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Mn-site doping induced CMR properties in calcium rich manganites $Pr_{1-x}Ca_xMnO_3$ ($0.6 \le x \le 0.7$)

A. Barnabé[a], A. Maignan, M. Hervieu, and B. Raveau

Laboratoire CRISMAT, ISMRA[b], 6 boulevard du Maréchal Juin, 14050 Caen Cedex, France

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Abstract. Doping of Mn-site by chromium, cobalt and nickel has been investigated in the calcium rich manganites $Pr_{0.4}Ca_{0.6}MnO_3$ and $Pr_{0.3}Ca_{0.7}MnO_3$. Whatever the nature of the doping element, a rapid disappearance of the charge ordered (CO) state is observed, T_{CO} decreasing as the doping rate increases. But the most important result concerns the Cr-doped compounds $Pr_{0.4}Ca_{0.6}Mn_{1-x}Cr_xO_3$ for which a re-entrant insulator to metal transition at 90-120 K is observed for $x = 0.10-0.12$, in a zero magnetic field. The possibility to induce colossal magnetoresistance (CMR) properties for high Mn(IV) contents (Mn(IV)/Mn(III) $\ge 3/2$) for $x = 0.07-0.12$ is shown for the first time, the resistance ratios R_0/R_{7T} reaching 2×10^6 at 30 K. This study also shows differently that the small size of the A-site cation (Pr, Ca) is not a redhibitory obstacle to the appearance of CMR properties in manganites, in contrast with previously established phase diagrams.

PACS. 71.30.+h Metal-insulator transitions and other electronic transitions – 75.30.Cr Saturation moments and magnetic susceptibilities – 75.70.Pa Giant magnetoresistance

Introduction

The numerous studies of the manganites $Ln_{1-x}A_xMnO_3$ performed these last years have shown that several factors should be taken into consideration for the appearance of colossal magnetoresistance (CMR) properties: average size of the interpolated cation (Ln, A), mixed valence of manganese (hole carrier density), size mismatch between the “A, Ln” cations in bulk materials [1–5] and also substrate-induced lattice distorsion in thin-films [6]. It has indeed been demonstrated by several authors that a minimum size of the “A, Ln” cations is necessary to obtain an insulator to metal (I/M) transition that coincides with a paramagnetic to ferromagnetic transition, T_c increasing with the size of the “A, Ln” cations [1–4]. Concerning the valence of manganese in these compounds, no CMR effect was detected for a Mn(IV)/Mn(III) ratio larger than 1 ($x > 0.50$). The size difference between the “A, Ln” cations called mismatch, was also found to be unfavourable to the I/M transition, leading to a substantial decrease of T_c [5].

Among the different manganites with the perovskite structure, the compounds $Pr_{1-x}Ca_xMnO_3$ are of great interest for the study of the magnetotransport mechanisms due to the fact that praseodymium and calcium exhibit the same size, so that there is no mismatch effect. In contrast to many other manganites, these materials are insulator at low temperature whatever x [7–9]. In fact, the absence of an I/M transition in a zero magnetic field in these oxides has been interpreted as the result of the too small size of the interpolated cations Pr^{3+} and Ca^{2+}. Nevertheless, such a transition could be induced for $x = 0.30$ by applying a magnetic field of several tesla [10,11]. Moreover doping of manganese sites with various cations (Mg^{2+}, Al^{3+}, Fe^{3+}, Ti^{3+} or Sn^{2+}) was found to suppress charge ordering in $Pr_{1-x}Ca_xMnO_3$ with $0.4 \le x \le 0.5$ [12]. Although the so doped phases remain insulators, they exhibit large magnetoresistance effects under 7 T, contrary to the undoped manganite. The most spectacular effect was recently observed by doping $Pr_{0.5}Ca_{0.5}MnO_3$ by cobalt, chromium and nickel [13]. An insulator to metal transition was indeed induced for the first time in this phase, and moreover CMR properties with resistance ratio $R_0/R_{H=7T}$ up to 10^7 were obtained. These results demonstrate that the size of the “Ln, A” cation is not a redhibitory parameter for the appearance or disappearance of CMR properties.

At this point of the investigations, we have to understand the exact role of hole carrier density in the magnetotransport properties of these oxides. One important issue concerns the possibility to obtain CMR properties for Mn(IV)/Mn(III) ratios larger than 1. The present study of the “Co, Ni, Cr” doped insulators $Pr_{1-x}Ca_xMnO_3$ shows for the first time that a re-entrant I/M transition, leading to CMR properties with resistance ratios up to 10^7, can

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[a] e-mail: `barnabe@crismat.ismra.fr`

[b] CNRS UMR 6508

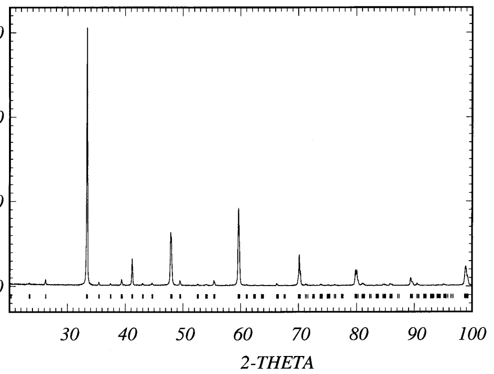


Fig. 1. Experimental X-ray diffractogram and corresponding Bragg sticks for $Pr_{0.4}Ca_{0.6}Mn_{0.93}Cr_{0.07}O_3$.

be induced in calcium rich compositions ($x = 0.60-0.70$), *i.e.* for Mn(IV)/Mn(III) ratios much larger than 1.

Results and discussions

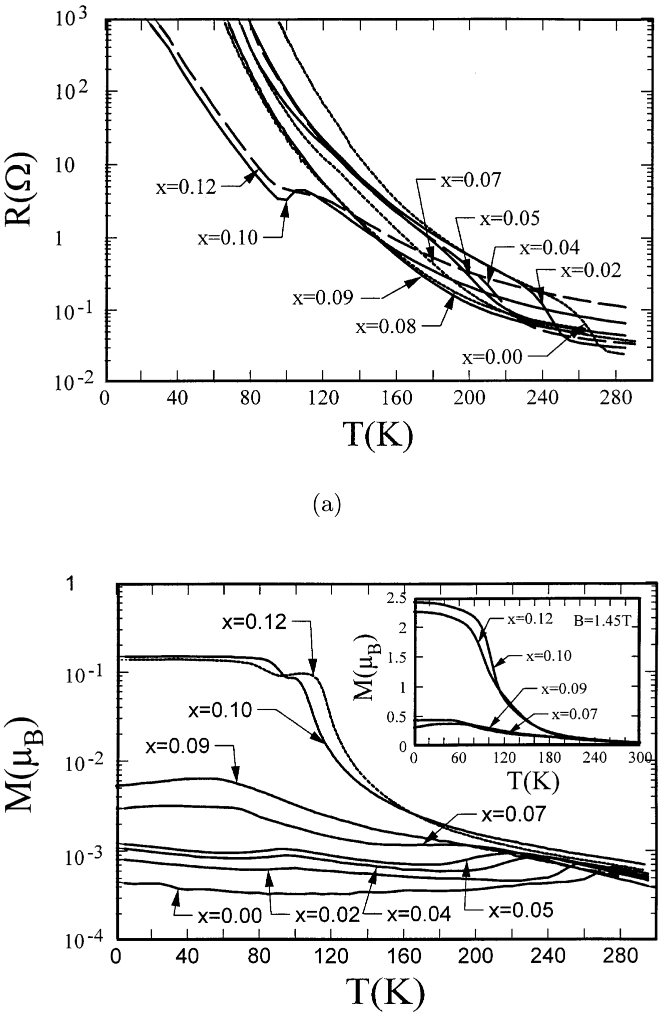
Experimental procedure

The synthesis of the calcium rich doped manganites $Pr_{0.4}Ca_{0.6}Mn_{1-x}M_xO_3$ and $Pr_{0.3}Ca_{0.7}Mn_{1-x}M_xO_3$ with M = {Co, Ni and Cr} was performed according to the procedure previously described for other doped $Pr_{1-x}Ca_xMnO_3$ manganites [13]. EDS analyses were performed with a Kevex analyser coupled with the TEM observations (JEOL 200 CX). X-ray diffraction studies were carried out with a Philips vertical diffractometer (CuKα radiation) and the corresponding patterns were collected by 0.04° step scanning.

The study of the resistance *versus* temperature $R(T)$ was performed with the classical four probe technique on bars with $2 \times 2 \times 10$ mm^3 dimensions. The magnetoresistance measurements were established with a Quantum Design Physical Property Measurements System. All the $R(T)$ curves were measured with decreasing temperature in magnetic field of 0 or 7 T. The magnetic curves *versus* temperature $M(T)$ were registered with a vibrating sample magnetometer in magnetic field of 10^{-2} T or 1.45 T.

Structural characterizations

The purity of the phases was systematically checked by recording X-ray diffraction patterns. All the samples were found to crystallize in an orthorhombic structure (space group Pnma) with no extra diffraction peaks indicative of impurities. A typical pattern corresponding to sample $Pr_{0.4}Ca_{0.6}Mn_{0.93}Cr_{0.07}O_3$ is given in Figure 1. The obtained cell parameters ($a = 0.5375$ nm, $b = 0.7575$ nm, $c = 0.5369$ nm) are found to be very close to that reported by Jirak *et al.* for $Pr_{0.4}Ca_{0.6}MnO_3$ [9] from a neutron diffraction study ($a = 0.5375$ nm, $b = 0.7601$ nm, $c = 0.5375$ nm).



(a)

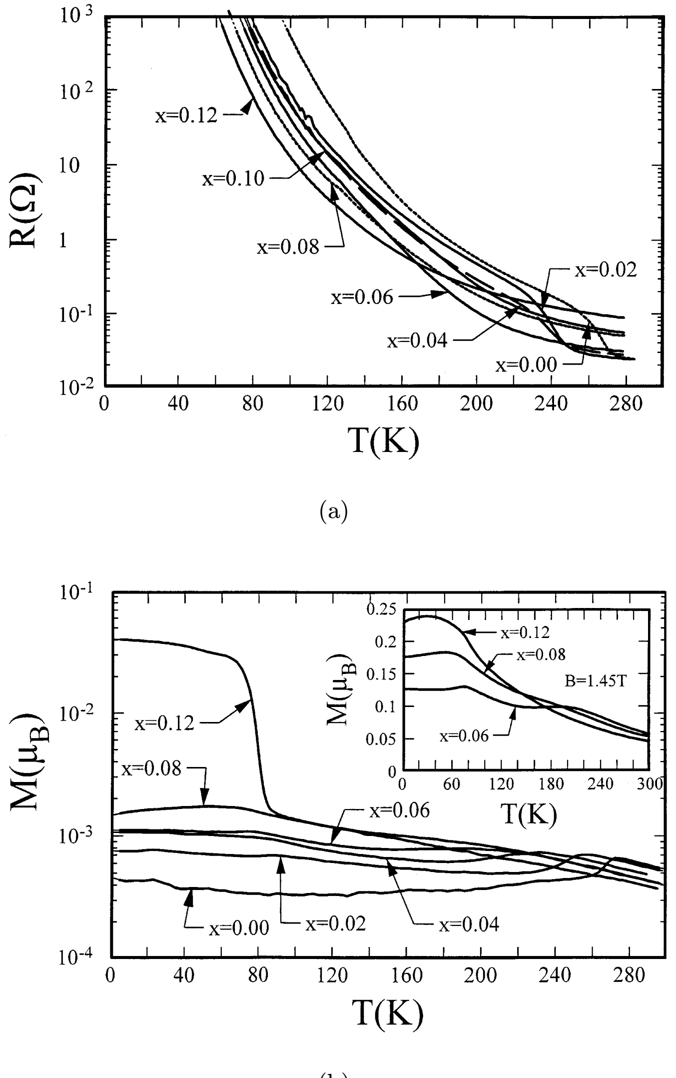
(b)

Fig. 2. $Pr_{0.4}Ca_{0.6}Mn_{1-x}Cr_xO_3$ series (x values are labelled on the graph). (a) Resistance (R) *versus* temperature (T). (b) Magnetization (M) *versus* T registered in a magnetic field of 10^{-2} T. Inset: $M(T)$ curves registered in 1.45 T.

The structural quality of the samples was further confirmed by systematic electron microscopy studies. For all doping elements, M = Cr, Co, Ni, and whatever the doping level (0 to 12%), the cationic compositions determined by EDS on more than hundred microcrystals were found to be similar to the nominal ones. Moreover, homogeneous cationic distributions were always observed. No traces of impurity phases have been detected.

The $Pr_{0.4}Ca_{0.6}Mn_{1-x}M_xO_3$ series

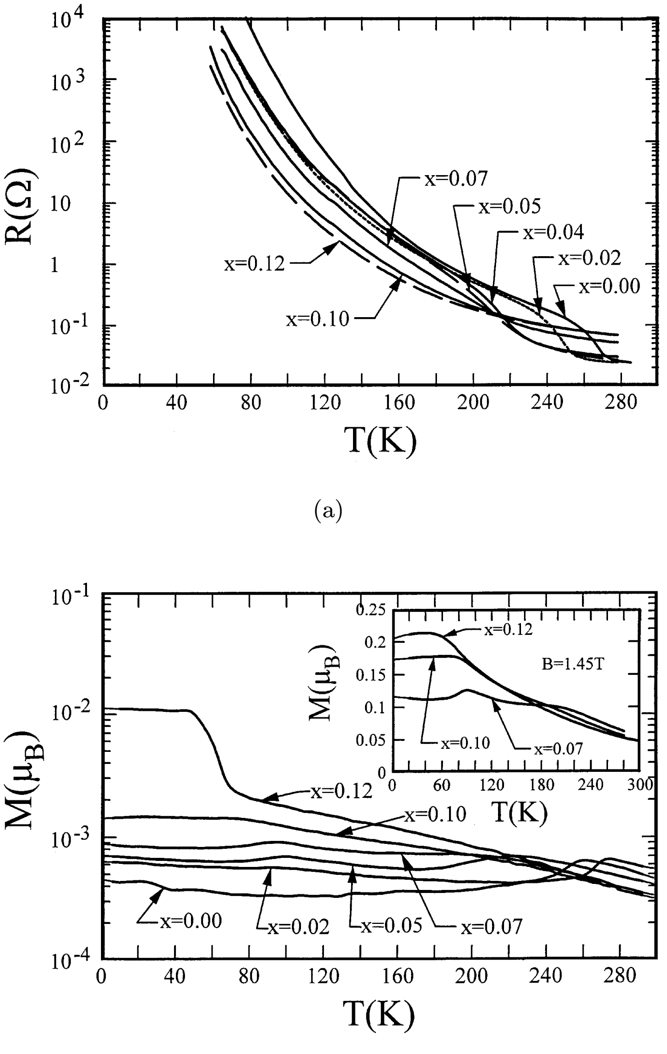
The $R(T)$ and $M(T)$ curves of the three series of samples $Pr_{0.4}Ca_{0.6}Mn_{1-x}M_xO_3$ with M = {Cr, Co and Ni} are displayed in Figures 2, 3 and 4 respectively. Considering the undoped phase, $Pr_{0.4}Ca_{0.6}MnO_3$, it can be seen that the latter exhibits, like other phases $Pr_{1-x}Ca_xMnO_3$,



(a)

(b)

Fig. 3. $Pr_{0.4}Ca_{0.6}Mn_{1-x}Co_xO_3$ series. (a) $R(T)$ curves. (b) $M(T)$ curves (10^{-2} T). Inset: $M(T)$ curves (1.45 T).



(a)

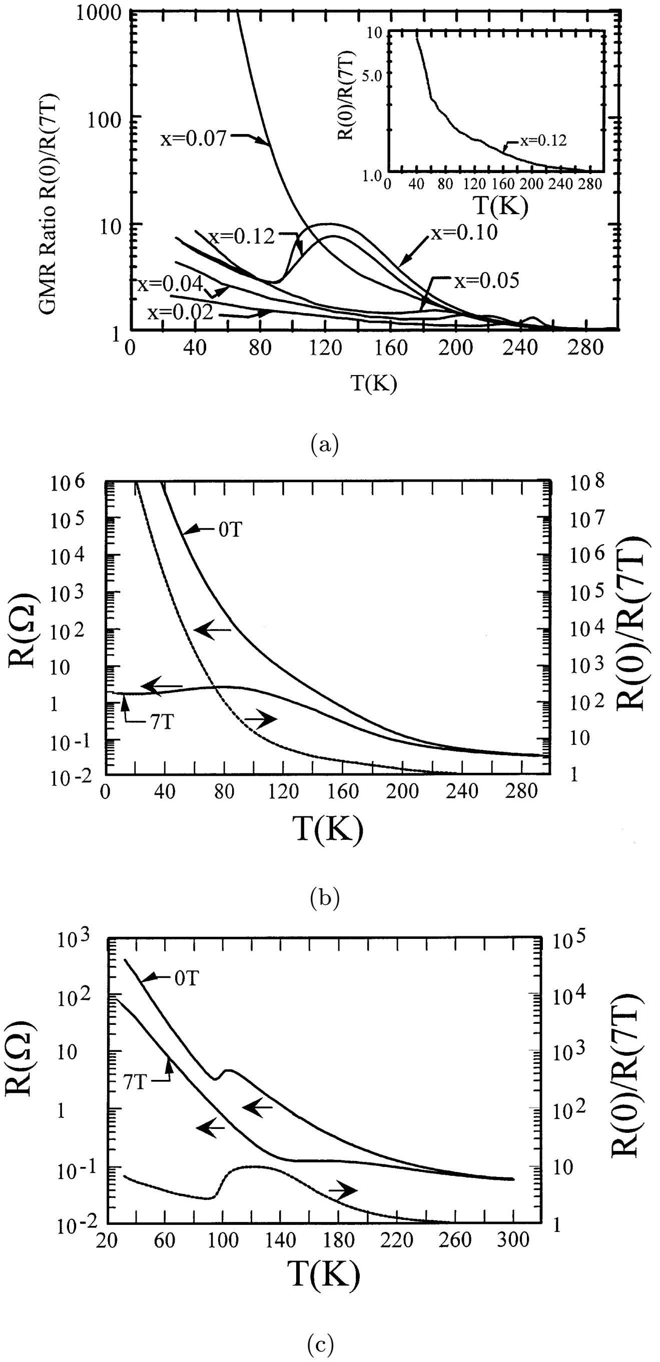
(b)

Fig. 4. $Pr_{0.4}Ca_{0.6}Mn_{1-x}Ni_xO_3$ series. (a) $R(T)$ curves. (b) $M(T)$ curves (10^{-2} T). Inset: $M(T)$ curves (1.45 T).

an insulating behaviour with a change of slope for $R(T)$ at 275 K, characteristic of charge ordering (Fig 2a). This charge ordering (CO) phenomenon can easily be identified on the $M(T)$ curve (Fig. 2b) by a peak at $T_{CO} = 275$ K. The latter has indeed been shown to correspond to a replacement of ferromagnetic spin correlations by antiferromagnetic spin fluctuations as T decreases below the charge ordering transition in (Bi,Ca)MnO_3 perovskite [14].

A first feature common to all the samples deals with the rapid disappearance of charge ordering by doping whatever the nature of the dopant, Cr, Co or Ni. One indeed observes that T_{CO} deduced from the $R(T)$ curves (Figs. 2a, 3a and 4a from Cr, Co and Ni respectively) or from the $M(T)$ curves registered under 10^{-2} T (Figs. 2b, 3b and 4b) decreases, and vanishes for $x \approx 0.07$. This behaviour is not unexpected: it has previously been observed for other doped manganites $Pr_{1-x}Ca_xMnO_3$ $(0.4 \leq x \leq 0.5)$ [12,13]. But more remarkable is the fact that for a same doping rate, one observes the same T_{CO} whatever the nature of the dopant, as shown for instance for $x = 0.05$ samples that exhibit a $T_{CO} \approx 225$ K for all three dopants. These results show that doping of the Mn-sites destroys charge ordering, in the same way independently of nature of the dopants Cr, Co or Ni.

At lower temperature, below 100-110 K, one observes a bump on the $M(T)$ curves (Figs. 2b, 3b and 4b), which corresponds to the appearance of a ferromagnetic contribution by doping, in contrast to the undoped phase. This increase of ferromagnetic correlations coincides with the disappearance of CO. Note that the Cr-doped phases exhibit a significantly higher magnetization (Fig. 2b) than the Co and Ni doped phases (Figs. 3b and 4b). This greater ability of the Cr-doped phase to display ferromagnetism at low temperature is confirmed by the $M(T)$ curves registered under 1.45 T (inset Fig. 2b), where one clearly observes a transition to a ferromagnetic state,



(a)

(b)

(c)

Fig. 5. $Pr_{0.4}Ca_{0.6}Mn_{1-x}M_xO_3$ series. (a) $R_0/R_{7T}(T)$ curves for $Pr_{0.4}Ca_{0.6}Mn_{1-x}Cr_xO_3$. Inset: $R_0/R_{7T}(T)$ curves for $Pr_{0.4}Ca_{0.6}Mn_{0.88}Co_{0.12}O_3$. (b) $R_0(T)$, $R_{7T}(T)$ and $R_0/R_{7T}(T)$ curves for $Pr_{0.4}Ca_{0.6}Mn_{0.93}Cr_{0.07}O_3$. (c) $R_0(T)$, $R_{7T}(T)$ and $R_0/R_{7T}(T)$ curves for $Pr_{0.4}Ca_{0.6}Mn_{0.90}Cr_{0.10}O_3$.

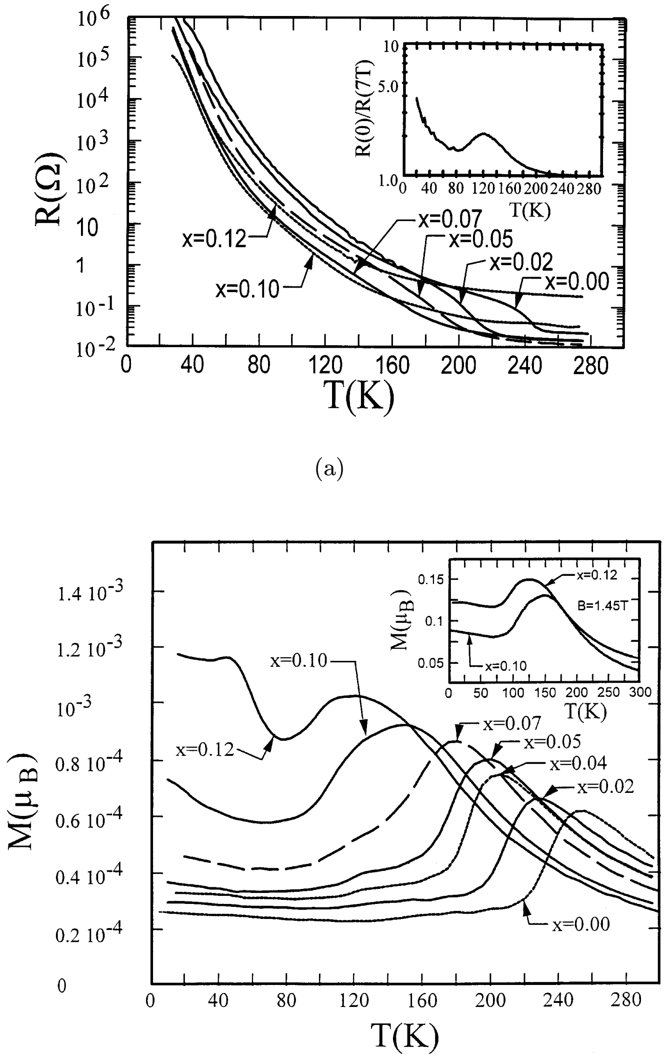
for $x = 0.10-0.12$, at low temperature with a magnetic moment of $2.4-2.2\mu_B$ at 5 K. In contrast, for the Co-doped phase (inset Fig. 3b) and the Ni doped phase (inset Fig. 4b), the magnetic moment at 5 K is ten times smaller (0.22 to $0.25\mu_B$), so that for these two series, one cannot talk about a transition to a ferromagnetic transition under 1.45 T.

The particular behaviour of the Cr-doped manganite with respect to the Co and Ni-doped phases is confirmed by the $R(T)$ curves. For $x = 0.10$, the Cr-doped phases shows clearly an I/M transition at $T = 100$ K followed by insulating behaviour at lower temperature (Fig. 2a). A similar tendency is observed for $x = 0.12$. In contrast, no anomaly is observed on the $R(T)$ curves of the Co and Ni-doped samples (Figs. 3a and 4a) that exhibit a semi-conducting behaviour whatever x. The remarkable coincidence of the re-entrant I/M transition (Fig. 2a) with the paramagnetic to ferromagnetic transition (Fig. 2b), at $T \approx 90$–120 K for $x = 0.10-0.12$, shows that for this optimum composition, chromium doping induces a paramagnetic insulating (PMI) to ferromagnetic metallic (FMM) transition in the calcium rich manganite $Pr_{0.4}Ca_{0.6}MnO_3$. This result is of capital importance since it is the first time that such an I/M transition is observed in systems with a so high Mn(IV) content, and a so small size of the interpolated cation. Thus the role of chromium appears as specific compared to cobalt or nickel for which no I/M transition has been observed here. Note that for the higher Cr doping rate ($x = 0.12$), the saturated magnetization at low temperature slightly decreases and the I/M transition tends to disappear (Figs. 2a and 2b).

The application of a magnetic field of 7 T shows that the Cr-doped manganites $Pr_{0.4}Ca_{0.6}Mn_{1-x}Cr_xO_3$ exhibit colossal magnetoresistance properties (Fig. 5a) with the largest resistance ratio R_0/R_{7T}, 2×10^6, for the $x = 0.07$ sample (Fig. 5b). Starting from an insulator, an I/M transition is induced by applying a magnetic field of 7 T. The latter is characterized by a flat maximum with $T_c \approx 90$ K. In contrast, for $x = 0.10$ (Fig. 5c), the maximum resistance ratio that is obtained is much smaller, *i.e.* 10 at 125 K. In that sample, the maximum which characterizes the I/M transition is also flat, and displaced toward higher temperatures ($T \approx 190$ K) with respect to the zero field $R(T)$ ($T \approx 110$ K). Note also that this sample is insulating at low temperature ($T < 120$ K) under 7 T, in agreement with the re-entrant character of the transition observed in a zero magnetic field. A very similar behaviour is observed for $x = 0.12$. In contrast, no I/M transition is induced by nickel or cobalt doping in the $Pr_{0.4}Ca_{0.6}MnO_3$ manganite. In these two series, the samples remain insulating in a magnetic field whatever x and the magnetoresistance ratio remains much smaller than 10, as shown for the Co-doped phase $Pr_{0.4}Ca_{0.6}Mn_{0.88}Co_{0.12}O_3$ (inset Fig. 5), which seems to be one of the best samples of these two series, and exhibits a resistance ratio close to 10 at 45 K.

The $Pr_{0.3}Ca_{0.7}Mn_{1-x}M_xO_3$ series

In order to test the possibility of inducing CMR properties for still higher Mn(IV) contents, we have investigated the doping of $Pr_{0.3}Ca_{0.7}MnO_3$ with Ni, Co and Cr. Whatever the nature of the dopant, no I/M transition can be induced in this manganite. The $R(T)$ (Fig. 6a) and $M(T)$ curves registered under 10^{-2} T (Fig. 6b) for the series $Pr_{0.3}Ca_{0.7}Mn_{1-x}Cr_xO_3$ exemplify the behaviour of



(a)

(b)

Fig. 6. $Pr_{0.3}Ca_{0.7}Mn_{1-x}Cr_xO_3$ series. (a) $R(T)$ curves. Inset: $R_0/R_{7T}(T)$ curves for $Pr_{0.3}Ca_{0.7}Mn_{0.90}Cr_{0.10}O_3$. (b) $M(T)$ curves (10^{-2} T). Inset: $M(T)$ curves (1.45 T).

these compounds. One observes that such a doping weakens the charge ordering, T_{CO} decreasing significantly from 250 K for $x = 0.00$ to 120 K for $x = 0.12$. However, in contrast to the $Pr_{0.4}Ca_{0.6}MnO_3$ series, no anomaly associated to the I/M transition is observed on the $R(T)$ curves (Fig. 6a). This is consistent with the $M(T)$ curves registered in a magnetic field of 1.45 T which show only small values of the magnetization at low temperature (see inset Fig. 6b), of about $0.10-0.15\mu_B$ against $2.40\mu_B$ for $Pr_{0.4}Ca_{0.6}Mn_{0.90}Cr_{0.10}O_3$. It turns out that the ferromagnetism is always very weak so that the decrease of T_{CO} can be observed for all compositions on the $M(T)$ curves registered under 10^{-2} T (Fig. 6b). In agreement with this behaviour, these compounds exhibit a low magnetoresistance effect as shown for example from the $R_0/R_{7T}(T)$ curve of $Pr_{0.3}Ca_{0.7}Mn_{0.90}Cr_{0.10}O_3$ (inset Fig. 6a) which shows a maximum resistance ratio R_0/R_{7T} of only 3 at 30 K.

Concluding remarks

The possibility to induce an I/M transition and consequently CMR properties in calcium rich manganites $Pr_{1-x}Ca_xMnO_3$ $(x > 0.50)$ is shown for the first time. Moreover we observe that the small size of the interpolated cation "Pr, Ca" is not a redhibitory obstacle for the obtention of CMR effect. These results confirm the great potentiality of the three magnetic ions — chromium, cobalt and nickel — for inducing ferromagnetism and metallic conductivity in those manganites, in agreement with previous studies of the doped $Pr_{0.5}Ca_{0.5}MnO_3$ systems [13]. Nevertheless from the present study, chromium appears the most promising doping agent to induce CMR properties in the perovskite manganites.

In the present state of the art, it is difficult to explain this spectacular influence of doping upon the magnetotransport properties of these compounds. Nevertheless it must be emphasized that chromium, cobalt and nickel are among the rare elements that exhibit "metastable" high valencies (Cr(IV), Co(IV) and Ni(III)) so that carriers may be introduced by these elements according to the following equilibria:

$$Cr^{4+} \leftrightarrows Cr^{3+} + p^+$$
$$Co^{4+} \leftrightarrows Co^{3+} + p^+$$
$$Ni^{3+} \leftrightarrows Ni^{2+} + p^+.$$

In this way, the charge ordered state, which would consist of a polaron lattice in agreement with the theories developed by Millis *et al.* [15], would be destroyed by any substitution (Fe, Al, Mg, Ni, Co, Cr, *etc...*), and possibly replaced by a delocalized charge state in the case of Cr, Co or Ni indicating that these cations participate to the double exchange mechanism. The ability of inducing a metallic state would be much higher for chromium than for the other species such as cobalt and nickel, in agreement with the weaker stability of Cr^{4+} species compared to Co^{4+} and Ni^{3+}.

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