JOURNAL OF SOLID STATE CHEMISTRY **130,** 162–166 (1997)
ARTICLE NO. SC977373

LETTER TO THE EDITOR

Insulator–Metal Transition Induced by Cr and Co Doping in $Pr_{0.5}Ca_{0.5}MnO_3$

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Communicated by J. M. Honig February 28, 1997; accepted March 4, 1997

The study of the perovskite manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ with M = Cr and Co has been carried out. It shows that the doping of the insulating antiferromagnetic phase $Pr_{0.5}Ca_{0.5}MnO_3$ with chromium or cobalt induces an insulator to metal transition. This behavior is exceptional since such a transition has never been observed to date in charge ordered manganites $Ln_{0.5}Ca_{0.5}MnO_3$ with an A-site cation of such a small size (Ln = Pr). The transition temperature to the ferromagnetic metallic state ranges from 110 to 150 K and from 60 to 80 K for chromium and cobalt, respectively. These Cr- and Co-doped manganites exhibit colossal magnetoresistance properties with resistance ratios (R_0/R_{7T}) ranging from 3×10^4 at 60 K to 30 at 150 K for chromium and from 3×10^6 at 60 K to 2×10^4 at 75 K for cobalt.

The recent studies of perovskite manganites ($Ln_{1-x}A_xMnO_3$) led to the discovery of colossal negative magnetoresistance (CMR) properties (1–8). Such CMR effects originate from a double exchange mechanism between Mn(III) and Mn(IV) species (9–11) that induces ferromagnetic correlations. The appearance of ferromagnetism is thus absolutely necessary for the occurrence of insulator–metal transitions (I–M), that coincide with T_C in these CMR oxides.

The investigation of the crystal chemistry of these mixed-valent manganites has shown that at least three factors govern the I–M transition in these materials (4, 12–16): the average size of the interpolated cations (A, Ln), the mixed valence state of manganese (hole carrier density), and the size mismatch between the A and Ln cations. The fact that the manganite $Pr_{1-x}Ca_xMnO_3$ remains insulating whatever the value of x (17–19) can be interpreted on this basis: the average size of the Pr^{3+} and Ca^{2+} cations are too small to develop the I–M transition. Nevertheless, such a transition can be induced by applying a magnetic field, as shown, for instance, for $Pr_{0.7}Ca_{0.3}MnO_3$ (20). However, for $x \cong 1/2$, the charge ordering between the Mn(III) and Mn(IV) species suppresses the I–M transition, so that $Pr_{0.5}Ca_{0.5}MnO_3$ remains an insulator whatever the value of the applied magnetic field up to 7 T.

The study of the substitution of various metallic elements for manganese in such perovskite manganites has shown that it was possible to modify dramatically their magnetic and transport properties (21–24). This is especially the case for doping of $Pr_{0.5}Ca_{0.5}MnO_3$ with Mg^{2+}, Al^{3+}, Fe^{3+}, Ti^{4+}, or Sn^{4+}, which suppresses charge ordering (24). Although these doped compounds remain insulating in a zero magnetic field, they exhibit huge magnetoresistance effects when subjected to a magnetic field of 7 T, in contrast to the pure phase $Pr_{0.5}Ca_{0.5}MnO_3$ that does not exhibit any CMR effect. Chromium and cobalt, owing to their various oxidation states, Cr(III), Cr(IV), Co(II), Co(III), and Co(IV), are susceptible to changes in magnetic and transport behavior. In the present letter, we report on the spectacular doping effect of cobalt and chromium upon the properties of $Pr_{0.5}Ca_{0.5}MnO_3$. An insulator–metal transition in the absence of magnetic field is indeed shown to occur for the first time, in spite of the small size of the interpolated cations (Pr, Ca). Large CMR effects with resistance ratios up to 10^6 in a magnetic field of 7 T are also observed.

The doped manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ with M = Cr, Co were synthesized in the form of bars, from mixtures of oxides Pr_6O_{11}, CaO, Mn_2O_3, and Cr_2O_3 or Co_3O_4, heated in air up to 1500°C, according to the experimental procedure previously described for the other manganites (21, 22).

The variation of the resistance versus temperature, measured with the four probe technique in the earth's magnetic field, is presented in Fig. 1. Doping with a small amount of chromium and cobalt leads to a rapid disappearance of the charge ordering for $x > 0.02$. The elimination of charge ordering by doping $Pr_{0.5}Ca_{0.5}MnO_3$ with a foreign element is not new: it has previously been observed for the manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ with M = Fe, Al, Ga, Ti (24).

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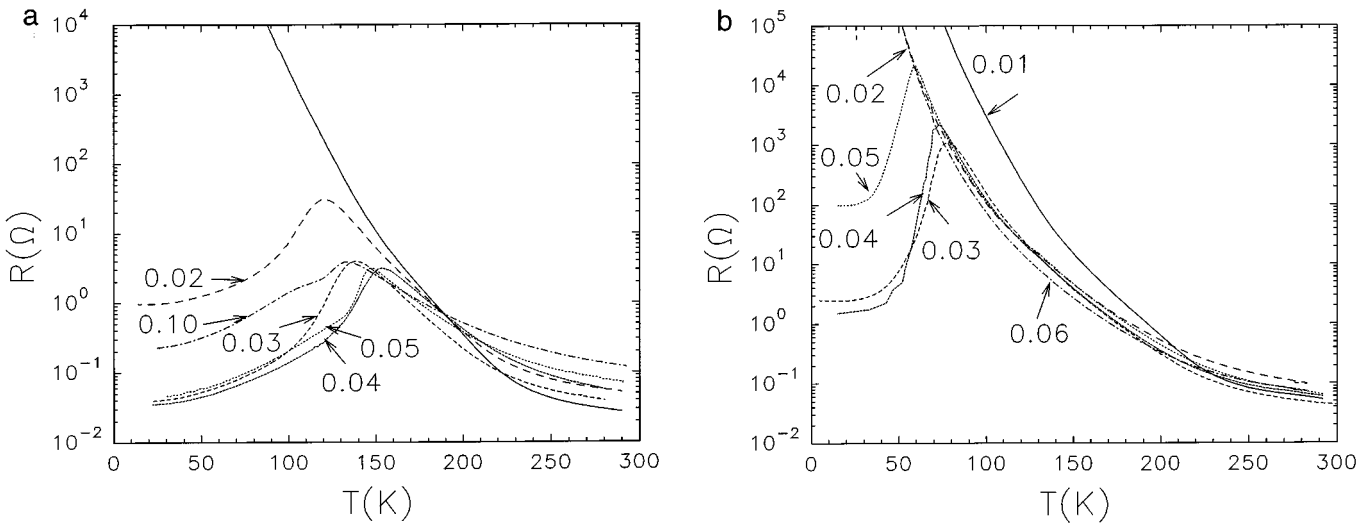

FIG. 1. (a) T dependence of the resistance R registered during cooling for the series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ (x values are labeled on the graph). (b) $R(T)$ curves for the series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Co_xMnO_3$.

But most surprising is the fact that the doping induces a resistance peak characteristic of an I–M transition as T decreases. This behavior is very different from that observed for other manganites, $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$, that remain insulating, like $Pr_{0.5}Ca_{0.5}MnO_3$, whatever M = Al, Fe, Ga, Ti and whatever the doping level. Such an I–M transition is remarkable since it had never been observed in manganese with an A-type cation of such a small average size. The second remarkable feature concerns the transition temperature T_{max} of the Cr-doped manganites (Fig. 1a), which increases significantly as the chromium content increases up to $T_{max} \cong 150$ K for $x = 0.05$ and then decreases for $x > 0.05$. For the Co-doped manganites (Fig. 1b), the transition temperature T_{max} is much smaller, ranging from 60 to 80 K, as against 110–150 K for the Cr doped phases. Consequently, the peak resistance is only observed in a narrow doping range: for $x \leq 0.02$ the Co-phase is insulating, as well as for $x \geq 0.06$, whereas for the intermediate Co content T_{max} seems to decrease from 80 K for $x = 0.03$ to 60 K for $x = 0.05$.

The magnetization curves $M(T)$ (Fig. 2) determined with a vibrating sample magnetometer in a magnetic field of

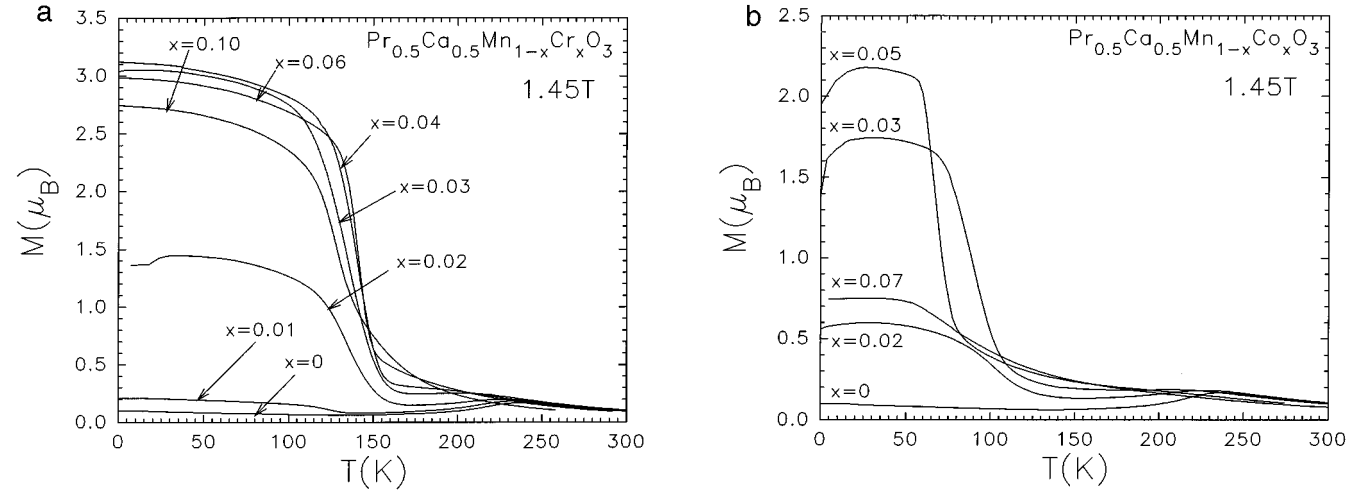

FIG. 2. (a) T dependence of the magnetization M registered in 1.45 T after zero field cooling for the series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$. (b) $M(T)$ curves for the series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Co_xO_3$.

1.45 T corroborate the $R(T)$ curves. One indeed observes a ferromagnetic contribution at low temperature by doping either with chromium or with cobalt, in contrast to the undoped phase $Pr_{0.5}Ca_{0.5}MnO_3$, which is antiferromagnetic at those temperatures. The Cr-doped manganites (Fig. 2a) show a rapid increase in their magnetic moment as x increases, reaching 3–3.10 μ_B for x ranging from 0.03 to 0.06; simultaneously, T_C increases up to 150 K as x increases to $x = 0.06$. T_C and ferromagnetism tend to decrease for x beyond $x = 0.06$, as shown for the $x = 0.10$ sample that exhibits a T_C of 125 K and a magnetic moment of 2.75 μ_B at 4.2 K. This trend is in perfect agreement with the $R(T)$ curves. In a similar manner, doping with cobalt (Fig. 2b) leads to a rapid increase in the magnetic moment up to 2.2 μ_B, as x increases up to $x = 0.05$, but the magnetic moment is significantly smaller than that observed for chromium. Beyond $x = 0.05$, the magnetic moment decreases as x increases, as shown, for instance, for $x = 0.07$, which exhibits a magnetic moment of 0.75 μ_B at 4.2 K. The Curie temperature does not vary considerably; it decreases from about 90 K for $x = 0.03$ to 65 K for $x = 0.05$, in agreement with the $R(T)$ curves.

This transition from an insulator to a ferromagnetic metal suggests that samples containing Cr and Co exhibit colossal magnetoresistance. The induced CMR effect is indeed spectacular as is seen by comparing the undoped $Pr_{0.5}Ca_{0.5}MnO_3$ manganite that is not magnetoresistant even under 7 T with the Cr- and Co-doped manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ (Figs. 3, 4). For very weak doping levels, i.e., $x = 0.01$, that correspond to insulators in zero magnetic field, one observes high resistance ratios (RR) of 3×10^4 for Cr (Fig. 3a) and 3×10^6 for Co (Fig. 4a) at 60 K, in spite of the fact that charge ordering has not completely disappeared. The highest RR value is observed for cobalt. The disappearance of charge ordering does not lead to an increase in RR, as shown for the $x = 0.02$ Co sample (Fig. 4b), which is still insulating in a zero magnetic field and exhibits a RR of 10^4 at 60 K. It is remarkable that as soon as

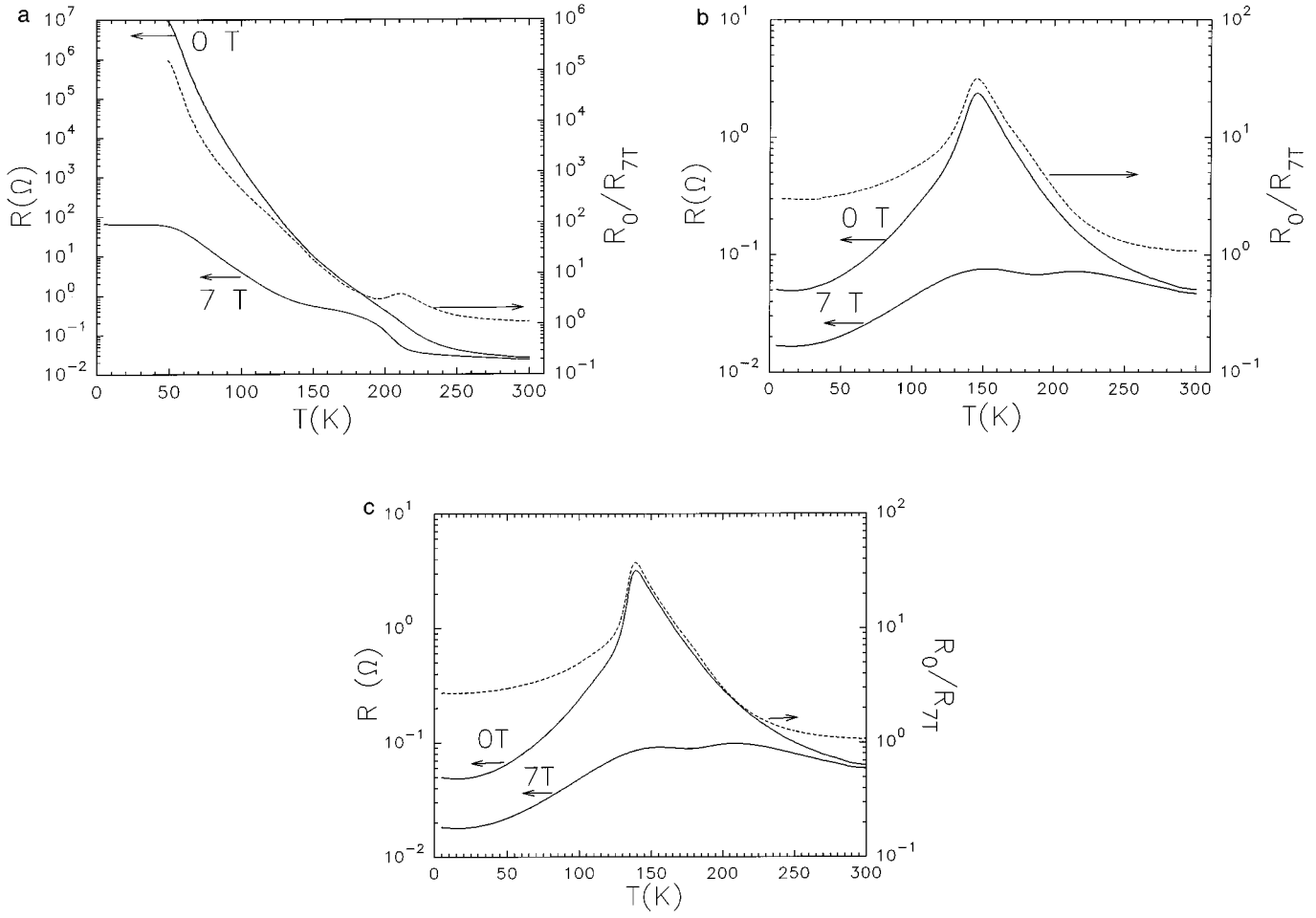

FIG. 3. $R(T)$ curves registered under 0 and 7 T by cooling the samples from 300 to 5 K. The corresponding resistance ratio R_{0T}/R_{7T} is also given (dashed line, right y axis). (a) $Pr_{0.5}Ca_{0.5}Mn_{0.99}Cr_{0.01}O_3$, (b) $Pr_{0.5}Ca_{0.5}Mn_{0.95}Cr_{0.05}O_3$, and (c) $Pr_{0.5}Ca_{0.5}Mn_{0.94}Cr_{0.06}O_3$.

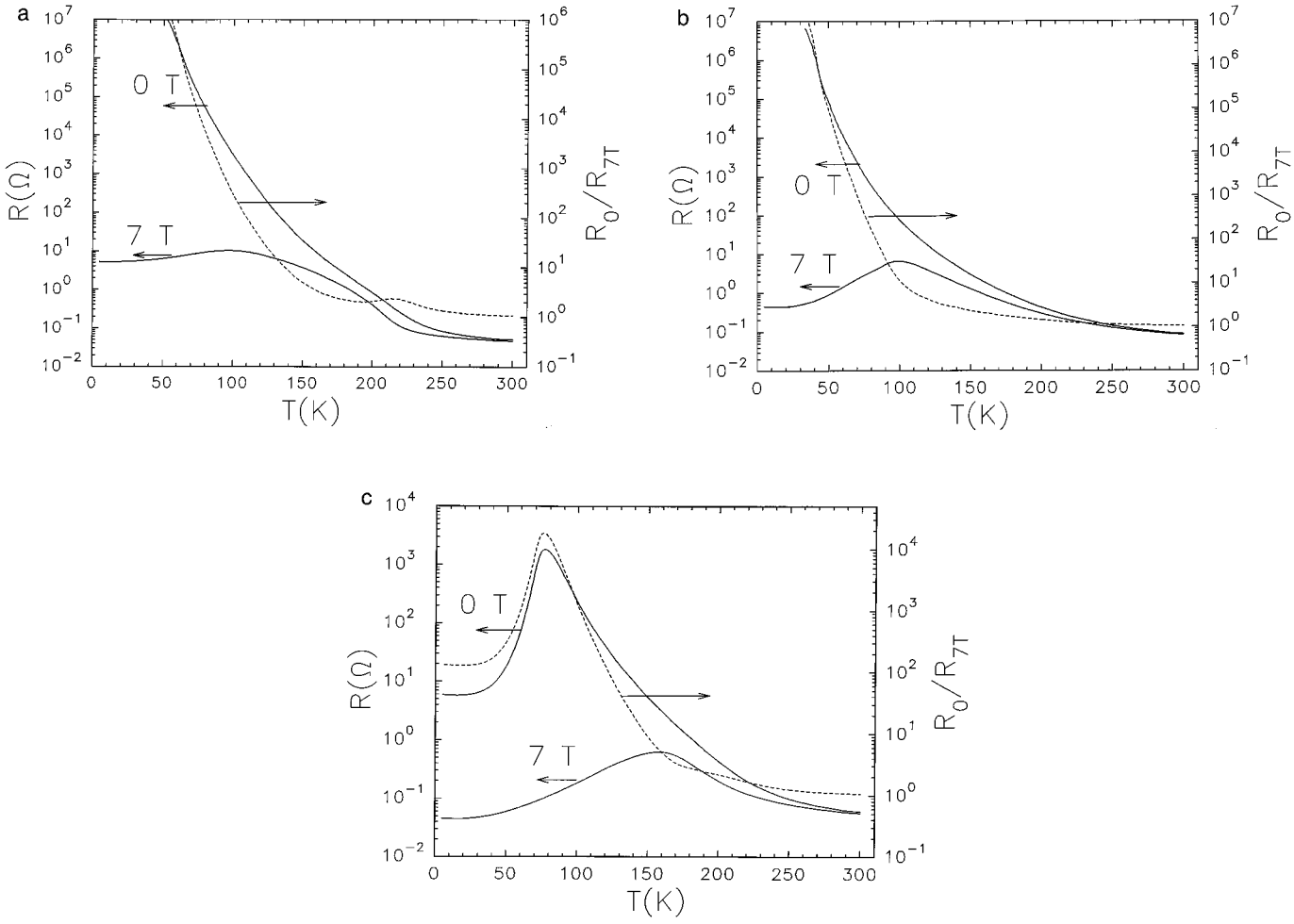

FIG. 4. $R_{0T}(T)$, $R_{7T}(T)$, and R_{0T}/R_{7T} curves for the following Co samples: (a) $Pr_{0.5}Ca_{0.5}Mn_{0.99}Co_{0.01}O_3$, (b) $Pr_{0.5}Ca_{0.5}Mn_{0.98}Co_{0.02}O_3$, and (c) $Pr_{0.5}Ca_{0.5}Mn_{0.97}Co_{0.03}O_3$.

the doped phase exhibits an I–M transition in zero magnetic field, the maximum RR value decreases significantly, following the T_{max} value: RR values of 30 and 40 are observed for the $x = 0.05$ (Fig. 3b) and 0.06 (Fig. 3c) Cr-doped phases at T_{max} values of 145 and 140 K, respectively, whereas a RR value of 2×10^4 is obtained for the $x = 0.03$ Co-doped phase (Fig. 4c) at $T_{max} = 75$ K.

This study shows the exceptional ability of chromium and cobalt doping to induce an insulator to ferromagnetic metal transition in the manganite $Pr_{1-x}Ca_xMnO_3$, counter-balancing the opposite effect arising from the small size of the *A*-site cations (Pr, Ca). It should be possible to apply such an effect to other perovskites $Ln_{0.5}Ca_{0.5}MnO_3$ with a smaller lanthanide cation, i.e., *Ln* = Nd, Sm, Gd, etc. The mechanism that governs such an effect is so far not understood; nevertheless, it is most probable that the mixed valence states of chromium Cr(III)/Cr(IV) and of cobalt Co(III)/Co(IV) will have to be taken into account to understand the competition between ferromagnetism and antiferromagnetism in these materials.

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