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LETTER TO THE EDITOR

Increase of the GMR Ratios up to 10^6 by Iron Doping in the Manganite $Sm_{0.56}Sr_{0.44}MnO_3$

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The possibility of increasing the resistance ratios of the giant magnetoresistance (GMR) manganites by several orders of magnitude through doping the Mn sites with a foreign cation is demonstrated for the first time. The perovskites $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ exhibit resistance maxima characteristic of the transition from a ferromagnetic metallic (FMM) to a paramagnetic semiconducting state (PMSC) for $0 \leq x \leq 0.03$. It is shown that T_{max} decreases dramatically as x increases, from 130 K for $x = 0$ to 55 K for $x = 0.03$; phases with $x \geq 0.04$ are semiconductors. The most spectacular effect is observed for the composition $Sm_{0.56}Sr_{0.44}Mn_{0.97}Fe_{0.03}O_3$, which exhibits a T_{max} of 55 K and a resistance ratio R_0/R_H of 8×10^5 at 55 K in a magnetic field of 5 T. Another important characteristic of the latter phase deals with the abrupt decrease of its resistance by more than one order of magnitude through application of a relatively low magnetic field, less than 0.2 T at 55 K.

Recent investigations of the manganese perovskites have shown the existence of a transition from a ferromagnetic metallic (FMM) to a paramagnetic semiconducting (PMSC) state with increasing temperature, characterized by a huge variation of the resistance ratio RR = R_0/R_H (R_0 is resistance in a zero magnetic field, R_H resistance in a magnetic field H) (1). The most spectacular variations of the RR ratios were reached in the praseodymium-based manganites $Pr_{1-x}(Ca,Sr)_xMnO_3$ with $x \sim 0.30$ with values ranging from 10^6 to 10^{11} (2, 3). Soon thereafter it was demonstrated that the transition temperature T_{max} of these phases can be tuned by changing either the average ionic radius of the interpolated cation or the hole doping level (Mn(IV)/Mn(III) ratio) (4–6).

From these studies it appears that the optimization of the GMR properties of these materials requires the simultaneous introduction of more than three metallic elements into the perovskite matrix. This is confirmed by the study of the pseudo-ternary system Sm–Sr–Mn–O (7, 8), which shows that the maximum RR ratio that can be reached is 10^3 at 65 K under 5 T, so that the introduction of calcium on the Sr sites was required to increase RR up to 10^5 at 75 K.

The recent study of the Al-doped manganites suggests that the substitution of a foreign element for manganese in these oxides may improve their GMR properties (9). For this reason we have investigated the substitution of iron for manganese in these materials. The present paper reports for the first time the spectacular increase of the RR ratio to 10^6 through doping of the GMR perovskite $Sm_{0.56}Sr_{0.44}MnO_3$ with iron.

The samples examined in this study correspond to the formula $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ with $0 < x \leq 0.10$. They were prepared by standard solid-state reaction in air from $SrCO_3$, MnO_2, Sm_2O_3, and Fe_2O_3 (8). Their powder X-ray diffraction patterns are characteristic of orthorhombic perovskites, with $a \cong b \cong a_p\sqrt{2}$ and $c \cong 2a_p$ (where a_p is the parameter of the cubic perovskite). The electron diffraction study attests to the high purity of these specimens.

Electrical resistance measurements were performed on sintered bars with $2 \times 2 \times 10$ mm dimensions, using the four-probe method, from 5 K to room temperature, both in the earth's magnetic field and in a magnetic field $\mu_0 H = 5$ T. The voltage contacts were separated by 4 mm so that the resistivity is given by $\rho\ (\Omega \cdot \text{cm}) = 10^{-1} \times R\ (\Omega)$. The samples were first zero-field cooled and then the magnetic field was applied. The magnetization was monitored with a vibrating sample magnetometer; after zero-field cooling down to 5 K a magnetic field of 1.4 T was applied and the magnetization was measured with increasing temperature.

The resistance curves versus temperature in a zero field (Fig. 1) exhibit maxima at T_{max} for $0 \leq x \leq 0.03$, characteristic of the transition from a metallic to a semiconducting state with increasing temperature. One observes that the

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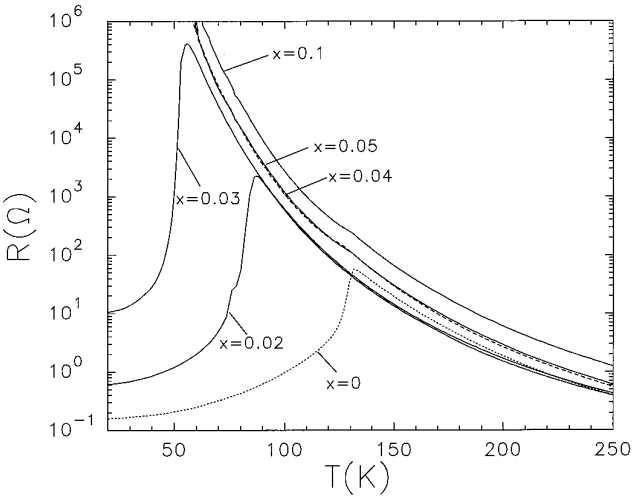

FIG. 1. Temperature dependence of the resistance R in the series $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.1$).

transition temperature T_{max} decreases dramatically from 130 K for $x = 0$ to 55 K for $x = 0.03$ as the iron content increases.

Similar behavior was previously observed for the Al-substituted manganites $Pr_{0.7}(Ca,Sr)_{0.3}Mn_{1-x}Al_xO_3$ [9]; however, the decrease of T_{max} was less dramatic, about 12 K per % Al substituted on the Mn sites, instead of about 25 K per % Fe. But the most important feature deals with the spectacular increase of the resistance peak by iron doping, several orders of magnitude higher than for the Al-substituted praseodymium manganites. For higher iron contents the transition has disappeared, yielding to a semiconducting behavior as shown for $x \geq 0.04$ (Fig. 1).

The magnetization curves versus temperature at 1.4 T (Fig. 2) confirm the ferromagnetic character of the samples

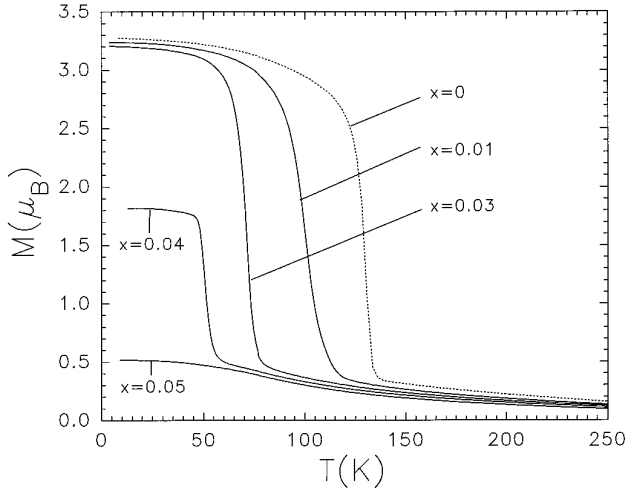

FIG. 2. Temperature dependence of the magnetic moment M per Mn atom under 1.4 T for the series $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.05$).

at low temperature for $0 \leq x \leq 0.03$, with a magnetic moment of 3.2 μ_B, close to the theoretical value of 3.56 μ_B per Mn atom. Although T_{max} does not coincide exactly with the Curie temperature T_C (because these temperatures are more or less shifted according to the applied magnetic field value), these compounds exhibit the characteristic FMM to PMSC transition. For higher x values the ferromagnetism vanishes rapidly, as shown for $x = 0.04$ and 0.05, and the FMM to PMSC transition is no longer observed.

The application of a magnetic field of 5 T displaces the resistance maxima toward higher temperatures, as shown, for instance, for $x = 0.02$ and $x = 0.03$ (upper part of Fig. 3), which exhibit a T_{max} of 135 and 115 K, respectively, instead of 85 and 55 K under zero magnetic field. Similarly, the semiconducting $R(T)$ curve corresponding to $x = 0.05$ in the earth's magnetic field is transformed into a $R(T)$ curve with a maximum at $T_{max} = 75$ K (upper part of Fig. 3). Consequently, one obtains exceptionally high RR ratios

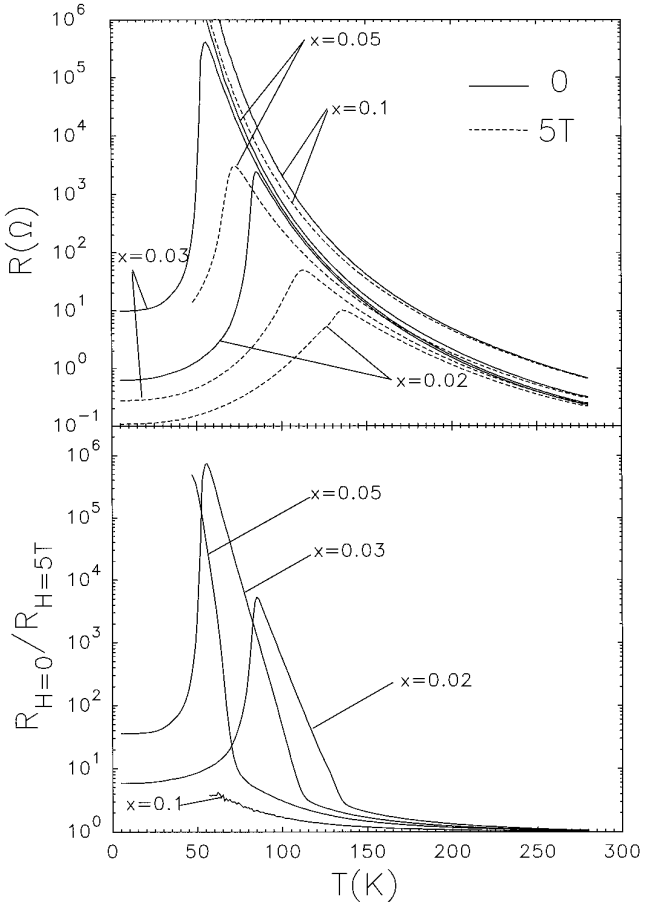

FIG. 3. (Upper part) Temperature dependence of the resistance R at $H = 0$ and at $H = 5$ T for the series $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ ($0.02 \leq x \leq 0.1$). (Lower part) RR ratios versus temperature for the same compounds and under the same magnetic fields.

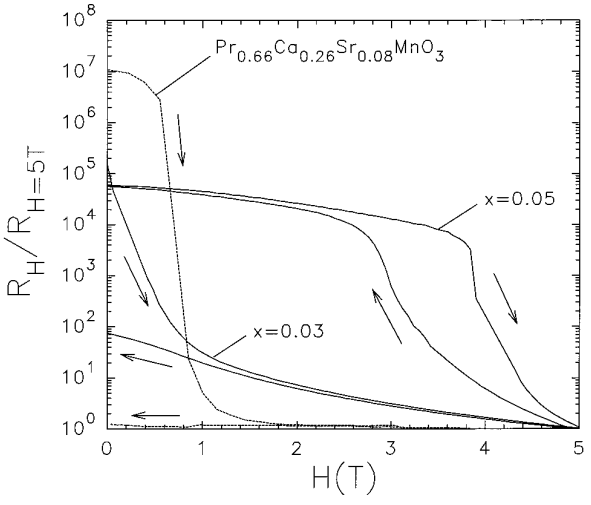

FIG. 4. Magnetoresistance ratios versus magnetic field H for $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ at 55 K ($x = 0.03$ and $x = 0.05$) and $Pr_{0.66}Ca_{0.26}Sr_{0.08}MnO_3$ at 50 K.

ranging from 5×10^3 at 85 K for $x = 0.02$, to 8×10^5 at 55 K for $x = 0.03$, or to 5×10^5 at 50 K for $x = 0.05$ (lower part of Fig. 3). Such results are quite remarkable, since it is the first time that such huge values of the resistance ratios have been observed in manganites involving only two cations (samarium and strontium) inserted in the perovskite cages.

Another important characteristic of these iron-substituted perovskites concerns the variation of resistance with applied magnetic field H. The $R(H)$ curves of the oxides $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ at 55 K compared to that of $Pr_{0.66}Ca_{0.26}Sr_{0.08}MnO_{3-\delta}$ (6) at 50 K, which also exhibits a huge GMR effect, illustrate this trend (Fig. 4). One indeed observes a very abrupt decrease of resistance for the phase $Sm_{0.56}Sr_{0.44}Mn_{0.97}Fe_{0.03}O_3$ in the range 0–0.2 T, compared to the two other phases $Sm_{0.56}Sr_{0.44}Mn_{0.95}Fe_{0.05}O_3$ and $Pr_{0.66}Ca_{0.26}Sr_{0.08}MnO_{3-\delta}$, for which the abrupt decrease of R appears only above 3.8 or 0.8 T, respectively. Such a decrease of resistance is of great interest for applications, but unfortunately appears at too low a temperature. Note also the irreversible behavior exhibited by all three compounds.

In conclusion, the possibility of inducing exceptionally high resistance ratios up to 10^6 in GMR pervoskites (A, A')MnO_3 involving only two cations in the A sites by doping the Mn sites with a foreign cation such as iron has been demonstrated for the first time. Though far from being understood, such a phenomenon may be related to the electronic configuration of the doping element rather than to its size. A Mössbauer study of these oxides is in progress in order to understand the role of iron in these properties. This dramatic effect of the doping of the Mn sites can be used from now on as a guide for the exploration and optimization of manganites with GMR properties.

REFERENCES

1. R. Von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71,** 2331 (1993).
2. B. Raveau, A. Maignan, and V. Caignaert, *J. Solid State Chem.* **117,** 424 (1995).
3. A. Maignan, Ch. Simon, and B. Raveau, *Solid State Commun.* **96,** 623 (1995).
4. A. Maignan, V. Caignaert, Ch. Simon, M. Hervieu, and B. Raveau, *J. Mater. Chem.* **5,** 1089 (1995).
5. R. Mahesh, R. Mahendiran, A. K. Raychaudhuri, and C. N. R. Rao, *J. Solid State Chem.* **120,** 204 (1995).
6. A. Maignan, Ch. Simon, V. Caignaert, and B. Raveau, *Z. Phys. B* **91,** 305 (1996).
7. V. Caignaert, A. Maignan, and B. Raveau, *Solid State Commun.* **95,** 357 (1995).
8. F. Damay, N. Nguyen, A. Maignan, M. Hervieu, and B. Raveau, *Solid State Commun.,* in press.
9. C. Martin, A. Maignan, and B. Raveau, submitted for publication.