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# LETTER TO THE EDITOR

# CMR Effect in Electron-Doped Manganites $Ca_{1-x}Sm_xMnO_3$

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**The magnetic and transport properties of the Mn(IV)-rich perovskites $Ca_{1-x}Sm_xMnO_3$ have been investigated for $x \leq 0.20$. These compounds exhibit very unusual magnetic behavior, especially for $0.14 \leq x \leq 0.20$, where a peak is observed on the $M(T)$ curves, whose temperature $T_{peak}$ increases with $x$, whereas their height decreases. Moreover, colossal magnetoresistance properties are exhibited for the first time in these electron-doped systems, as shown for $x = 0.15$, which exhibits resistance ratios $R_0/R_{7T}$, of $10^2$ and 10 at 50 and 100 K, respectively. These properties are interpreted in terms of a competition between ferromagnetism and antiferromagnetism, in connection with two opposing factors, namely, electron delocalization and charge ordering.** © 1997 Academic Press

Recent studies of the manganese perovskites have shown that one can induce colossal magnetoresistance (CMR) properties in lanthanide manganites $LnMnO_3$ by hole doping. In these systems, starting from the electronic configuration of Mn(III), $(t_{2g})^3(e_g)^1$, mobile holes are created in the $e_g$ band of manganese, either by partly replacing the lanthanide element with a divalent cation $A$, according to the formula $Ln_{1-x}A_xMnO_3$ (1–7), or by introducing a lanthanide deficiency, as in $La_{1-x}MnO_3$ (8, 9). The realization of such properties requires a high Mn(III) content, i.e., a lanthanide-rich composition, in order to avoid the charge ordering phenomena that appear for the oxides $Ln_{0.5}A_{0.5}MnO_3$ (10, 11).

In contrast, no CMR effect has been noted to date in Mn(IV)-rich manganites, i.e., manganites containing only a few percent of lanthanide. The investigation of such compounds should be fruitful since they correspond to the doping of a Mn(IV) insulating matrix by electrons, so that a transition toward a metallic or semimetallic state should be induced. The recent evidence for large negative magnetoresistance in $Bi_{1-x}Ca_xMnO_3$ (12), although modest compared to lanthanide manganites, i.e., $R_0/R_{7T} \sim 3$ at 50 K, is in agreement with this viewpoint. For this reason we have revisited the $LnMnO_3$–$CaMnO_3$ system on the calcium-rich side. In the present letter, we report on the electron-doped manganites $Ca_{1-x}Sm_xMnO_3$ ($0 < x \leq 0.20$) that exhibit a semimetallic to insulating transition in the temperature range 100–150 K, together with an induced ferromagnetic component at low temperature, so that CMR properties with resistance ratios $R_0/R_{7T}$ larger than $10^2$ can be obtained at 50 K.

The oxides $Ca_{1-x}Sm_xMnO_3$ were prepared from mixtures of CaO, $Sm_2O_3$, and $MnO_2$ heated at 1000°C in air, pressed into the form of bars, heated at 1200°C, and then sintered 12 h at 1500°C. The purity, homogeneity, and composition of the samples were checked by X-ray diffraction, electron diffraction, and EDS analysis.

Resistivity measurements (four-probe method) were performed with a physical properties measurement system (PPMS, Quantum Design), on $2 \times 2 \times 10$ mm bars, so that the resistivity $\rho(\Omega.cm) = 10^{-1} \times R(\Omega)$. Curves were obtained on cooling, the 7-T magnetic field being applied at 300 K. Magnetization measurements were obtained by means of a SQUID magnetometer.

The magnetization curves $M(T)$ in a magnetic field of 1.45 T (Fig. 1) show that for low $x$ values ($0 < x \leq 0.12$) a ferromagnetic state is induced at low temperature, i.e., for $T \leq 100$ K. The corresponding $R(T)$ curves (Fig. 2) clearly establish that, for this composition range, the resistance of the samples is significantly decreased with respect to that of $CaMnO_3$, tending toward semimetallic behavior between 110 and 300 K, for $x$ ranging from 0.075 to 0.12. The properties of this first series of samples can be explained by the fact that doping with samarium introduces mobile electrons into the $e_g$ band, so that the interaction of these carriers via $t_{2g}$ spins induces ferromagnetic coupling. The tendency to exhibit a transition toward a ferromagnetic metallic state is clearly seen by the anomaly in the $R(T)$ curve of the $x = 0.1$ sample (inset Fig. 2), which appears at $T_C = 110$ K, in agreement with the $M(T)$ curve (Fig. 1).

For higher $x$ values ($0.14 \leq x < 0.20$) the $M(T)$ curves are quite unusual (Fig. 1). One observes an abrupt collapse



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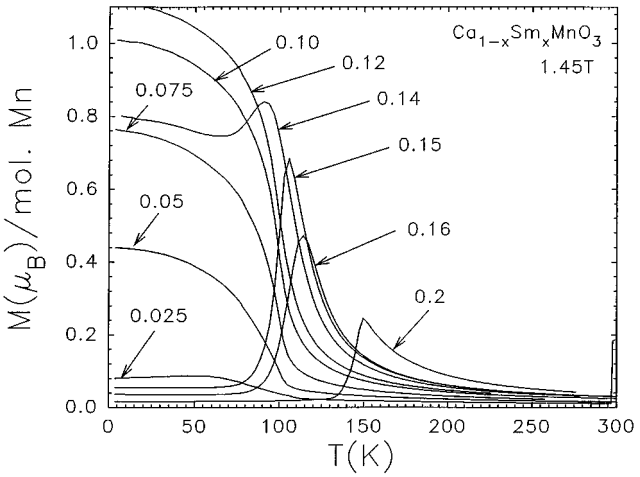


**FIG. 1.** Temperature dependence of the magnetization $M$ registered under 1.45 T for the series $Ca_{1-x}Sm_xMnO_3$ ($x$ values are labeled on the graph).

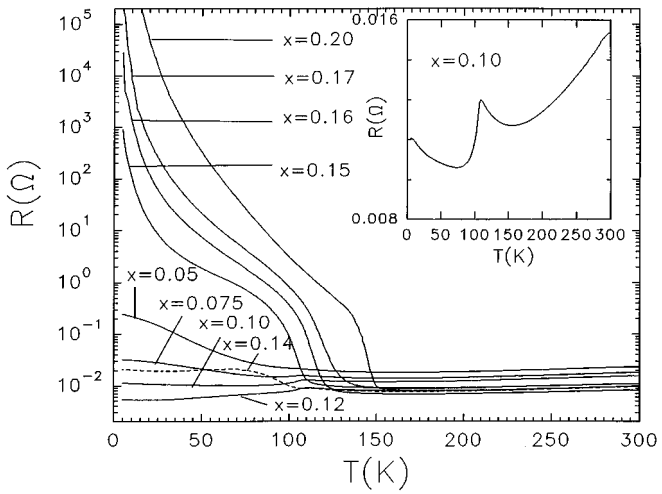


**FIG. 2.** Temperature dependence of the resistance $R$ for the series $Ca_{1-x}Sm_xMnO_3$ ($x$ values are labeled on the graph). Inset: Enlargement of the $x = 0.1$ curve.

of the magnetic moment at low temperature, for $x$ larger than 0.14, indicating a return to the antiferromagnetic state for $T < 100$ K. But the most striking feature concerns the $M(T)$ peak, which is rather sharp for $0.15 \leq x \leq 0.20$. This phenomenon, also observed for $Bi_{0.2}Ca_{0.8}MnO_3$ (12, 13) for $x$ ranging from 0 to 0.25, can be explained by competition between electron delocalization and charge ordering. The introduction of electrons at the $e_g$ level of Mn(III) favors electron delocalization and consequently induces the ferromagnetic component. By contrast the tendency to charge ordering and consequently to antiferromagnetism is favored as $x$ increases and approaches $x = 0.25$, in agreement with the neutron diffraction study previously made for $(La, Ca)MnO_3$ (14). The competition between these two opposing effects favors electronic delocalization for low $x$ values (far from $x = 0.25$), leading to ferromagnetism, whereas charge ordering becomes predominant for higher $x$ values, i.e., as $x$ tends to 0.25, leading to antiferromagnetism. The increase of the $T_{peak}$ from 105 K for $x = 0.15$ to 150 K for $x = 0.20$ and the decrease of the peak intensity as $x$ increases is thus easily explained by a rapid expansion of the antiferromagnetic state (charge ordering) at the expense of ferromagnetism (electronic delocalization). The $R(T)$ curves observed for $x = 0.14$ and 0.20 (Fig. 2) are also in agreement with this interpretation: they show a transition (at 100 and 150 K) from a semimetallic to a semiconducting state as $T$ decreases, similar to that observed in the charge-ordered manganites $Ln_{0.5}A_{0.5}MnO_3$ (10, 11).

The $R(T)$ curves in a 7 T magnetic field (Fig. 3) exhibit negative magnetoresistance over the whole domain $0 < x \leq 0.20$. The low $x$ values $0 < x < 0.12$, which exhibit a ferromagnetic transition, are characterized by small magnetoresistance ratios $R_0/R_{7\,T}$, ranging from 1.8 for $x = 0.05$ (Fig. 3a) to 1.5 for $x = 0.10$ (Fig. 3b) at 50 K. Such a small effect is comparable to that described for the bismuth manganite $Bi_{1-x}Ca_xMnO_3$ (12), for which a resistance ratio (RR) of 3 is observed at 50 K. This can be explained by the fact that the resistance in the ferromagnetic state and near the ferromagnetic state (i.e., above $T_C$) is rather low, so that the application of a magnetic field cannot dramatically modify the resistance. In contrast, as soon as we reach the peak region on the $M(T)$ curves, i.e., $0.14 \leq x < 0.20$, involving a competition between ferromagnetism and antiferromagnetism, much higher RR are obtained. The RR value increases to 6 at 50 K for $x = 0.14$ (Fig. 3c), whereas the sample $x = 0.15$ exhibits CMR with resistance ratios of $10^2$ at 50 K and larger than 10 at 100 K (Fig. 3d). A further increase of $x$ leads to a decrease of RR at 50 K, as shown for $x = 0.16$ (Fig. 3e) and $x = 0.17$ (Fig. 3f) for which the RR is equal to 10 and 3 at 50 K respectively. Note, however that the RR at 110 K (near the $M(T)$ peak) of the two latter samples are still high, i.e., 15 and 7 respectively. Finally, for $x = 0.20$, the magnetoresistance effect completely disappears below 120 K, but the resistance ratio still remains high, close to 10, around 140 K, the temperature which corresponds to the $M(T)$ peak (Fig. 3g). The phases $Ca_{1-x}Sm_xMnO_3$ are very similar to the charge-ordered manganites $Ln_{0.5}A_{0.5}MnO_3$ (10, 11) which also exhibit CMR properties, in connection with the ferromagnetic metallic to antiferromagnetic insulating transition at low temperature. However in the latter, a much larger interpolated cation is required for the appearance of such an effect, since, for example, the manganite $Ca_{0.5}Pr_{0.5}MnO_3$ does not exhibit any CMR effect below

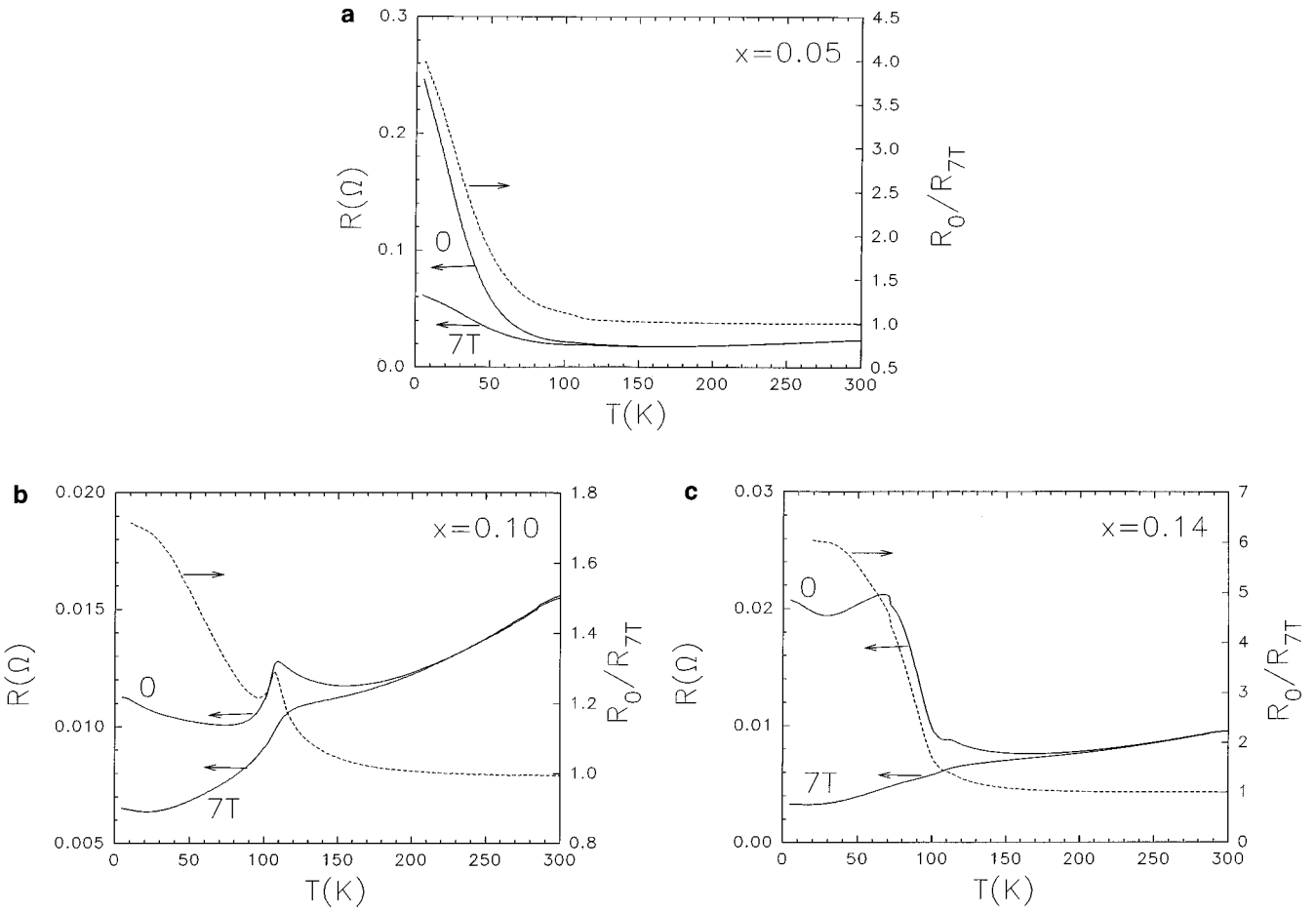


**FIG. 3.** $R(T)$ curves registered under 0 and 7 T (left axis) and $R_{B=0}/R_{B=7\,T}$ ratio (right axis) for the series $Ca_{1-x}Sm_xMnO_3$ with $x = 0.05$ (a), $x = 0.1$ (b), $x = 0.14$ (c), $x = 0.15$ (d), $x = 0.16$ (e), $x = 0.17$ (f), $x = 0.2$ (g).

7 T. Moreover, it is remarkable that the pure ferromagnetic metallic state is in fact not observed in the electron-doped manganites $Ca_{1-x}Sm_xMnO_3$. Consequently, it can be stated that the presence of ferromagnetic interactions within an antiferromagnetic insulating matrix is sufficient to induce the CMR effect.

Inspection of half-hysteresis loops registered at 10 and 100 K for $Ca_{0.85}Sm_{0.15}MnO_3$, which is the most CMR compound, is very instructive (Fig. 4). At 10 K (Fig. 4a) the magnetization values are limited to less than 0.12 $\mu_B$ per Mn. The first magnetization curve, with an abrupt increase below 0.2 T indicating the existence of a weak ferromagnetic component, shows only a slight upturn for magnetic fields higher than 3 T. At this temperature, the sample is thus an antiferromagnet with a weak ferromagnetic component strengthened by the magnetic field. The slight change of the slope observed for $H > 3$ T induces irreversible modifications of the $M(H)$ loops, leading to higher $M$ values for the decreasing branch of the magnetic field. As $T$ is increased, the effectiveness of the magnetic field in inducing a ferromagnetic component increases. On the $M(H)$ half-loop registered at 100 K (Fig. 4b), one can see that the magnetization reaches values up to 0.8 $\mu_B$/Mn in 5 T. Here again, hysteresis exists for the largest magnetic field values, but in low magnetic fields ($H \leq 0.2$ T) the curves become reversible, so that the sample state is not modified after a complete cycle, in contrast to the behavior observed at 10 K. Finally, it appears thus that the magnetic behavior of this CMR compound is that of an antiferromagnet, where a weak ferromagnetic component exists, so that it can be considered as a ferrimagnet. The application of a magnetic field tends to reinforce the ferromagnetic component at the expense of antiferromagnetism; this effect is amplified as the temperature is increased. Nevertheless, the lack of magnetization saturation even in 5 T and at $T = 100$ K suggests that higher magnetic fields are required to reach the expected

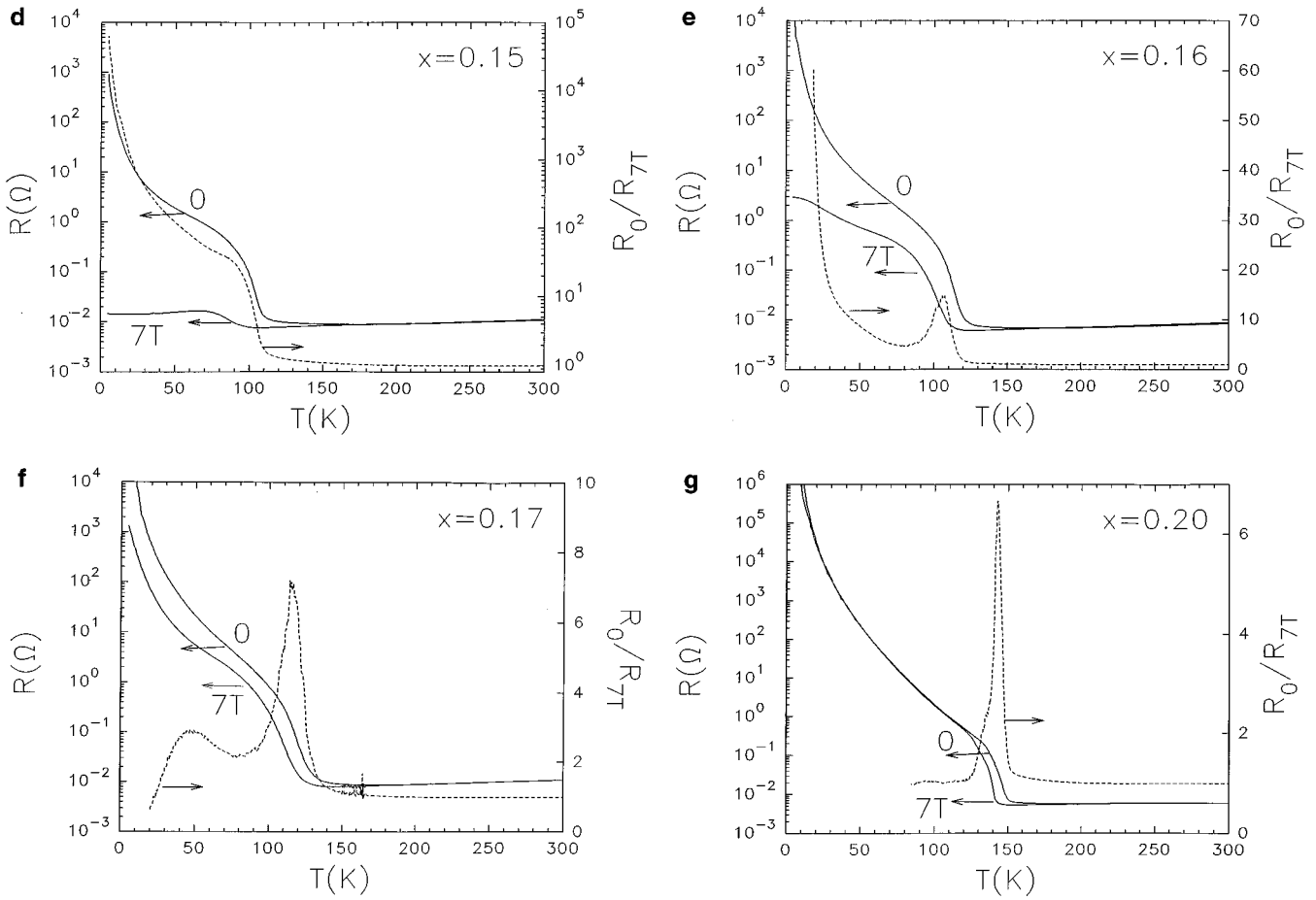


**FIG. 3**—*Continued*

magnetic moment of $\sim 3\,\mu_B$/Mn. The physical properties of $Ca_{0.85}Sm_{0.15}MnO_3$ may be explained via a double exchange (DE) model (15). The magnetic field application reinforces the ferromagnetic component, so that the carrier scattering decreases, thereby inducing negative magnetoresistance.

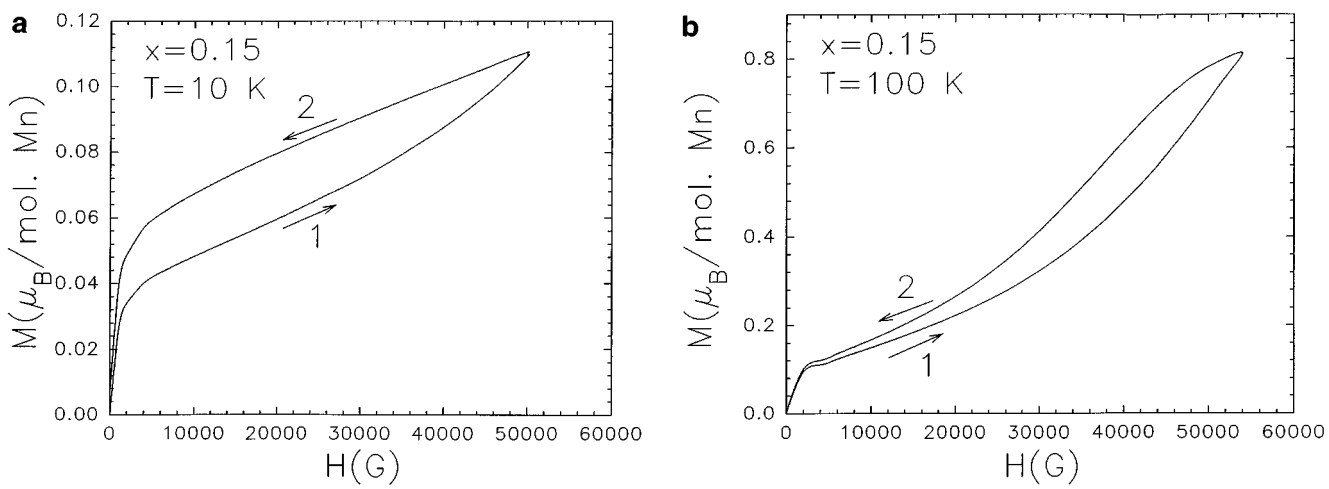


**FIG. 4.** Magnetic field dependence of the magnetization $M$ for $Ca_{0.85}Sm_{0.15}MnO_3$ ($x = 0.15$) at 10 K (a) and 100 K (b).

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