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LETTER TO THE EDITOR

Spectacular Giant Magnetoresistance Effects in the Polycrystalline Perovskite $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_{3-\delta}$

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A polycrystalline manganite with spectacular magnetoresistive properties, $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_{3-\delta}$ has been synthesized. This perovskite-type phase exhibits a resistance variation up to 2.5×10^7% at 85 K with $\mu_0 H = 5$ T, i.e., one order of magnitude larger than has been observed on the best manganite thin films to date. The size of the interpolated cations, in addition to the mixed valence Mn(III)–Mn(IV), is a crucial parameter for the GMR effect. A route to the utilization of manganite perovskites for device applications is thereby opened. © 1995 Academic Press, Inc.

Mixed valence manganese perovskites $La_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr, Ba), synthesized several years ago in the form of thin films (1–7), have shown remarkable giant magnetoresistance (GMR) properties. These can be characterized by ratios $(R_0/R_H)_{T_c}$ near the Curie temperature T_c, where R_0 and R_H represent the resistance in zero magnetic field and in an applied field H, respectively. These films exhibit ferromagnetic properties and metallic conductivity simultaneously; $(R_0/R_H)_{T_c}$ ratios up to 10^4 have been observed. This 10^6% variation in resistivity is of the greatest interest for device applications.

The transfer of such properties to bulk materials in the form of ceramics is a challenge. The existence of the GMR effect in bulk samples of perovskites has indeed recently been observed in four series of manganites. Two of these compounds, $La_{1-x}Sr_xMnO_{3-\delta}$ (8) and $Pr_{0.75-x}La_xSr_{0.25}MnO_{3-\delta}$ (9), exhibit $(R_0/R_H)_{T_c}$ ratios of 3 and 8, respectively, for T_c ranging from 200 to 250 K. The two other phases, $La_{0.6}Y_{0.07}Ca_{0.33}MnO_{3-\delta}$ (10) and $Sm_{2/3}Sr_{1/3}MnO_{3-\delta}$ (11), appear most promising, since $(R_0/R_H)_{T_c}$ ratios of 100 near $T_c = 77$ K and of 500 near $T_c = 92.5$ K, respectively, are observed.

The latter studies show that the T_c of these phases decreases dramatically as the size of the interpolated cation decreases (9, 11). They also suggest that the ratio (R_0/R_H) near T_c depends on the nature of the interpolated cations, so that an optimization of this GMR ratio should be possible by introducing various cations in the perovskite cages, keeping the mixed valence Mn(III)–Mn(IV) unchanged. We report herein on spectacular GMR properties in a polycrystalline ceramic of the perovskite $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_{3-\delta}$, which exhibits a GMR ratio $(R_0/R_H)_{T_c}$ near $T_c = 85$ K of 250,000, i.e., 20 times larger than that obtained for the best manganite films fabricated up to now.

The perovskite $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_{3-\delta}$ was prepared by mixing $SrCO_3$, CaO, Pr_6O_{11}, and MnO_2 in appropriate proportions. The mixture was first heated in air to 900°C for 12 hr for decarbonation. The preheated phases were then pressed in the form of bars at 1 ton/cm^2, sintered at 1500°C for 12 hr, and finally cooled slowly to room temperature.

The cationic composition of the sintered bars as determined by SEM, coupled with EDS analysis, was found to be identical to the nominal composition before heating. The X-ray diffraction analysis carried out with a Guinier camera shows that the phase crystallizes as a pure pseudocubic perovskite.

The plot of dc resistivity versus temperature (Fig. 1), measured between 10 and 290 K in the earth's magnetic field on parallelepiped bars of dimensions $0.2 \times 0.2 \times 1$ cm using a standard four-point method, shows metallic behavior at low temperature and a transition to the semiconducting state, characterized by a resistivity peak, at $T_{max} = 80$ K. Note the huge amplitude of the variation close to T_{max}, which corresponds to more than five orders of magnitude in resistivity: $\rho = 4\ \Omega \cdot$cm at 50 K before the transition in contrast to $\rho = 2 \times 10^5\ \Omega \cdot$cm at the maximum for T_{max} at 85 K. The magnetization versus temperature measurements (Fig. 2), performed with a SQUID magnetometer from 5 to 300 K, provide evidence of ferromagnetic behavior of this phase at low temperature, with a transition to the paramagnetic state at around 90 K.

The magnetoresistance curves (Fig. 3) confirm the spec-

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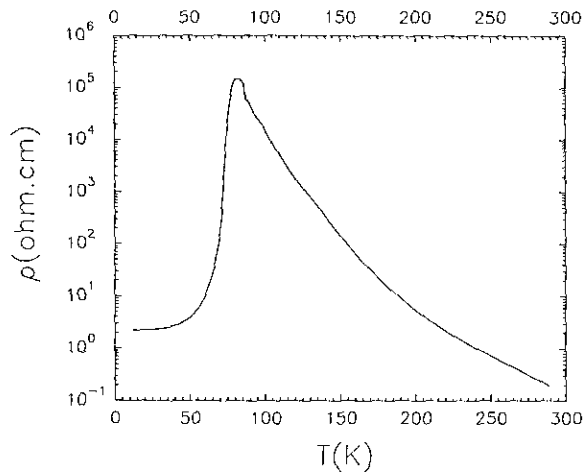

FIG. 1. Temperature dependence of the resistivity for the ceramic $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$.

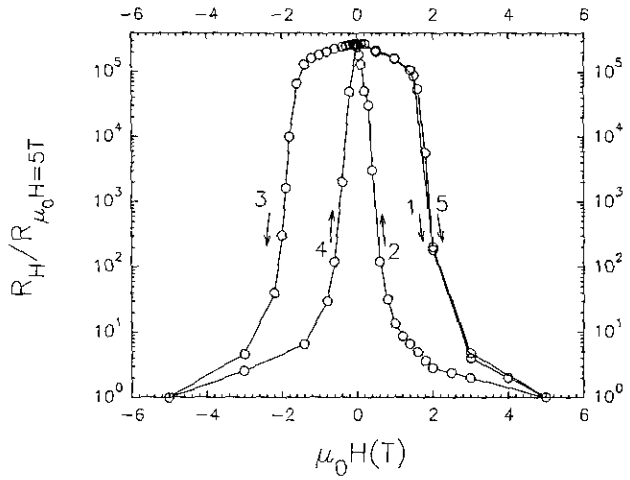

FIG. 4. Magnetic field dependence of the $R_H/R(\mu_0 H = 5\ T)$ ratio for $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$ registered at 85 K.

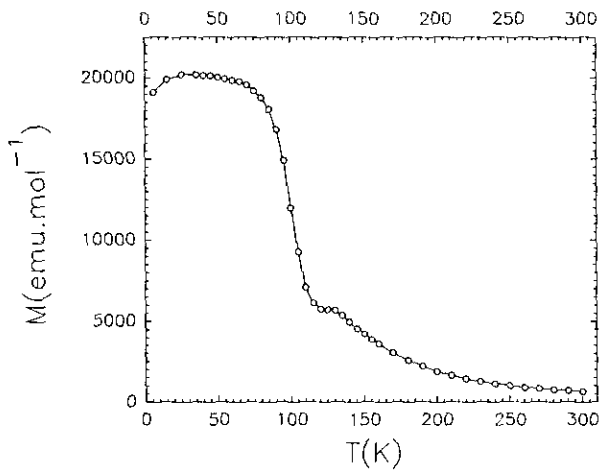

FIG. 2. Temperature dependence of the magnetization for a sample of $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$ (registered with $\mu_0 H = 1.4$ T after zero field cooling).

tacular GMR effect compared to that in other polycrystalline samples and even in manganite films. One observes a peak for R_0/R_H at $T_c = 85$ K, corresponding to a variation in resistance of $2.5 \times 10^7\%$, compared to $5 \times 10^4\%$ for the best ceramic $Sm_{2/3}Sr_{1/3}MnO_{3-\delta}$ (11) and to $1.06 \times 10^6\%$ for the best films of $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$, which were recently prepared (12) but with a lower T_c of 60 K and in a magnetic field of 8 T. This effect is confirmed by the changes in the R_0/R_H ratio ($\mu_0 H = 5$ T) at 85 K, which shows a spectacular drop in the range 0–2 T (Fig. 4), and by the hysteretic nature of the phenomenon.

To test the sensitivity of the GMR effect to variations in the interpolated cation, solid solutions of $Pr_{0.7}Sr_{0.30-x}Ca_xMnO_{3-\delta}$ were studied for $x = 0.10$, 0.15, 0.20, and 0.25. The resistivity curves versus temperature are shown in Fig. 5. In all cases one observes a peak which corre-

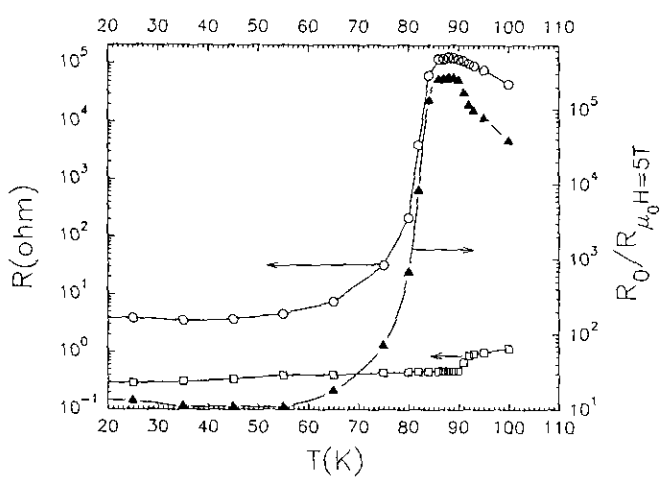

FIG. 3. Temperature dependence of R_0 ($H = 0$), R_H ($\mu_0 H = 5$ T) and R_0/R_H for $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$: $R_0(0)$, R_H (□) and $R_0 + R_H$ (▲).

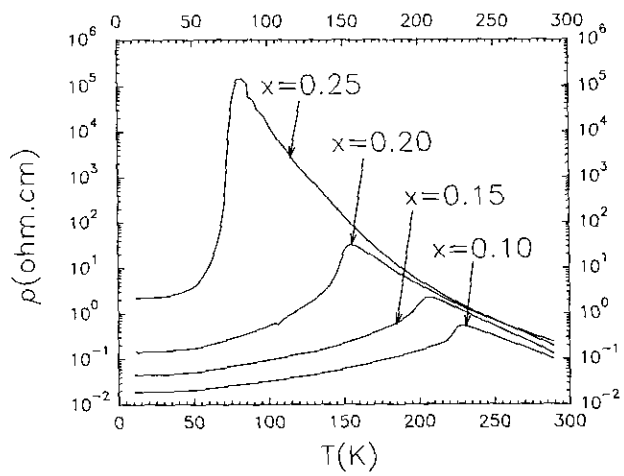

FIG. 5. Temperature dependence of the resistivity for different samples of the series $Pr_{0.7}Sr_{0.3-x}Ca_xMnO_3$; the different x values ($0.05 \leq x \leq 0.25$) are labeled on the graph.

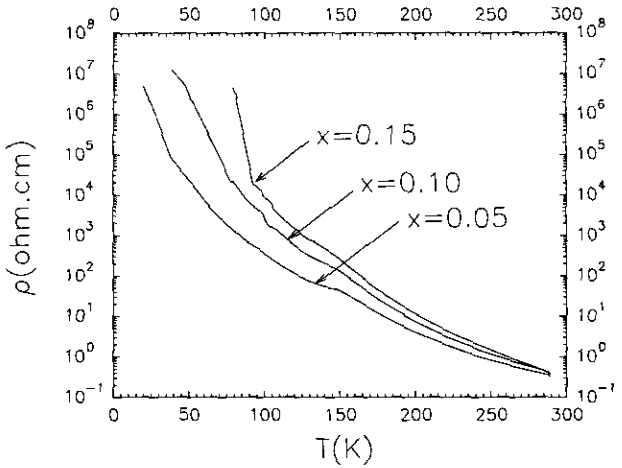

FIG. 6. Temperature dependence of the resistivity for different samples of the series $Pr_{0.8}Sr_{0.2-x}Ca_xMnO_3$ with $x = 0.05, 0.1, 0.15$.

sponds to a transition from the metallic to the semiconducting state when T is increased. The transition temperature T_{max} decreases dramatically from 225 K for $x = 0.10$ to 155 K for $x = 0.20$ as strontium is replaced by calcium; $x = 0.25$ corresponds to the title compound with T_c = 85 K. This confirms our previous statement (9, 11) that T_c in these phases decreases dramatically as the size of the interpolated cations decreases. Of great interest is the fact that all the compositions of this solid solution, except $x = 0.25$, exhibit a weak drop in resistivity, with a variation in resistivity smaller than one order of magnitude close to the maximum. This effect is very sensitive to the molar ratios Pr/(Sr + Ca), as shown for the series $Pr_{0.8}Sr_{0.2-x}Ca_xMnO_{3-\delta}$ with $x = 0.05, 0.10$, and 0.15, which are all semiconductors (Fig. 6).

In conclusion, this study demonstrates that exceptionally large magnetoresistance effects, considerably higher than those in thin films, can be obtained in bulk polycrystalline manganite samples. This result is of the greatest interest in device applications. Although the phenomenon is not yet understood, it appears that the size of the interpolated cation plays a dominant role in the magnitude of the GMR effect, with the mixed valence Mn(III)–Mn(IV) also being an important factor. This opens the route for the generation of new manganites, taking into consideration the relative size of the lanthanide alkaline earth ions. Nevertheless, a large effort will have to be mounted to explore the role of oxygen deficiences and of extended defects in these phases.

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