovskite layers in $SrO \cdot (La_{1-x}Sr_xMnO_3)_n$ causes an increase in electrical conductivity as well as ferromagnetic interaction. The oxide becomes a highly conducting ferromagnet when $n \geq 2$. © 1987 Academic Press, Inc.

Introduction

Electrical and magnetic properties of the quasi-two-dimensional oxides, A_2BO_4, of the K_2NiF_4 structure are distinctly different from those of the corresponding perovskites, ABO_3 (*1*). Recent studies in this laboratory (*2*) have shown the evolution of metallic conductivity as one goes from La_2NiO_4 ($n = 1$) to the higher members of the $LaO \cdot (LaNiO_3)_n$ family. We considered it most worthwhile to carry out a comparative investigation of the quasi-two-dimensional $La_{1-x}Sr_{1+x}MnO_4$ system and the corresponding three-dimensional $La_{1-x}Sr_xMnO_3$ system. Members of the latter system are well-known metallic ferromagnets (*3*),

the ferromagnetic ordering being caused by double exchange (*4*) involving electron hopping between Mn^{3+} and Mn^{4+} ions with conservation of the spin angular momentum. The $La_{0.5}Sr_{1.5}MnO_4$ which is the two-dimensional analog of $La_{0.5}Sr_{0.5}MnO_3$, on the other hand, seems to show no evidence for long-range ferromagnetic ordering (*5*). The point of interest to us was to examine the two-dimensional $La_{1-x}Sr_{1+x}MnO_4$ or $SrO \cdot La_{1-x}Sr_xMnO_3$ system with regard to its ferromagnetic as well as electrical transport properties over a wide range of compositions. The effect of Ba substitution in the $La_{0.5}(Sr_{1-x}Ba_x)_{1.5}MnO_4$ system was also of interest. We then investigated how the electrical and magnetic properties of the $SrO \cdot (La_{1-x}Sr_x MnO_3)_n$ system vary with three-dimensional character. This system belongs to the family of intergrowth structures (*6*) of the

general formula $A_{n+1}B_nO_{3n+1}$ and provides an excellent means of following the evolution of ferromagnetism and itinerant electron properties with an increase in three-dimensional character brought about by an increase in the number of perovskite layers.

Experimental

$La_{1-x}Sr_{1+x}MnO_4$ with $0.25 \leq x \leq 0.75$ and $SrO \cdot (La_{1-x}Sr_xMnO_3)_n$ with $x = 0.5$, $n = 2,3$, as well as $x = 0.3$, $n = 2$, were prepared by the decomposition of the coprecipitated carbonates obtained by adding an aqueous solution of the nitrates of the corresponding metal ions (in the required stoichoimetry) to a solution of $(NH_4)_2CO_3$ taken 10 times in excess. The resulting precipitates were dried and decomposed at 1250 K after which they were pelletized and heated at 1500–1600 K for 24–72 hr. These methods of preparation are different from the ceramic methods reported earlier (5, 7) involving the grinding and firing of the component oxides. $La_{0.5}(Sr_{1-x}Ba_x)_{1.5}MnO_4$ (1.5 $\leq x \leq 0.25$) could not be prepared by the above method. These oxides were prepared by heating the stoichiometric amounts of the component oxides at 1500 K for 48 hr with repeated grinding and pelletizing. The stoichiometry of these compounds was determined by iodimetric titrations, and the titrable oxygen content corresponded to the formal oxidation states expected in most of the cases when heated in air alone. The deviation from stoichiometry, δ, in $La_{1-x}Sr_{1+x}MnO_{4\pm\delta}$ was generally below 0.04.

X-ray lattice parameters were determined using a JEOL diffractometer. The lattice parameters are given in Table I. Magnetic susceptibility of these oxides were measured by the Faraday method using a Cahn RG electrobalance. Magnetization measurements were carried out with a PAR vibrating sample magnetometer in conjunction with a closed cycle refrigeration (AIR Products Displex) unit. Electrical

Compound	$a = b$ (Å) ($\pm$ 0.001)	c (Å) ($\pm$ 0.003)	c/a
$La_{0.25}Sr_{1.75}MnO_4$	3.822	12.378	3.239
$La_{0.4}Sr_{1.6}MnO_4$	3.844	12.344	3.212
$La_{0.5}Sr_{1.5}MnO_4$	3.858	12.378	3.209
$La_{0.6}Sr_{1.4}MnO_4$	3.845	12.386	3.222
$La_{0.75}Sr_{1.25}MnO_4$	3.848	12.443	3.233
$LaSr_2Mn_2O_7$	3.870	20.069	5.186
$La_{1.5}Sr_{2.5}Mn_3O_{10}$	3.872	27.970	7.224
$La_{1.4}Sr_{1.6}Mn_2O_7$	3.868	20.086	5.193
$La_{0.5}Ba_{0.25}Sr_{1.25}MnO_4$	3.882	12.476	3.214
$La_{0.5}Ba_{0.5}Sr_{1.0}MnO_4$	3.890	12.596	3.238
$La_{0.5}BaSr_{0.5}MnO_4$	3.922	12.800	3.264

resistivity studies were carried out by four-probe dc method.

Results and Discussion

$La_{1-x}Sr_{1+x}MnO_4$

High-temperature ($T > 300$ K) magnetic susceptibility, χ, data of some of representative oxides of this family are shown as χ^{-1} vs T plots in Fig. 1. The plots show curvature toward higher slopes with increasing temperature especially when x is close to 0.5. Curie–Weiss behavior is observed only at high temperatures and the C values calculated from the slopes in this region correspond closely to those expected from the spin-only value of the Mn ions. The calculated and observed spin-only values of μ_{eff} are given in Table II. The paramagnetic Curie temperatures, θ, obtained from the Curie–Weiss regions of the plots are also given in Table II. We notice a marked decrease in the θ values with increasing x for $x > 0.5$. These θ values are compared with those for the corresponding members of the three-dimensional $La_{1-x}Sr_xMnO_3$ system (3) in Table II. There is a definite decrease in θ on going from the three-

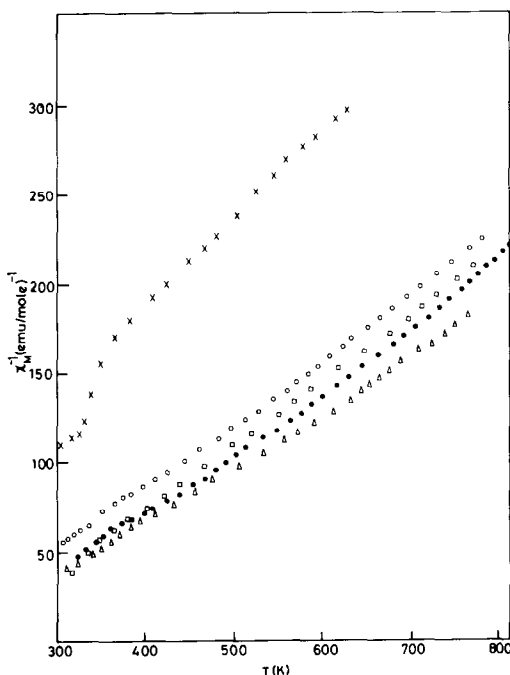FIG. 1. Plots of χ_M^{-1} vs T (K) ($T > 300$ K) of La$_{1-x}$Sr$_{1-x}$MnO$_4$ system. $x = 0.75$ (crosses), $x = 0.6$ (open circles), $x = 0.5$ (closed circles), $x = 0.4$ (squares), and $x = 0.25$ (triangles).

dimensional to the two-dimensional system.

Room-temperature resistivity data of La$_{1-x}$Sr$_{1+x}$MnO$_4$ show a maximum around $x = 0.5$ (see Table II). All these two-dimensional oxides show semiconducting behavior with fairly high activation energies. The

TABLE II

MAGNETIC SUSCEPTIBILITY AND RESISTIVITY DATA
OF La$_{1-x}$Sr$_{1+x}$MnO$_4$ SYSTEM

Compound	μ_{eff} in BM		θ^a (K)	Room temperature resistivity (ohm-cm)
	Observed	Calculated		
La$_{0.25}$Sr$_{1.75}$MnO$_4$	4.06	4.66	30	4.9
La$_{0.4}$Sr$_{1.6}$MnO$_4$	4.50	4.52	210	29.4
La$_{0.5}$Sr$_{1.5}$MnO$_4$	4.21	4.42	310 (312)	47.3
La$_{0.6}$Sr$_{1.4}$MnO$_4$	3.94	4.31	250 (360)	20.9
La$_{0.75}$Sr$_{1.25}$MnO$_4$	3.66	4.15	240 (350)	8.4

^{a} Values in parentheses are for the corresponding values of x in the three-dimensional La$_{1-x}$Sr$_x$MnO$_3$ system.

three-dimensional oxides, on the other hand, are metallic (3) especially when $x \simeq 0.3$. The temperature coefficient of resistivity changes sign at the magnetic ordering temperature for $x \leq 0.2$.

Magnetic susceptibility data of the La$_{1-x}$Sr$_{1+x}$MnO$_4$ system below room temperature ($T < 300$ K) are given in Fig. 2. None of the samples show a divergence in the susceptibility indicative of ferromagnetic ordering in the temperature range studied. There is a definite trend toward long-range antiferromagnetic ordering with an increase in x. Thus, oxides with $x = 0.25$ and 0.4 seem to show superparamagnetic behavior with two or more manganese ions coupling ferromagnetically to give rise to a giant moment; the $x = 0.25$ sample is, however, slightly nonstoichiometric (oxygen excess). The $x = 0.75$ sample, however, shows a marked
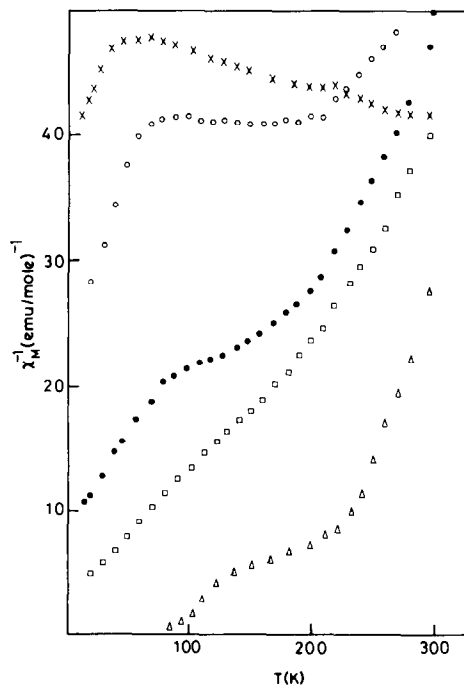

FIG. 2. Plots of χ_M^{-1} vs T (K) ($T < 300$ K) of La$_{1-x}$Sr$_{1+x}$MnO$_4$ system. $x = 0.75$ (crosses), $x = 0.6$ (open circles), $x = 0.5$ (closed circles), $x = 0.4$ (squares), and $x = 0.25$ (triangles).

antiferromagnetic type of behavior with the susceptibility decreasing with decreasing temperature as in the case of Sr_2MnO_4 (8). Thus, lower dimensionality seems to suppress the ferromagnetic ordering found in the corresponding three-dimensional oxides, even though the θ values are comparable. More interestingly, despite the nonintegral occupancy of electrons, antiferromagnetic ordering seems to manifest itself in these systems, a behavior that is not predicted by the double-exchange model of Zener as applied to the three-dimensional perovskite oxides (9).

$La_{0.5}(Sr_{1-x}Ba_x)_{1.5}MnO_4$

The χ^{-1} vs T plots of a few members of this series of solid solutions are shown in Fig. 3. Substitution of Sr by Ba ions leads to an increase in the a parameters (Table I)
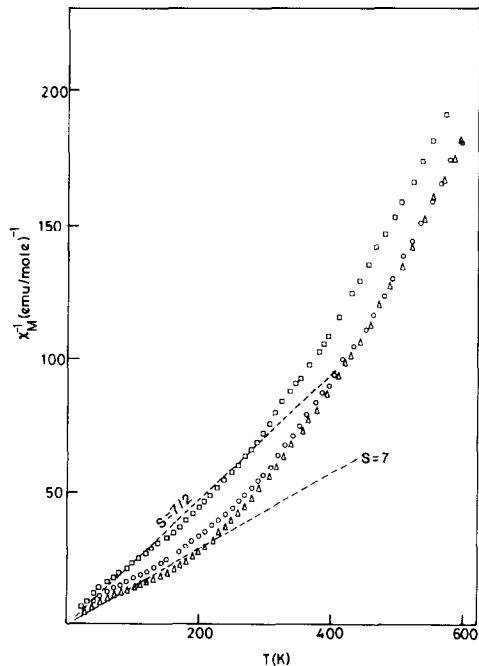
and a decrease in the paramagnetic Curie temperature. In none of the solid solutions do we observe a divergence in the susceptibility typical of ferromagnetic or ferrimagnetic ordering. For small values of x, there seems to be a temperature range where the susceptibility behavior suggests ferromagnetic coupling of the spins of two or more manganese ions. The expected slope for two Mn ions being coupled ferromagnetically to give a $S = 7/2$ system (Mn^{3+} and Mn^{4+} ions per pair) and another for four manganese ions ($S = 7$ system) are also shown in Fig. 3. It seems that when $x = 0$, there are at most four Mn ions coupled ferromagnetically and as x increases, there are at most two Mn ions coupled ferromagnetically. Thus, increasing the proportion of Ba appears to decrease the strength of ferromagnetic interaction; compared to the three-dimensional systems, the decrease is more prominent in the two-dimensional systems. For instance, Jonker and Van Santen (3) observed only a decrease of 20 K on replacing Sr by Ba in $La_{0.6}Sr_{0.4}MnO_3$. In the present study, the decrease is more than 100 K. The other characteristic feature in these oxides is the large deviation from the Curie–Weiss law at high temperatures. Such a deviation is not found in the case of the three-dimensional oxides. The deviation observed in the present study may possibly arise from short range effects.

FIG. 3. Plots of χ_M^{-1} vs T (K) for $La_{0.5}Ba_{0.25}Sr_{1.25}MnO_4$ (triangles), $La_{0.5}Ba_{0.5}SrMnO_4$ (circles), and $La_{0.5}BaSr_{0.5}MnO_4$ (squares).

$SrO \cdot (La_{0.5}Sr_{0.5}MnO_3)_n$

We have carried out magnetization measurements on members of this series to investigate the effect of dimensionality on the evolution of ferromagnetism. When $n = 1$, the oxide is two dimensional with the K_2NiF_4 structure. The magnetization results shown in Fig. 4 are interesting. Magnetization behavior of the $n = 1$ oxide (K_2NiF_4 structure) is close to that reported by MacChesney et al. (10) with respect to the magnitude of the magnetization. The n

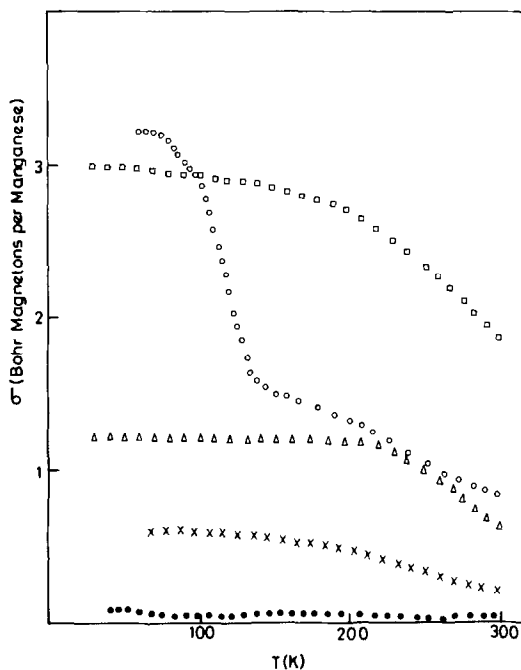FIG. 4. Plots of σ vs T (K) for $La_{0.5}Sr_{0.5}MnO_3$ (squares), $La_{1.4}Sr_{1.6}Mn_2O_7$ (open circles), $La_{1.5}Sr_{2.5}Mn_3O_{10}$ (triangles), $LaSr_2Mn_2O_7$ (crosses), and $La_{0.5}Sr_{1.5}MnO_4$ (closed circles).

$= \infty$ member, which is the three-dimensional perovskite, $La_{0.5}Sr_{0.5}MnO_3$, has a magnetization value (extrapolated to 0 K) close to that reported by Jonker and Van Santen (3). The $n = 2$ and $n = 3$ members show increasing magnetization with increasing n. Neither of these solids, however, shows a substantial increase in the magnetization around 120 K as reported by MacChesney et al. (10). Magnetization of the $n = 2$ member is much larger than that reported by these workers. This discrepancy is not apparently due to the presence of an $n = \infty$ phase. For this to be so, nearly 15 mole% of the $n = \infty$ phase would have to be present and this is detectable even by X-ray diffraction. Since X-ray studies show the $n = 2$ composition to be monophasic, the discrepancy between our results and those of MacChesney seems to

be real; the $n = 3$ oxide, however, exhibits a comparable magnitude of magnetization at low temperatures. The $n = 2$ member of the SrO $\cdot$ $(La_{0.7}Sr_{0.3}MnO_3)$ series, on the other hand, shows nearly the same value of magnetization as the $n = \infty$ phase reported by Jonker and Van Santen (3). This sample shows the rapid increase in magnetization around 120 K reported by MacChesney et al. χ^{-1} vs T plots of these oxides do not show deviation from the Curie–Weiss law observed in the two-dimensional $La_{1-x}Sr_{1+x}MnO_4$.

Electrical resistivities of these oxides (Fig. 5) show a progressive decrease with an increase in n, similar to the LaO $\cdot$ (La $NiO_3)_n$ system investigated in this laboratory (2). In none of the present series of oxides did we find a positive temperature coefficient of resistivity expected of metals.
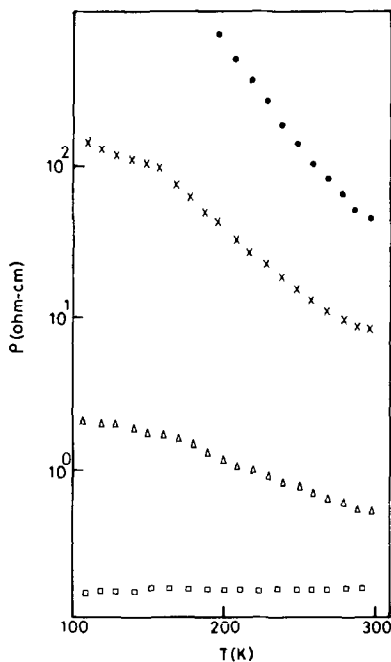

FIG. 5. Plots of ρ vs T (K) for $La_{0.5}Sr_{1.5}MnO_4$ (closed circles), $LaSr_2Mn_2O_7$ (crosses), $La_{1.5}Sr_{2.5}Mn_3O_{10}$ (triangles), and $La_{0.5}Sr_{0.5}MnO_3$ (squares).

Concluding Remarks

Studies comparing the quasi-two-dimensional $La_{1-x}Sr_{1+x}MnO_4$ system and the corresponding three-dimensional $La_{1-x}Sr_x$ MnO_3 system show the absence of ferromagnetic ordering in the former. While the three-dimensional perovskites ($x \simeq 0.3$) are metallic, the two-dimensional systems are all semiconducting. Magnetic properties of $SrO \cdot (La_{0.5}Sr_{0.5}MnO_3)_n$ system, wherein the number of perovskite layers can be changed to vary the dimensionality, show interesting features. With increasing the number of perovskite layers (increase in the three-dimensional character), n, the material becomes increasingly ferromagnetic. Electrical resistivity also decreases progressively with n. The present results clearly demonstrate the effect of three-dimensional character on the electrical and magnetic properties of the La–Sr–Mn–O system. Comparative studies of other two-dimensional and three-dimensional oxide systems are necessary before a fuller explanation of the results can be provided.

Acknowledgments

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