Magnetic and transport properties of polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$

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The effect of Fe doping ($\leqslant 10\%$) on polycrystalline samples of $La_{0.7}Sr_{0.3}MnO_3$ has been studied by means of x-ray diffraction, resistivity, ac susceptibility, magnetization, and magnetoresistance measurements. Fe doping does not affect the lattice structure, but it weakens the ferromagnetism and substantially augments the resistivity of the samples. The magnetoresistance of a sample with 10% Fe doping, in a 5 T magnetic field, was 4 times greater than that of the undoped sample near the peak in the resistivity. The results were explained in terms of the formation of antiferromagnetic clusters of Fe ions. At 5 K the magnetoresistance showed no significant dependence on Fe doping, but it displayed large variations in fields below 0.5 T for all samples. This behavior was attributed to spin-polarized tunneling at the grain boundaries of the polycrystalline samples. A variable-range hopping behavior in the resistivity was also encountered in all the samples at low temperatures.

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Compounds of the type $A_{1-x}B_xTO_3$ (A represents a lanthanide, B an alkali metal, and T a transition metal) have been the subject of intense research in recent years.[1–12] These materials have proved to be an ideal natural laboratory for the study of strongly correlated electronic systems, since they incorporate a wide variety of interactions and effects. A detailed study of these materials should therefore bring about a profound understanding of solid-state physics, opening up new opportunities for technological applications.

At room temperature, the perovskite compound $LaMnO_3$ is an insulator in which Mn is trivalent. The partial substitution of trivalent La ions with divalent ions such as Ca, Ba, Sr, Pb, and Cd (Refs. 1–5, 13, and 14) yields a new compound capable of exhibiting strong ferromagnetism and high metallic conductivity. For example, in the compound $La_{1-x}Sr_xMnO_3$ with the ideal stoichiometry, both Mn^{+3} and Mn^{+4} coexist, allowing the hopping of electrons between them. This phenomenon is usually explained using Zener's[15] theory of double exchange (DE). However, there is a growing body of evidence that suggests that the double-exchange model is insufficient to explain the rich variety of phenomena observed in these oxides. Perovskites of this type have been shown to exhibit the effect known as colossal magnetoresistance (CMR). In this phenomenon the application of a magnetic field near the Curie temperature T_C induces up to a thousandfold decrease in the material resistivity.[1] The effect was first observed in thin films of the oxides,[1,14] but also occurs in polycrystals[2,3] and monocrystals.[5] Another strong effect is spin-polarized tunneling across grain boundaries in polycrystalline samples.[6,7] Among other things, such as the above-mentioned intergranular effect in polycrystalline substances, it is now clear that lattice strain and deformation, which affect the Mn^{+3}–O–Mn^{+4} bond angle and length, have dramatic consequences on the properties of these systems.[16]

Another interesting way of modifying the properties of these systems is to dope the Mn site, which is the heart of DE.[3,8,17] Most investigations of Fe-doped CMR materials (or materials doped with other transition metals[8]) have been performed on oxides whose undoped compound has a ferromagnetic transition (where the CMR is more pronounced) well below room temperature.[3,8] Ahn *et al.*[3] observed that the substitution of Mn by Fe encourages an antiferromagnetic insulator behavior which opposes the DE effects. Simopoulos *et al.*[18] studied Fe doping of the compound $La_{1-x}Ca_xMnO_3$ by means of Mössbauer spectroscopy and observed that Fe is coupled antiferromagnetically to its Mn neighbors. Ogale *et al.*[19] studied the effect of doping the compound $La_{0.75}Ca_{0.25}Mn_{1-x}Fe_xO_3$ with Fe and observed the occurrence of a localization-delocalization transition in the system at a critical concentration. Ghosh *et al.*[8] studied the effect of doping in the compound $La_{0.6}Ca_{0.3}MnO_3$ with various transition elements on the CMR properties. They observed that the effects of local strains induced by the size mismatch between the dopant and the host lattice dominate the magnetotransport properties of such materials.

In this work we present results, obtained from measurements of x-ray diffraction, resistivity, ac susceptibility, magnetization, and magnetoresistance (MR), on the influence of Fe doping ($\leqslant 10\%$) on the magnetic and transport properties

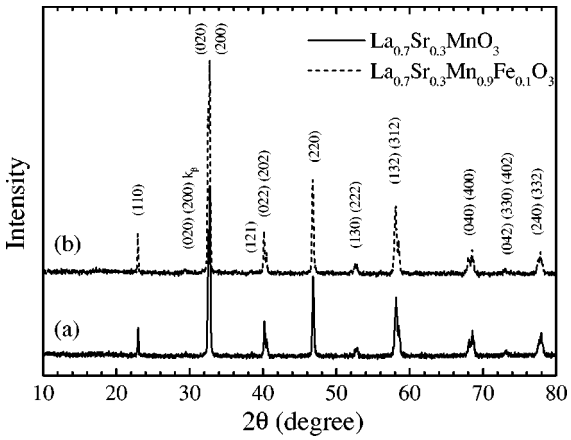

FIG. 1. X-ray diffraction pattern of polycrystalline (a) $La_{1-x}Sr_xMnO_3$ and (b) $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ fired at 1000 °C in air for 20 h, showing the Miller index of the corresponding plans.

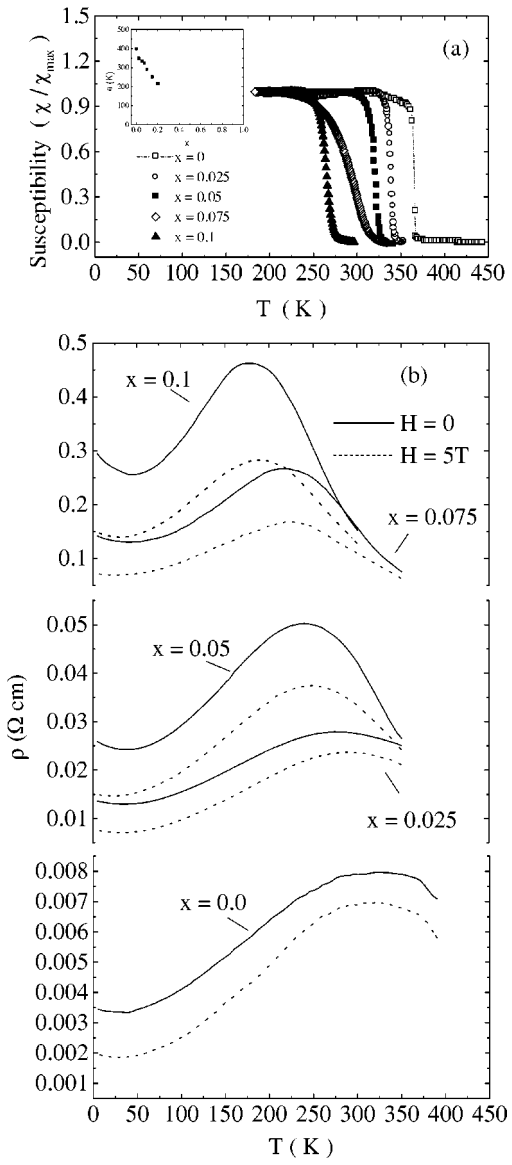

FIG. 2. Temperature dependence of χ_{ac} (a) and ρ (b) of polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ for five different values of x. Inset of (a): Weiss constant as a function of x.

of polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ ($T_C = 360$ K). There are two principal reasons why a study of this type is important: (1) Both Fe and Mn have similar ionic radii, so the crystalline structure is not modified by the addition of Fe. (2) The manganite $La_{0.7}Sr_{0.3}MnO_3$ possesses a large bandwidth which is free of phenomena such as electron-phonon interactions characteristic of narrow-bandwidth materials. Consequently, lattice effects may be ignored and effects due to the variation in electronic structure become accessible. Fe may therefore be used as a control parameter to vary only the magnetic and transport properties of these manganites.

The polycrystalline samples were prepared using the sol-gel process,[20,21] which offers unique advantages such as low sinterization temperature, precise composition control, and versatile powder formation. The precusor gel was heated to 100 °C for 20 h after which the powder was fired at 1000 °C for 20 h. The samples, in the form of compressed tablets,

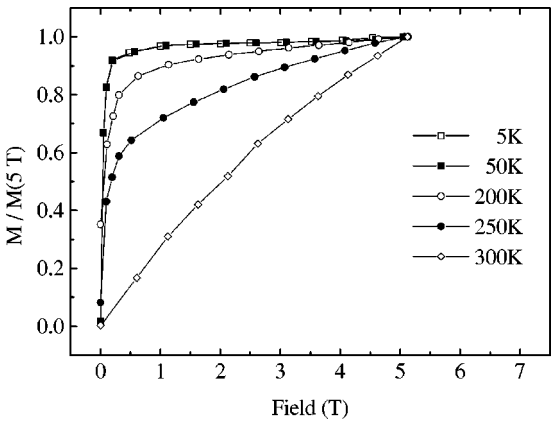

FIG. 3. Magnetic field dependence of magnetization for five different values fixed of temperature of polycrystalline $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$.

were sintered at 1000 °C and then cut into rectangular slices on which the measurements were performed. The x-ray diffraction results showed that all the samples had the perovskite structure in the absence of any secondary phases or impurities (Fig. 1).

In order to verify the effect of oxygen stoichiometry, some of the samples were exposed to a pressure of 1 atm of oxygen at a temperature of 1000 °C. No significant change in their physical properties was observed.

Resistivity ρ (in zero and 5 T fields) and MR (in fields up to 7 T) were measured using the standard four-contact technique. A conventional ac susceptometer was used to measure the magnetic susceptibility χ at a frequency of 17.5 Hz using a field of 1.5 Oe. Magnetization was measured using a superconducting quantum interference device (SQUID) from Quantum Designs Inc.

Figures 2(a) and 2(b) show representative curves demonstrating the temperature dependence of χ and ρ, respectively. As the Fe concentration x in the compound $La_{0.7}Sr_{0.3}MnO_3$ is increased up to 0.1, we observe an atypical increase in ρ accompanied by a decrease in T_C. All the samples display a maximum in ρ at some temperature $T_{max} < T_C$ (see Table I). It is interesting to note that, for each increase of 0.05 in x, the sample resistivity increases by at least an order of magnitude. The magnetoresistance (MR $= \rho_{H=0} - \rho_H / \rho_{H=0}$) near T_{max} for $x = 0.1$ is 4 times greater than that of the undoped sample.

TABLE I. Values of the Curie temperature T_C, resistivity peak temperature T_{max}, MR $= \Delta\rho/\rho_0$ at $T = T_{max}$ and 5 K, and resistivity at zero field ρ_0, for five different values of x of polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$.

x	T_C (K)	T_{max} (K)	MR $T = T_{max}$	MR $T = 5$ K	ρ_0 (Ω cm)
0.000	366	324	0.11	0.44	0.008
0.025	339	275	0.17	0.44	0.028
0.050	322	238	0.26	0.44	0.050
0.075	299	217	0.39	0.48	0.268
0.100	265	179	0.40	0.50	0.462

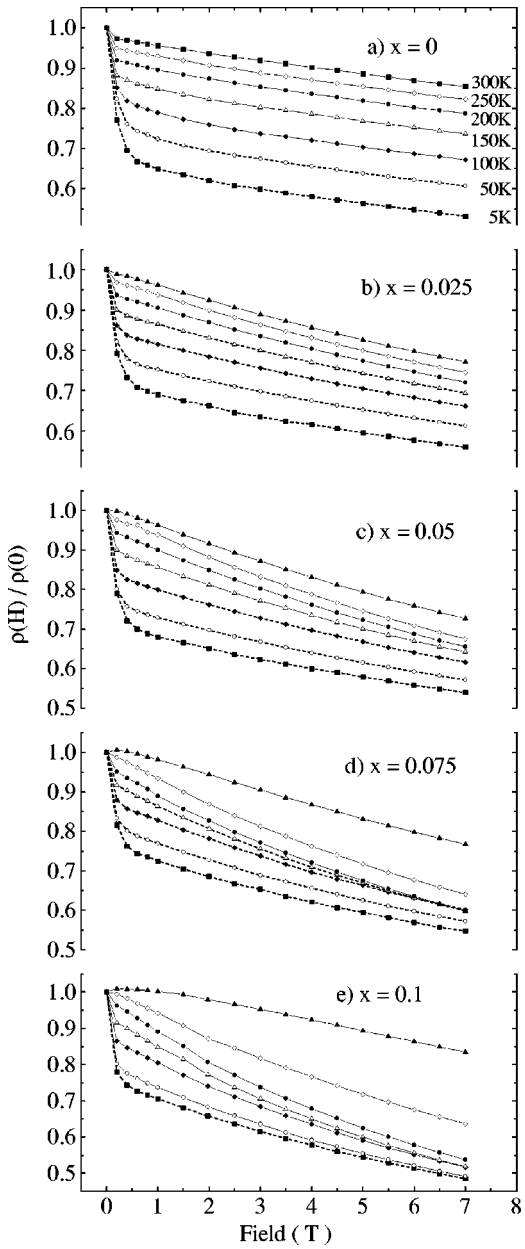

FIG. 4. Magnetic field dependence of MR for five different values of x of polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$, measured at seven different values of temperature each one.

The variations of the resistivity and of the MR due to the addition of Fe are intimately linked, as already discussed. For $T<T_{\max}$, ρ displays a metallic behavior ($\partial\rho/\partial T>0$), but at low temperatures all samples clearly show an increase in resistivity which decreases with the application of a magnetic field. This effect is characteristic of polycrystalline manganites,[12] and has been attributed to variable-range hopping of electrons in the region of disordered grain boundaries. There does not appear to be a clear correlation between a large decrease in ρ in the metallic state [Fig. 2(b)] and the ferromagnetic transition temperature as measured from the susceptibility data [Fig. 2(a)]. However, it is worth noting that the relationship between $T_{\max}$ and T_C depends on phenomena such as the effect of surface phonons associated with the grain size[10] and the oxygen stoichiometry.[11] Since the latter affects $T_{\max}$ and T_C equally, we conclude that the discrepancies between Figs. 2(a) and 2(b) are due solely to surface effects.

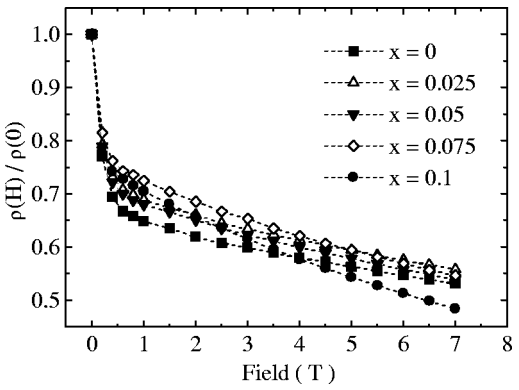

FIG. 5. Magnetic field dependence of MR for five different values of x of polycrystalline $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ measured at 5 K.

The dependence of magnetization (normalized to the value at 5 T) on magnetic field for the $x=0.1$ sample is shown in Fig. 3 at five different temperatures. The dependence of the resistivity (normalized to the zero-field value) on magnetic field is shown in Fig. 4 for five different values of x. For each x value the resistivity was measured as a function of field at seven fixed temperature values. A sharp variation in MR ($>30\%$) was observed at low fields (<5 T) for all the samples. This effect decreased as the temperature was increased. The pronounced change in resistance over this field range is associated with a field-induced reduction in the scattering from the domain walls at the grain boundaries of the polycrystalline samples. This interpretation is confirmed by the absence of such effects in epitaxial films and monocrystals.[7,9] As can be seen in Figs. 3 and 4(e), the magnetoresistance varies rapidly throughout the region in which the domains undergo rotation. The same behavior was studied, and explained as spin-polarized tunneling, by Hwang *et al.*[7] in a similar polycrystalline sample and by Li *et al.*[9] in polycrystalline films of such oxides.

For $x=0$ the MR above 0.5 T appears to be independent of temperature, but we observed an interesting temperature dependence for the Fe-doped samples. This dependence appears to be intimately related to the resistivity variation near $T_{\max}$ [cf. Figs. 2(b) and 4], as discussed below.

Previous studies have shown that, for light Fe doping ($x \leqslant 0.1$), Mn^{3+} is directly substituted by Fe^{3+} (Ref. 22). Despite the coexistence of both Mn^{3+} and Mn^{4+} in $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$, almost all the Fe is present as Fe^{3+}, as confirmed by our own Mossbäuer spectra[23] and other studies.[24] Recent Mössbauer results[18] indicate that Fe couples antiferromagnetically with its Mn neighbors. The sharp increase in the resistivity of the Fe doped samples could be related to the appearance of local antiferromagnetic (AF) ordering of the Fe atoms and their Mn neighbors. The presence of antiferromagnetic interactions was checked by measuring the Weiss constant (θ) as a function of x, from a fit to reciprocal susceptibility in the paramagnetic phase [in-

set to Fig. 2(a)]. It is seen that θ decreases rapidly with increasing x, tending towards a negative value. We note that at low concentrations in which the atoms are highly dilute, minimizing the probability of appreciable AF clusters, there should be no increase in resistivity (other than that due to the increase a reduction in the quantity of Mn^{3+}, since Fe^{3+} does not participate in the DE mechanism[3]). At the other extreme ($x \geqslant 0.2$), the AF clusters dominate the system, which becomes insulating.[23] In the range $0.05 \leqslant x \leqslant 0.1$, at which some clusters are already present, the Fe clusters depolarize the spins of their Mn neighbors. Hence, we believe that conduction, in this doping regime, is reduced by scattering off these depolarized spins. This mechanism explains the large values of MR of these samples at temperatures near T_{max}. In this range, thermal fluctuations are very strong. Application of intense magnetic fields (~ 1 T) realigns the Mn spins, favoring hopping of electrons between Mn ions and significantly decreasing the resistivity of the samples. At low temperatures AF order is fairly stable, and the magnetic field is less able to realign the spins. In this case the MR is almost solely associated with spin tunneling, and is practically independent of Fe concentration (Fig. 5).

In summary, the effect of Fe doping in $La_{0.7}Sr_{0.3}MnO_3$ on transport and magnetic properties has been studied. An increase in Fe concentration in this material decreased ferromagnetic ordering, increased resistivity, and produced large values of MR near the resistivity peak. These results were explained as due to AF Fe cluster formation. Large values of MR at low temperatures and low fields, attributed to spin-polarized tunneling at the grain boundaries, were observed. Finally, a variable-range hopping behavior was observed in the all samples at low temperatures.

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