

Colossal magnetoresistance in $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$

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 (Received 27 January 1997)

A new manganite $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ has been discovered that exhibits colossal magnetoresistance (CMR) near the Curie temperature and semiconductor-metal transition temperatures similar to that of $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ ($D=\text{Ca}^{2+}$, Pb^{2+} , etc.) or ABO_3 compounds. X-ray photoelectron spectra establish the presence of four valent Sn and Mn ions; thus the electrical conductivity is n type rather than p type as for the ABO_3 material. Also, x-ray powder diffraction indicates that the crystal structure is monoclinic. Magnetic susceptibility and Mössbauer spectra of ^{57}Fe -doped samples have also been investigated. Although the resistivity of the iron-doped manganite is now larger, the CMR is actually increased. [S0163-1829(97)04921-7]

The large magnetoresistance of the single-crystal manganites $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ was discovered at the University of Manitoba in 1969.¹ Since about 1994, the compounds $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ ($D=\text{Ca}$, Sr , Ba , Pb , and Cd , all divalent ions) and their magnetoresistance have become a lively research topic.² This resurgence of interest has occurred because the detailed mechanism of this phenomenon is not fully understood and because there are numerous potential sensor applications. All these compounds have a distorted perovskite structure³ and the electrical conductivity that is p type. More recently, large magnetoresistance has been observed in other crystal structures, namely, the pyrochlore $\text{Tl}_2\text{Mn}_2\text{O}_7$ (Refs. 4 and 5) and $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$.⁶ In this paper we report on a new manganite compound, $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ that has properties similar to the $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ compounds. However, the crystal structure is different and the Sn ion is the four-valence state so that the electrical conductivity is n type. The new compound exhibits a semiconductor-metal transition at about 245 K. At low temperatures the manganese ions are ordered ferromagnetically from the double-exchange interaction; the Curie temperature is about 254 K. In addition, samples in which 1.5% of the Mn ions have been replaced by the isotope ^{57}Fe have been studied.

Samples of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ were synthesized by the conventional ceramic technique. A mixture of the oxides (La_2O_3 , SnO_2 and MnO_2) of stoichiometric composition was

shaped by pressure and presintered at 800 °C for 8 h. Then the samples were sintered at 1250 °C for 5 h in air, below their melting point of about 1330 °C. Wet chemical analysis showed that the atomic ratio of (La,Sn) to Mn is very close to unity. In order to employ Mössbauer spectroscopy,

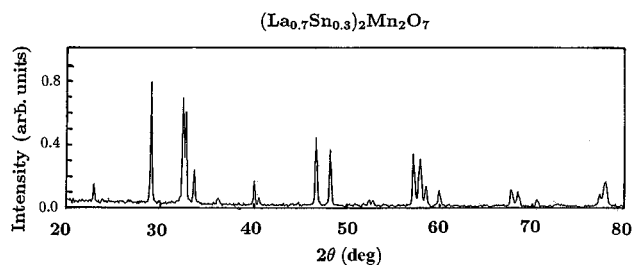


FIG. 1. X-ray diffractogram of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$; here θ is the Bragg angle.

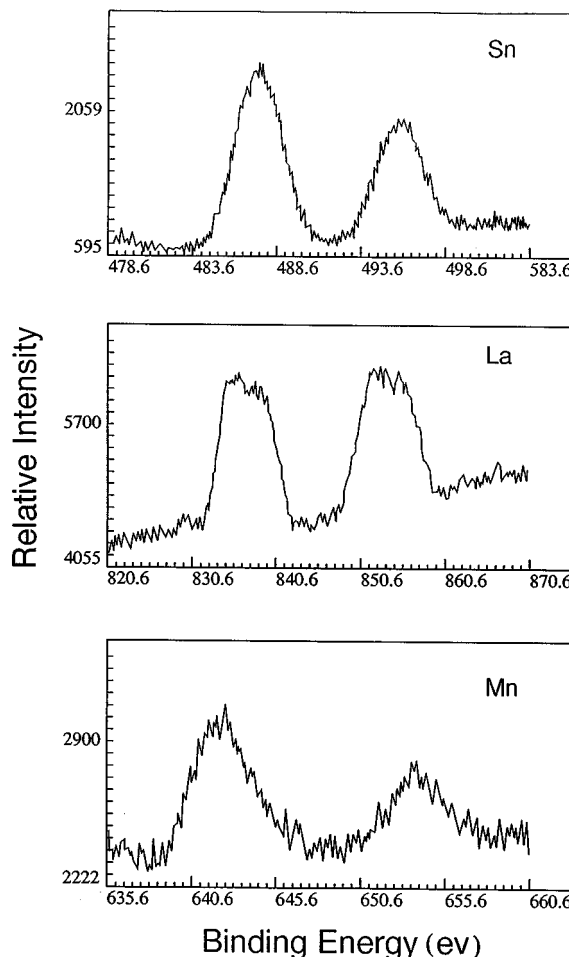


FIG. 2. X-ray photoelectron spectra for the cations of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$.

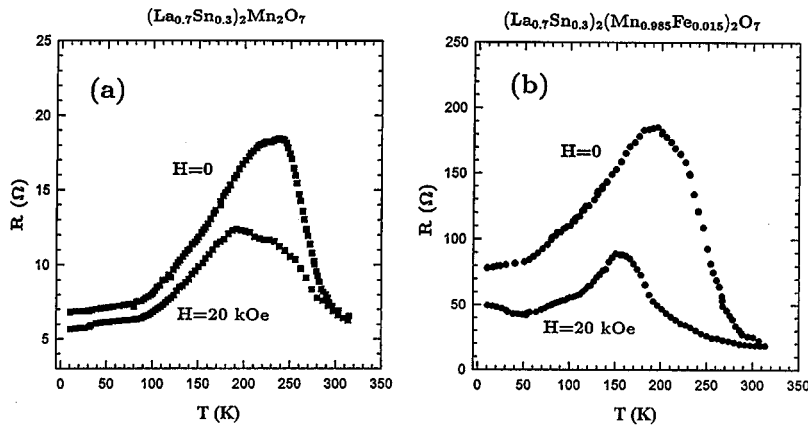


FIG. 3. Resistance-temperature curve (a) for $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ and (b) for $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$ in zero and a 20 kOe applied magnetic field.

samples with the stoichiometric composition $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$ were synthesized using the same technology.

It is well known that compounds of the $A_2B_2O_7$ type have a structure that is a three-dimensional network of corner sharing (BO_6) octahedra. The A ions and the seventh oxygen ion occupy large open spaces in this network. An x-ray powder diffractogram of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ is shown in Fig. 1. A computer program⁷ using an accuracy of 0.0008 showed that the structure could be indexed as monoclinic with the lattice parameters $a=6.4385$ Å, $b=10.7168$ Å, $c=4.9686$ Å, and $\alpha=91.48^\circ$ and a unit cell volume of 342.7 Å³. These parameters show that the unit cell is seriously distorted in comparison with a cubic structure, probably because the ionic radii of La^{3+} and Sn^{4+} are appreciably different. The strong lines of MnO_2 or Mn_2O_3 were not detected. However, there are some traces (or vestiges) of an unknown compound; these traces have not been considered in the indexing procedure.

As is well established, the electronic state of an internal orbit of an ion depends on the valence state of the ion. X-ray photoelectron spectra (XPS) of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ obtained with an ESCA-LAB5 are shown in Fig. 2. After surface stripping with Ar ions for 5 min at 1 kV at $5 \mu\text{A}$, the peak position of the $3d_{5/2}$ state of Sn is at 487.65 eV. This is consistent with the Sn $-3d_{5/2}$ state of SnF_4 ,⁸ and so it follows that the Sn ions are in the 4+ valence state. Under the same conditions, the peak position of La $3d_{5/2}$ is at 835.8 eV, which is the same as for LaF_3 ; hence the La ion is the 3+ valence state. For the manganese ions, the $2p_{3/2}$ is at 642.05 eV, the same as for Mn $2p_{3/2}$ in MnO_2 . However, the position of Mn $2p_{3/2}$ in Mn_2O_3 is at about 641.5 eV, that is, just at the lower-energy side of the observed peak. Consequently, we think that most of the manganese ions are in a four-valence state and the remainder are in the 3+ valence state. Based on charge neutrality, about 30% of the Mn ions are in the 3+ state from the electron transfer between the Sn and Mn ions.

The electrical resistance was measured by the standard four-probe method. The data for $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ for $H=0$ are displayed in Fig. 3(a). On cooling, a semiconductor-metal transition occurs at about 245 K and may be an Anderson-Mott transition, as discussed in depth by Beltz and Kirkpatrick.⁹ The ac susceptibility is shown in Fig. 4. The Curie temperature is about 254 K and the material appears to be in a ferromagnetic state. The correlation

between the resistance and the magnetization is very similar to that observed in the $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ compounds by van Santen and Jonker¹⁰ and which led Zener and others¹¹ to propose the double-exchange interaction.

After doping with 1.5 at. % /f.u. of ^{57}Fe atoms, the semiconductor-metal transition moves downwards to about 186 K, as shown in the resistance data of Fig. 3(b). Since now the electron concentration, correlation, and disorder are changed, it is to be expected that the Fermi level and mobility edge will also be changed. In the range of 190–300 K the electrical resistance versus temperature of $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$ can be fitted by the equation $R=a+b \exp(c/T)$ where $a=-30.5$, $b=27.2$, and $c=434 \text{ K}^{-1}$. In other words, this material behaves as a typical semiconductor in this temperature range. The ac susceptibility of the sample is plotted in Fig. 4 and indicates that the Curie temperature occurs at about 235 K. A similar behavior was observed earlier for the $\text{La}_{1-x}\text{Pb}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ compounds¹² and interpreted in terms of a model that considers the antiferromagnetic Fe-O-Mn superexchange interaction in addition to the ferromagnetic double-exchange interaction.

The magnetoresistive properties will now be presented. The resistance of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ in an applied magnetic

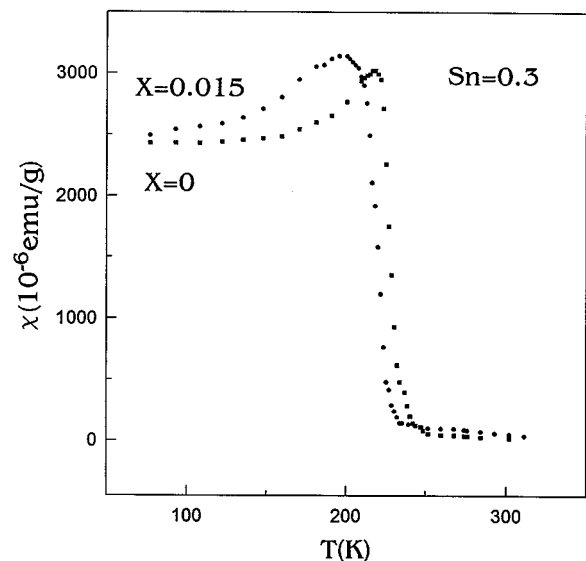


FIG. 4. The ac magnetic susceptibility of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ and a sample doped with 1.5 at. %/f.u. of ^{57}Fe .

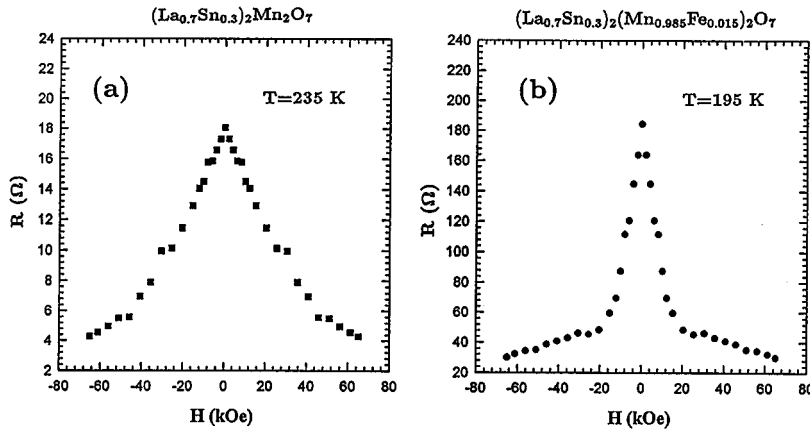


FIG. 5. The magnetoresistance (a) of $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ at the temperature 235 K and (b) of $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$ at the temperature 195 K.

field of 20 kOe is also shown as a function of temperature in Fig. 3(a). The decrease in resistivity when a field is applied is to be expected since the magnetic order is increased. The maximum occurs close to the Curie temperature. For the iron-doped sample, the general shape of the resistance versus temperature curve at $H=20$ kOe is qualitatively similar, as shown in Fig. 3(b).

The magnetoresistance at a temperature close to where the maximum effect occurs is shown for $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ in Fig. 5(a) and for the iron-doped sample in Fig. 5(b) in applied fields up to 70 kOe. The resistance of the iron-doped sample in the applied fields is higher than that of the pure sample, a result also expected because the iron ions will act as additional scattering centers for the itinerant double-exchange electrons.

The classical definition of the magnetoresistivity coefficient is given by

$$-\frac{\Delta\rho}{\rho(0,T)}100\% = -\frac{\rho(H,T) - \rho(0,T)}{\rho(0,T)}100\%, \quad (1)$$

where $\rho(0,T)$ is the resistivity evaluated in zero field and $\rho(H,T)$ is the resistivity evaluated in the applied field H . Equation (1) then expresses the fractional change in resistance expressed in present and is always less than 100%. For $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ with $H=70$ kOe this coefficient is $\sim 77\%$. It is interesting that although the absolute values of the resistance are much higher for the Fe-doped compound, the magnetoresistivity coefficient is now larger, $\sim 84\%$. A modern definition of the magnetoresistivity coefficient is the fraction

$$-\frac{\Delta\rho}{\rho(H,T)}100\% = -\frac{\rho(H,T) - \rho(0,T)}{\rho(H,T)}100\% \quad (2)$$

and can be several factors larger than 100%. This has led to the introduction of the expression ‘‘colossal magnetoresistance’’ (CMR) into the literature.

Since the Mössbauer effect is a powerful way to study the interactions between ions, ^{57}Fe spectra have been taken for $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$. The data at $T=300$ K and 77 K are shown in Fig. 6(a) and 6(b), respectively. At room temperature the ^{57}Fe ions are in a paramagnetic state, as expected. At 77 K, there are clearly two hyperfine-field split patterns and a central absorption; it follows that at least three subspectra are present, viz., two six-line patterns and a cen-

tral doublet. The spectrum at room temperature was therefore fitted with three overlapping doublets; it is possible of course that more than three subpatterns are actually present. The Mössbauer parameters obtained from the computer fitting are list in Table I.

The value of the isomer shift δ shows that all the iron ions are in the ferric (Fe^{3+}) state. Subpattern 1, with a hyperfine field of 507 kOe at 77 K, is reasonably similar to the subpattern identified as Fe ions replacing Mn ions in $\text{La}_{1-x}\text{Pb}_x\text{Mn}_{0.97}\text{Fe}_{0.03}\text{O}_3$.¹² Subpattern 2, with a hyperfine field of 479 kOe, is somewhat similar to a pattern observed for the $(\text{LaPb})(\text{MnFe})\text{O}_3$ compound¹² and tentatively identified as iron associated with oxygen vacancies primarily at or near the surface; however, the quadrupole splitting of subpattern 2 is much smaller. The amount of iron doping is too small for any appreciable number of Fe-Fe neighbor pairs,

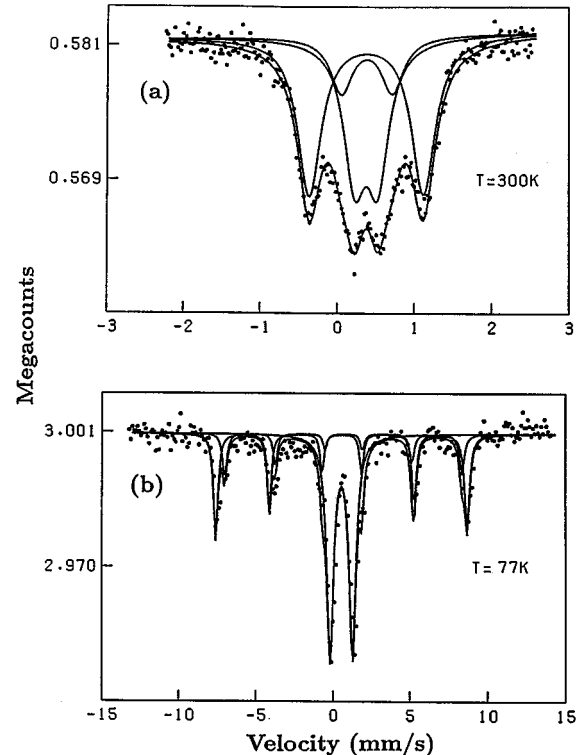


FIG. 6. ^{57}Fe Mössbauer spectra of $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$ (a) at $T=300$ K and (b) $T=77$ K.

TABLE I. Mössbauer parameters for $(\text{La}_{0.7}\text{Sn}_{0.3})_2(\text{Mn}_{0.985}\text{Fe}_{0.015})_2\text{O}_7$. Here, δ is the isomer shift with respect to α -Fe, ϵ is the quadrupole splitting, H_{hf} is the hyperfine field, Γ is the linewidth, and A is the subspectral area.

$T=77\text{ K}$					
	δ (mm/s)	ϵ (mm/s)	H_{hf} (kOe)	Γ (mm/s)	A (%)
1	0.50	-0.02	507	0.35	32.6
2	0.62	-0.02	479	0.35	13.7
3	0.49	1.47		0.35	53.7
$T=300\text{ K}$					
	δ (mm/s)	ϵ (mm/s)	H_{hf} (kOe)	Γ (mm/s)	A (%)
1	0.37	0.30		0.35	37.3
2	0.37	0.67		0.35	15.7
3	0.37	1.49		0.37	47.1

and so this cannot be the origin of subpattern 2. The large central doublet, subpattern 3, was not observed in the ABO_3 Fe-doped compound. This doublet cannot be associated with unreacted α -Fe, which has a quadrupole splitting close to zero. Its origin may be Fe ions located in the large spaces in the 2-2-7 structure. Future experiments with larger

iron dopings and at lower temperature with and without an applied field should be instructive.

The compound, $\text{La}_2\text{Mn}_2\text{O}_7$ is not easy to make since La and Mn in oxygen at high temperatures will always form the LaMnO_3 compound. However, by using a four-valence metal T such as Sn, the compound $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ can be obtained. Several of the Mn^{4+} ions are then transformed into Mn^{3+} ions. The physical properties of the $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ compound are analogous to those for $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ ($D = \text{Ca, Sr, Ba, Pb, and Cd}$). Both possess a semiconductor-metal transition and magnetic ordering below a certain temperature. However, there are important differences between the two compounds, including the crystal structure and the electronic state. Therefore $(\text{La}_{0.7}\text{Sn}_{0.3})_2\text{Mn}_2\text{O}_7$ is a new material with a fully polarized narrow conduction band. Such materials are potential sources of polarized electron beams, an application Searle attempted to achieve with the ABO_3 -type manganites in unpublished research in the 1970s.¹³

To conclude, there exist manganite compounds in addition to the ABO_3 type. New insights into the basic properties are likely to emerge from investigations on the new materials and some of them may be more useful for applications.

This research received funding from the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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