LETTER TO THE EDITOR

Giant Magnetoresistance in Bulk Samples of La$_{1-x}$A$_x$MnO$_3$ (A = Sr or Ca)

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Magnetoresistance measurements have been carried out on bulk samples of several members of the La$_{1-x}$A$_x$MnO$_3$ family (A = Sr and Ca) with varying x or Mn^{4+} content. The magnitude of magnetoresistance (MR) is highest at the insulator–metal (I–M) transition when the transition temperature is relatively low (≤250 K). The relative MR (%MR) is essentially the same (40–50%) at 4.2 K for all the compositions showing the I–M transition, namely ~15% at $T ≳ 300$ K. Insulating compositions (small or large x) show smaller %MR than the compositions that undergo the I–M transition. © 1995 Academic Press, Inc.

Giant magnetoresistance (GMR) has been observed recently in films of perovskites of the general formula La$_{1-x}$A$_x$MnO$_{3-\delta}$ (A = Ca or Ba) (1–3). The GMR in these films occurs in the temperature range 77–300 K when the material is nearly metallic and ferromagnetic. La$_{1-x}$A$_x$MnO$_3$ perovskites become ferromagnetic at relatively low temperatures because of Mn^{3+}–O–Mn^{4+} interactions. Fast hopping of the d-electrons between the two oxidation states of Mn produces metallic behavior as the materials become ferromagnetic (4–7), giving rise to an insulator–metal (I–M) transition at temperatures slightly below the ferromagnetic Curie temperature. We have investigated the occurrence of GMR in bulk samples of La$_{1-x}$A$_x$MnO$_3$ (A = Ca or Sr) in order to compare the results reported for the films of these oxides and to establish the general features of the GMR phenomenon in these perovskites. Thus, it was our objective to establish how factors such as the Mn^{4+} content and the associated electronic and magnetic properties of these oxides determine the magnitude of the magnetoresistance. Furthermore, the magnetoresistance behavior of the La$_{1-x}$Sr$_x$MnO$_3$ system, either in bulk or in film form, has not been investigated hitherto.

La$_{1-x}$A$_x$MnO$_3$ (A = Ca or Sr) samples were prepared by heating stoichiometric mixtures of La$_2$O$_3$, CaCO$_3$, SrCO$_3$, and MnO$_2$ at 1223 K for 12 hr. The powder thus obtained was ground, pelletized, and heated for another 12 hr at the same temperature. The phase purity of the samples was checked using powder X-ray diffraction techniques. The Mn^{4+} content in the samples was determined by redox titrations using potassium permanganate and ferrous sulfate. Magnetoresistance measurements were carried out on bar-shaped samples (0.5 mm × 1 mm × 10 mm). A maximum magnetic field of 6 T was applied, using a superconducting solenoid perpendicular to the direction of the current. The resistance of the sample was measured by the standard four-probe method, by the low frequency (~20 Hz) ac method, and by the dc method. The magnitude of the magnetoresistance is then defined as $[\Delta\rho/\rho(0)] = [\rho(H) - \rho(0)]/\rho(0)$, where $\rho(H)$ and $\rho(0)$ are the resistivities at magnetic field H and at zero field, respectively.

The unit cell parameters and the crystal structures of various La$_{1-x}$A$_x$MnO$_3$ compositions are presented in Table 1, along with the Mn^{4+} content. With the increase in Mn^{4+} content, the oxides become cubic, as expected. La$_{1-x}$Sr$_x$MnO$_3$ is rhombohedral when $x = 0.1, 0.2$, and 0.3, with %Mn^{4+} values of 27, 34, and 37, respectively. It becomes cubic only when $x ≳ 0.4$ (%Mn$^{4+} > 40$). La$_{1-x}$Ca$_x$MnO$_3$ is rhombohedral when $x = 0.1$ (%Mn = 19) and becomes cubic even at $x = 0.2$, when %Mn$^{4+} = 25$. The parent LaMnO$_3$ is known to become cubic when %Mn$^{4+} = 33$ (7).

Four-probe resistivity measurements on La$_{1-x}$Sr$_x$MnO$_3$ samples indicate an I–M transition at ~215 K (T_{IM}) when $x = 0.1$ and around 325 K when $x = 0.3$. The $x = 0.5$ composition was insulating in the 325–4 K range. The resistivity and resistivity anomaly of these samples at T_{IM} decreases with increasing x.

In Fig. 1, we show the temperature variation of the resistivity of La$_{0.9}$Sr$_{0.1}$MnO$_3$ at H = 0 and 6 T. We ob-

TABLE 1

Structure Data and %Mn^{4+} in $La_{1-x}A_xMnO_3$

x	A = Sr			A = Ca		
	%Mn^{4+}	Crystal structure[a]	Lattice parameters	%Mn^{4+}	Crystal structure[a]	Lattice parameters
0.0	12	O	$a = 5.543$ Å $b = 5.494$ Å $c = 7.805$ Å	—	—	—
0.1	27	R	$a = 5.523$ Å $\alpha = 60.60°$	19	R	$a = 5.480$ Å $\alpha = 60.40°$
0.2	34	R	$a = 5.482$ Å $\alpha = 60.40°$	25	C	$a = 7.744$ Å
0.3	37	R	$a = 5.454$ Å $\alpha = 60.14°$	33	C	$a = 7.699$ Å
0.4	41	C	$a = 7.721$ Å	39	C	$a = 7.677$ Å
0.5	47	C	$a = 7.714$ Å	44	C	$a = 7.668$ Å

[a] O, orthorhombic; R, rhombohedral; C, cubic.

serve a significant decrease in resistivity at T_{IM} on application of a magnetic field. The temperature variation of magnetoresistance (Fig. 2) clearly shows that %MR is maximum at T_{IM} (40%) and decreases at higher temperatures. The variation of %MR with magnetic field at 4.2 K (Fig. 3) shows a maximum value of 45% at this temperature.

$La_{0.7}Sr_{0.3}MnO_3$ with $T_{IM} = 325$ K shows a small change in MR (~20%) at T_{IM} (Fig. 1). Furthermore, the %MR decreases monotonically with increasing temperature (Fig. 2). The %MR at 4.2 K is, however, nearly the same as that of the $x = 0.1$ composition (Fig. 3). The $x = 0.5$ composition, which is an insulator, showed low magnetoresistance, the %MR being 8 at 265 K and 35 at 4.2 K.

Some important conclusions from the magnetoresistance measurements on $La_{1-x}Sr_xMnO_3$ compositions are the following: all compositions show comparable %MR at high temperatures (~15% at $T \gtrsim 300$ K) at 4.2 K (35–45%). It is in the intermediate temperature range, especially close to T_{IM}, that the %MR differs significantly from one composition to another. The $x = 0.1$ composition with the highest resistivity, as well as the largest resistivity anomaly at T_{IM} (at zero field), shows the highest %MR, the low T_{IM} also being favorable for this to happen. Clearly, a GMR effect is favored when T_{IM} is relatively low (<250 K).

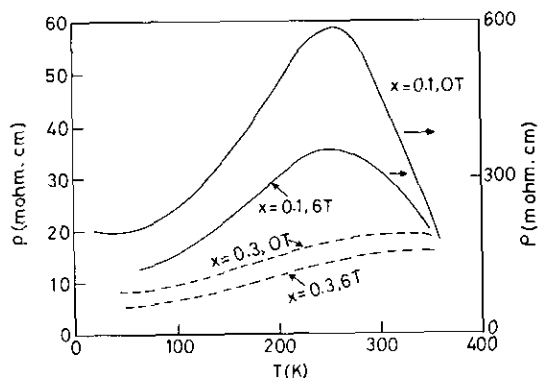Our investigations of the $La_{1-x}Ca_xMnO_3$ compositions corroborate the results obtained with $La_{1-x}Sr_xMnO_3$.
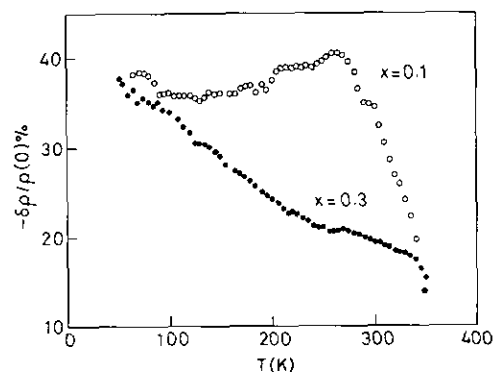

FIG. 1. Magnetoresistance behavior of $La_{1-x}Sr_xMnO_3$ samples.

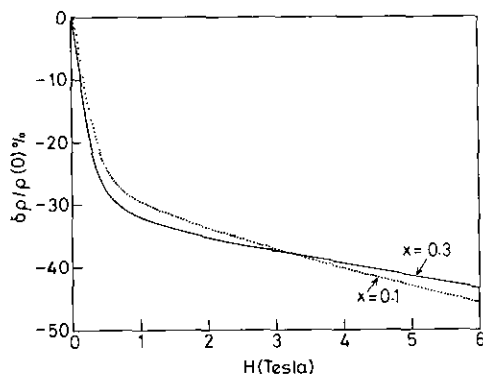FIG. 2. Temperature variation of %MR in $La_{1-x}Sr_xMnO_3$ samples at 6 T.

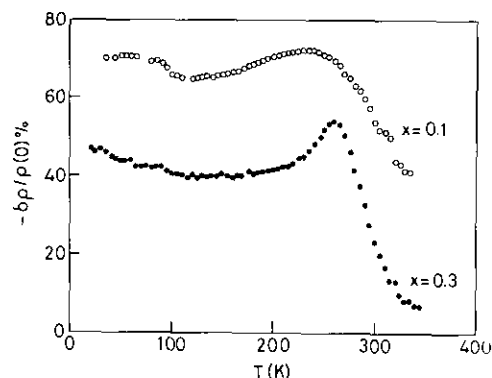FIG. 3. Variation of %MR in $La_{1-x}Sr_xMnO_3$ with applied field at 4.2 K.

FIG. 4. Temperature variation of %MR in $La_{1-x}Ca_xMnO_3$ samples at 6 T.

The $x = 0.1$ composition of $La_{1-x}Ca_xMnO_3$ shows an I–M transition around 220 K with a significant resistivity anomaly, whereas the $x = 0.3$ composition shows a transition around 260 K, with a smaller resistivity anomaly. The resistivity of the $x = 0.1$ composition is also considerably higher (~4000 mohm cm) at T_{IM} than that of the $x = 0.3$ composition (~200 mohm cm). In Fig. 4, we show the temperature variation of %MR for these two compositions. We see that at T_{IM}, the $x = 0.1$ composition has a much higher magnetoresistance (70%) compared to the $x = 0.3$ composition (56%). At 4.2 K, however, both the $x = 0.1$ and 0.3 compositions show a similar %MR (~44). It appears that the actual crystal structure is not as crucial as the occurrence of the I–M transition at relatively low temperatures. The Mn^{4+} content should, however, be sufficient to generate a transition associated with ferromagnetism. In the parent $LaMnO_3$, %MR is found to be 70% at T_{IM} (220 K) when %Mn^{4+} is 33 (8).

Two other features of the GMR phenomenon in $La_{1-x}A_xMnO_3$ systems are noteworthy. The first is the appearance of a peak in the variation of magnetoresistance with temperature (Figs. 2 and 4) in some of the compositions. Apparently, there are two competing contributions, one in which %MR decreases smoothly with increasing temperature and another which gives a peak at T_{IM}, the two contributions being controlled by different factors. The second contribution is apparently more sensitive to stoichiometry, homogeneity, and other such factors. The second feature is the sharp drop in %MR in small magnetic fields (Fig. 3), which is likely to be associated with the properties of domains. Further studies are in progress to understand the GMR phenomenon in these oxide systems in greater detail.

REFERENCES

1. R. Van Helmolt, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
2. K. Chanara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. 63, 1990 (1993).
3. M. McCormack, S. Jin, T. H. Tiefel, R. M. Fleming, J. M. Phillips, and R. Ramesh, Appl. Phys. Lett. 64(22), 3045 (1994).
4. G. H. Jonker and J. H. Van Santen, Physica 16, 337 (1950).
5. E. O. Wollan and W. C. Koehler, Phys. Rev. 100, 545 (1955).
6. J. B. Goodenough, Prog. Solid State Chem. 5, 149 (1971).
7. M. Verelst, N. Rangavittal, C. N. R. Rao, and A. Rousset, J. Solid State Chem. 104, 74 (1993).
8. R. Mahendiran, R. Mahesh, A. K. Raychaudhuri, and C. N. R. Rao, to be published.