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What about the role of B elements in the CMR properties of ABO_3 perovskites?

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Abstract

A lot of progress has been made these last years about the understanding of colossal magnetoresistance (CMR) properties of manganites with the perovskite structure. The role of the interpolated cation (size, mismatch effect) is now well established, whereas the mixed valency of manganese Mn(III)–Mn(IV) is primordial for the appearance of this phenomenon which originates from double exchange between Mn^{3+} and Mn^{4+} species. The present paper is focused on the possibility to introduce other elements on the Mn-sites of the perovskite to enhance their CMR properties. The doping of manganites with various elements (Al, Ga, In, Ti, Sn, Fe, Cr, Co, Ni, Mg) is first reviewed. This study allows some spectacular effects to be evidenced for several perovskites (increase of T_C and of CMR effect by several orders of magnitude, induced CMR effects in insulating perovskites). Clearly, the doping of the Mn-sites modifies dramatically the magnetic phase diagrams established on the only basis of the size effect by different authors. The second point deals with the synthesis of new magnetoresistant oxides without manganese: the 112-type cobaltites $LnBaCo_2O_{5.4}$ (Ln=Eu, Gd) which are oxygen deficient perovskites and the 1201-type oxide $Tl_{0.94}Sr_2Cu_{0.4}Co_{0.6}O_{5-\delta}$ whose magnetotransport properties are studied. © 1998 Elsevier Science S.A.

Keywords: Magnetoresistance; Perovskite; Manganese; Cobalt; Oxide

1. Introduction

A great deal of work has been carried out on the manganites $Ln_{1-x}A_xMnO_3$ since the discovery of colossal magnetoresistance properties in these compounds [1,2]. It has been recently shown that three parameters govern the magnetotransport properties of these materials: the average size of the interpolated cation [3–9], the hole carrier density, i.e. the mixed valence of manganese [3–5], and the size mismatch between the interpolated cations [10].

Although the mechanisms that are at the origin of these properties are still subject to discussion, it seems clear that the double exchange between Mn^{3+} and Mn^{4+} species plays an important role [11–13], whereas Jahn Teller type distortions [14] should also be involved. Such features are specific of manganese so that the CMR properties of these materials should be considerably modified by doping the Mn sites with different elements. In the present study, we report the recent trends concerning the role of the B elements in the CMR properties of the ABO_3 perovskites. The preparation of the samples is described elsewhere [15–17,31–33].

2. The substitution of trivalent and tetravalent elements for manganese in $Pr_{1-x}(Ca, Sr)_xMnO_3$

The systematic study of the substitution of various M elements for Mn in the CMR perovskite $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ has been performed for M=Al, Ga, In, Ti, Sn [15,16]. It shows that whatever the element, the transition temperature T_C (or T_{max}) from the ferromagnetic metallic (FMM) to the paramagnetic insulating (PMI) state decreases dramatically as the content of the doping element increases. This is illustrated by the $R(T)$ curves of the series $Pr_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Al_xO_3$ (Fig. 1) where it can be seen that T_{max} is decreased by about 12 K per percent of Al atom introduced on the Mn site. The corresponding magnetoresistance, calculated by dividing the $R(T)_{H=0}$ values by the $R(T)_{H=7T}$ ones, is in fact correlated to T_C: it increases significantly as x increases, R_0/R_{7T} reaching 10^3 at 71 K for 6% Al per Mn.

A very different behaviour is observed for the charge

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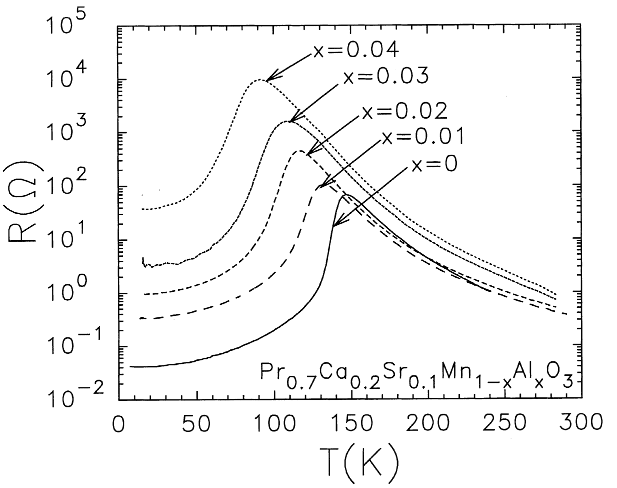


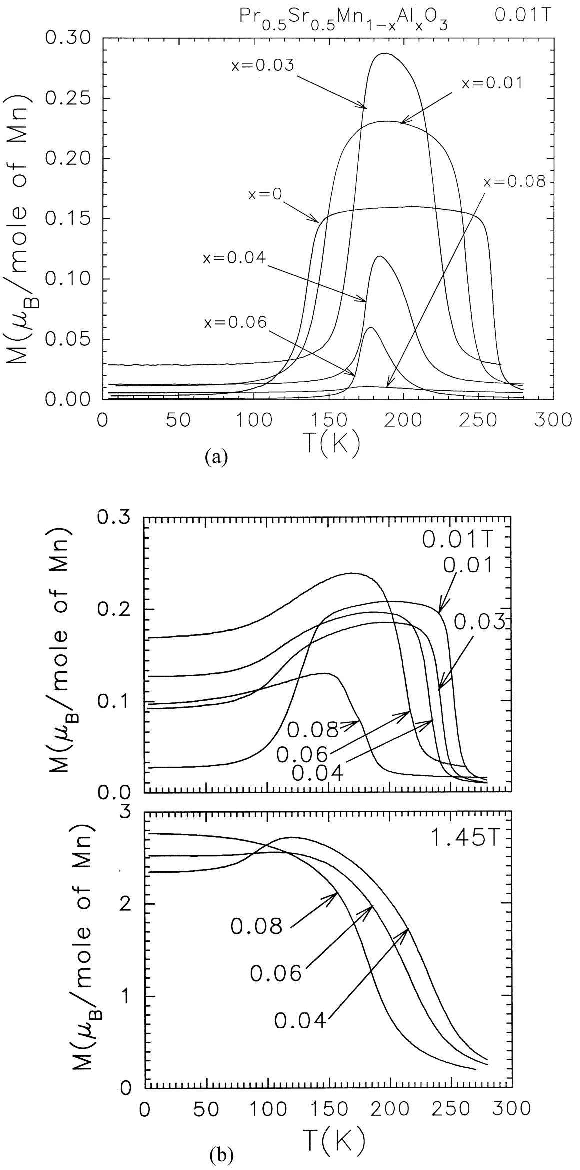
Fig. 1. T dependence of resistance (R) for different x values (labelled on the graph) for the $Pr_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Al_xO_3$ samples.

ordered phase $Pr_{0.5}Sr_{0.5}MnO_3$, which exhibits two different effects according to the valence of the doping element M. Doping with trivalent elements (M=Al, Ga, In) increases the antiferromagnetic insulating (AFMI) and the PMI state at the expense of the FMM state as shown from the M(T) magnetisation curve for M=Al, where a substantial increase of T_N is observed from 135 K for $x=0$ to 170 K for $x=0.06$ (Fig. 2a). On the opposite, doping with tetravalent elements (M=Ti, Sn) tends to suppress the AFMI state, whereas the FMM to PMI transition still exists (Fig. 2b).

3. The increase of CMR effect by iron and magnesium doping in some manganites

The substitution of magnesium for manganese in $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ [17] leads also to a decrease of T_C which is even larger than that observed with trivalent or tetravalent dopants. But the most remarkable feature deals with the jump of resistance near the transition temperature, which is the highest that has been observed to date in the manganites $Pr_{0.7}(Ca, Sr)_{0.3}Mn_{1-x}M_xO_3$. Resistance peaks close to four orders of magnitude are obtained at temperatures ranging from 70 K to 108 K for x~0.005–0.02 (Fig. 3), suggesting that the Mg doped phases exhibit very promising CMR properties. The resistance curve registered in a magnetic field of 7 T (Fig. 4) confirms this viewpoint: a resistance ratio R_0/R_{7T} of 4×10^5 at 70 K is obtained for $Pr_{0.7}Ca_{0.2}Sr_{0.1}Mn_{0.98}Mg_{0.02}O_3$, to be compared to 230 at 150 K for the undoped phase $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$. In contrast, the $Pr_{0.5}Sr_{0.5}Mn_{1-x}Mg_xO_3$ manganites are very similar to the phases $Pr_{0.5}Sr_{0.5}Mn_{1-x}M_xO_3$ with M=Al, Ga, In, differing from the homologous series doped with tetravalent elements (M=Ti, Sn).

The doping of manganites by iron is also susceptible to enhance the CMR effect in the manganites. This is the case of the perovskite $Sm_{0.56}Sr_{0.44}MnO_3$ [18]. The perovskites $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ exhibit resistance maxima characteristic of a FMM- to a PMI transition for very low doping ($0\leq x\leq0.03$) as shown in Fig. 5. Like doping with other elements, it can be seen that T_{max} (i.e. T_C) decreases dramatically as x increases, from 130 K for $x=0$, to 55 K for $x=0.03$, the phase with $x=0.04$ being a semiconductor. But the most spectacular effect concerns the magnetoresistance effect that is considerably increased. For instance, R_0/R_{7T} reaches 8×10^5 at 55 K for $x=0.03$. Another important characteristic deals with the evolution of the resistance versus the applied magnetic field. One observes a very abrupt decrease of the resistance for the



(a)

(b)

Fig. 2. (a) T dependence of magnetization for different x values (labelled on the graph) for the $Pr_{0.5}Sr_{0.5}Mn_{1-x}Al_xO_3$ series. (b) T dependence of M for $Pr_{0.5}Sr_{0.5}Mn_{1-x}Ti_xO_3$; $\mu_0H=0.01$ T, and $\mu_0H=1.45$ T.

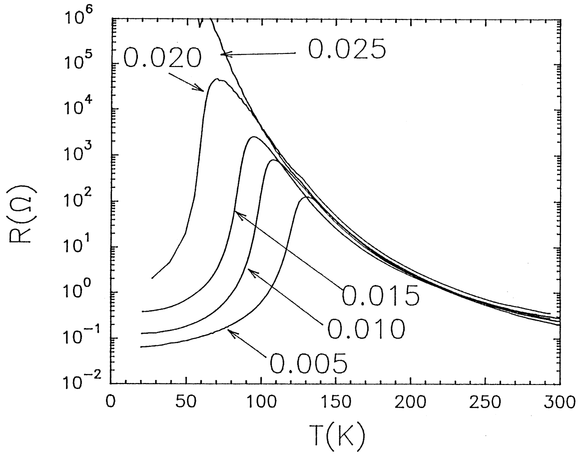


Fig. 3. T dependence of the resistance $R_{(H=0)}$ for $Pr_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Mg_xO_3$ samples, x values are labelled on the graph.

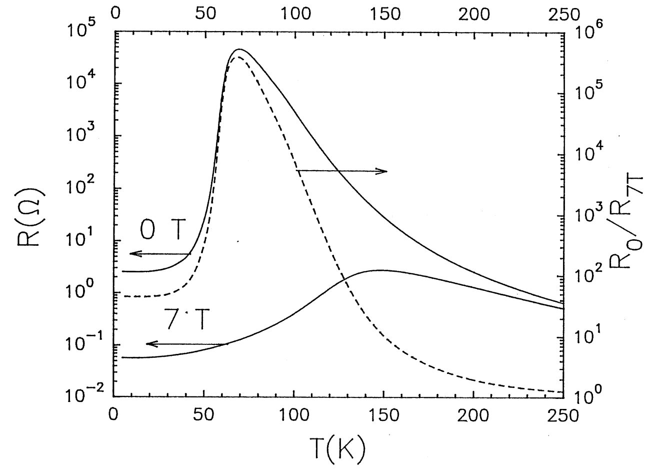


Fig. 4. T dependence of the resistance registered under 0 and 7 T and corresponding R_0/R_{7T} (T) ratio for sample $Pr_{0.7}Ca_{0.2}Sr_{0.1}Mn_{0.98}Mg_{0.02}O_3$.

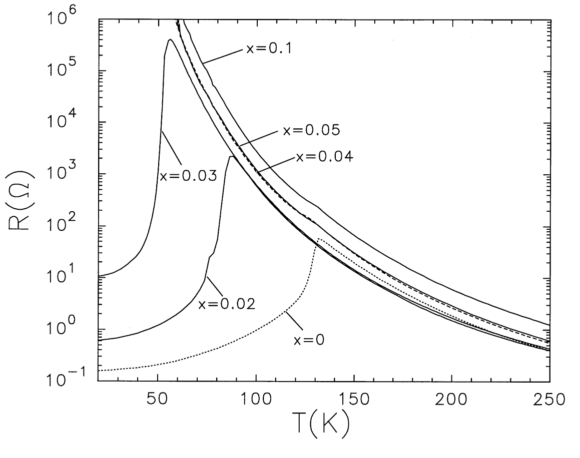


Fig. 5. Temperature dependence of the resistance R in the series $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.1$).

phase $Sm_{0.56}Sr_{0.44}Mn_{0.97}Fe_{0.03}O_3$ (Fig. 6) in the range 0–0.02 T. Such a decrease of R has never been observed below 1 T in other manganites to date.

4. The spectacular insulator–metal (I–M) transition induced by ‘Cr, Co, Ni’ doping in $Pr_{0.5}Ca_{0.5}MnO_3$

In contrast to many other manganites with the perovskite structure, the manganite $Pr_{1-x}Ca_xMnO_3$ remains insulating whatever x [19–23]. Such a behaviour has been explained by the fact that the size of the interpolated cations Ca^{2+} and Pr^{3+} is too small to develop the I–M transition.

Nevertheless, such a transition can be induced by applying a magnetic field, as shown for $Pr_{0.7}Ca_{0.3}MnO_3$ [22,23], so that the latter compound exhibits CMR properties in spite of its insulating properties. Nevertheless, for the particular value $x \sim 1/2$, the charge ordering between the Mn(III) and Mn(IV) species reinforces the capitulation of the I–M transition so that $Pr_{0.5}Ca_{0.5}MnO_3$ does not exhibit CMR properties, i.e. remains insulator whatever the value of the applied magnetic field up to 7 T.

The study of the doping of $Pr_{0.5}Ca_{0.5}MnO_3$ with chromium, cobalt or nickel leads to a rapid disappearance of the charge ordering phenomenon [24,25]. This is illustrated by the $R(T)$ curves (Fig. 7a) and $M(T)$ curves (Fig. 7b) of the series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ [24]. The fact that charge ordering vanishes by doping with a foreign element is not particular to Cr, Co or Ni: it is also observed for the manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ with M=Fe, Al, Ga, Ti [26]. But most important is the fact that this ‘Cr, Co or Ni’ doping induces a resistance peak characteristic of an I–M transition as T decreases (Fig. 7a). This behaviour is very different from that observed for other manganites, $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$, that remain insulator, whatever M=Fe, Al, Ga, Ti and whatever x. Such an I–M transition is remarkable since it has never been observed to date in manganites with a small average size of the A-site cation. Another remarkable feature concerns the transition temperature T_{max} of the Cr-doped phases (Fig. 7a) which increases significantly as the chromium content increases up to $T_{max}=150$ K for $x=0.05$ and then decreases for $x>0.05$. A similar evolution is observed for Co and Ni doped manganites. The $M(T)$ curves (Fig. 7b) corroborate the $R(T)$ curves. One indeed observes the appearance of a ferromagnetic contribution at low temperature by doping with Cr, Co or Ni, in contrast to the undoped phase which is antiferromagnetic at those temperatures. This is illustrated in Fig. 7b for the Cr-doped manganites that show a rapid increase of 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 up to $x=0.06$. Then, T_C and ferromagnetism tend to decrease as x increases 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. Very similar behaviours are observed

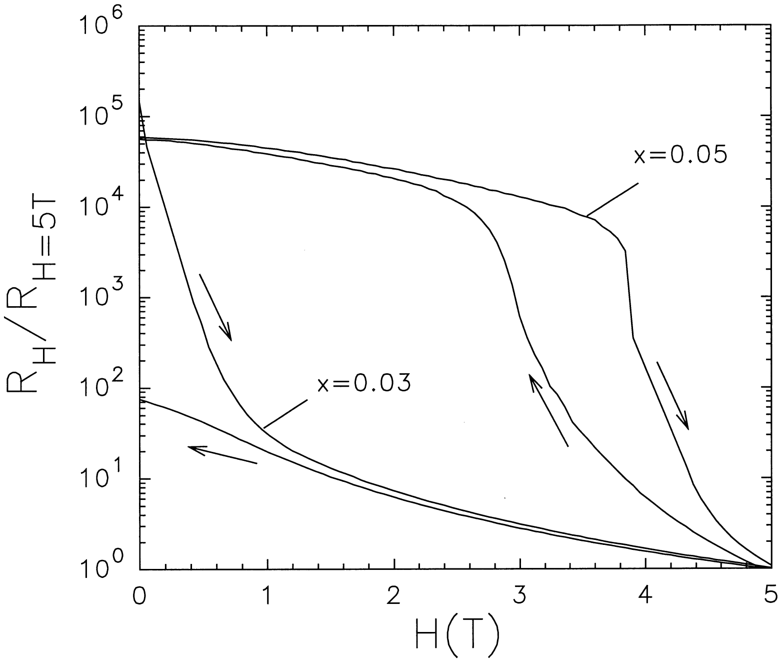
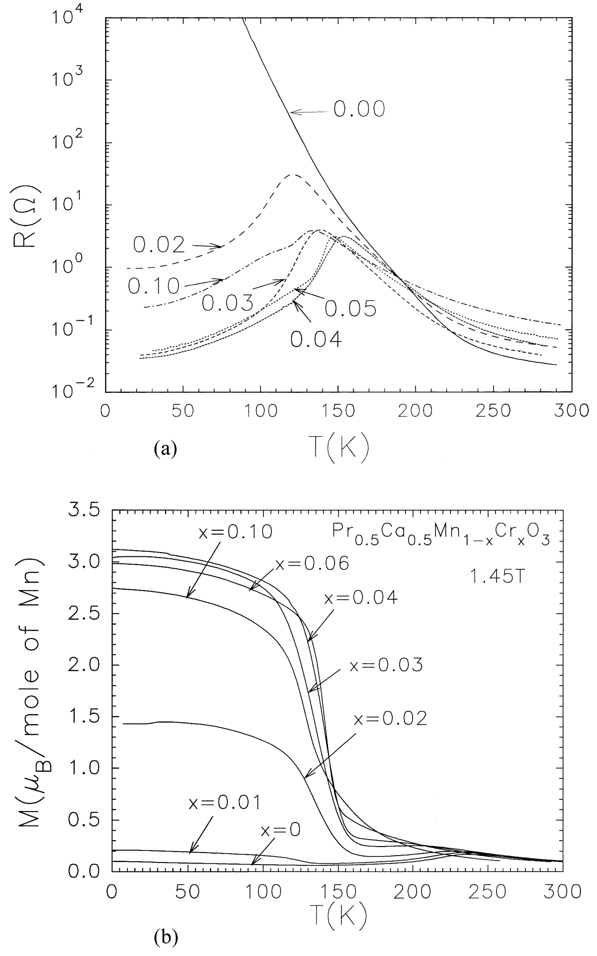


Fig. 6. Magnetoresistance ratios versus magnetic field H for $Sm_{0.56}Sr_{0.44}Mn_{1-x}Fe_xO_3$ at 55 K ($x=0.03$ and $x=0.05$).



(a)

(b)

Fig. 7. $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$: T dependence of the resistance R registered during cooling (a), and T dependence of the magnetization in 1.45 T after zero field cooling (b).

for cobalt and nickel, except that the maximum value of the magnetic moment is significantly smaller than for chromium. This transition from an insulator to a ferromagnetic metal suggests that the so doped samples exhibit colossal magnetoresistance properties. The induced CMR effect is indeed spectacular as shown by comparing the undoped $Pr_{0.5}Ca_{0.5}MnO_3$ manganite that is not magnetoresistant even under 7 T, with the Cr doped manganites $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ (Fig. 8). 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 (Fig. 8a) at 60 K, in spite of the fact that charge ordering has not completely disappeared. It is remarkable that as soon as the doped phase exhibits an I–M transition in a 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. 8b) and 0.06 Cr-doped phases at $T_{\max}$ values of 145 K and 140 K respectively. It is worthy to note, that among these three dopants, cobalt exhibits the highest resistance ratios with $RR\sim3\times10^6$ at 60 K under 7 T for $Pr_{0.5}Ca_{0.5}Mn_{0.99}Co_{0.01}O_3$.

The possibility of applying such an effect to other perovskites, $Ln_{0.5}Ca_{0.5}MnO_3$, with a smaller lanthanide cation has been demonstrated for the series $Ln_{0.5}Ca_{0.5}Mn_{1-x}Ni_xO_3$ [25]. Nevertheless, it is observed that the ability to suppress charge ordering decreases as the size of Ln^{3+} decreases from Pr^{3+} to Sm^{3+}. In the same way, the difficulty to induce an I–M transition increases from Pr^{3+} to Sm^{3+}.

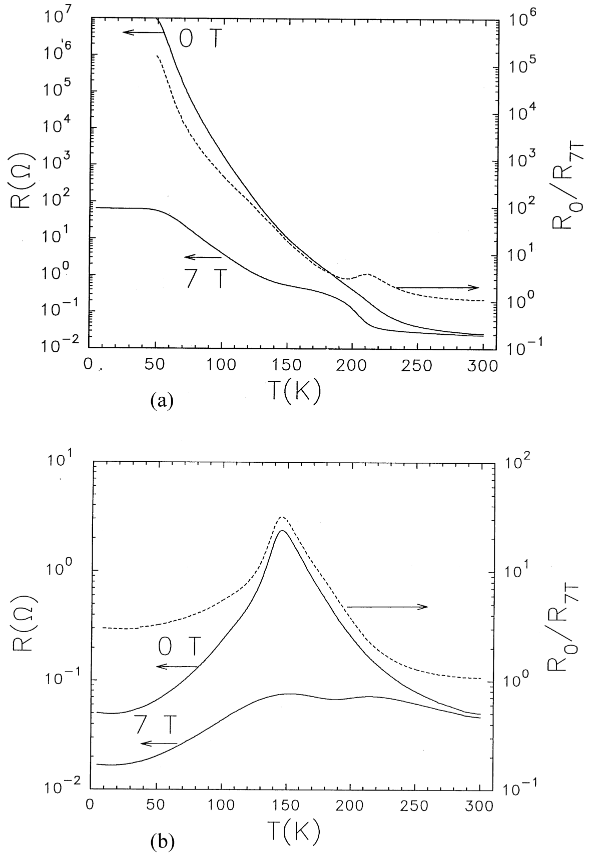


Fig. 8. $R(T)$ curves registered under 0 T and 7 T by cooling the samples from 300 K to 5 K. The corresponding resistance ratio R_{0T}/R_{7T} is also given (dashed line, right y-axis). (a) $Pr_{0.5}Ca_{0.5}Mn_{0.99}Cr_{0.01}O_3$ and (b) $Pr_{0.5}Ca_{0.5}Mn_{0.95}Cr_{0.05}O_3$.

5. Non-manganese perovskites and relatives

The possible mixed valence of cobalt makes this element appear as a potential for the generation of CMR materials. The recent discovery of magnetoresistance properties for the cobalt perovskite $La_{1-x}Sr_xCoO_3$ [27–30] supports this viewpoint. Nevertheless, the resistance ratios observed for the latter is small, i.e. R_0/R_H is smaller than 2 whatever the temperature is, in a magnetic field of 6 T. In order to understand the role of cobalt in such properties, cobalt based systems were investigated. Two new phases, $LnBaCo_2O_{5.4}$ (Ln=Eu, Gd) [31] and $Tl_{0.94}Sr_2Cu_{0.4}Co_{0.6}O_{5-\delta}$ [32,33] have been shown to exhibit CMR properties.

5.1. The 112-type $LnBaCo_2O_{5.4}$

These new phases, isolated for Ln=Eu, Gd, exhibit an ordered oxygen deficient perovskite structure derived from the 112-structure of $YBaFeCuO_5$ [34,35]. It consists of double pyramidal cobalt layers $[BaCo_2O_5]_\infty$ interleaved with $[LnO_y]_\infty$ layers (y=0.40). The resistivity curves of these compounds show that a metal-insulator transition (MI) occurs at T_{MI}~360 K, separating a nearly constant ρ region (10^{-3} $\Omega\,cm^1$ for $T>360$ K) from an insulating region below 360 K, which cannot be described with one activation energy (Fig. 9). The application of a magnetic field of 7 T demonstrates that this phase exhibits a negative magnetoresistance for $T<250$ K. The resistivity ratios R_0/R_{7T} (T) show that this effect is at least 'giant' since ratios higher than 10 are obtained at low temperature. The magnetic field dependence of the normalized resistance R_H/R_{7T} shows that the magnetoresistance percentages $(R_0-R_{7T}/R_0)\times100$ ranging from 15% to 41% according to the temperature, are at least comparable to the highest values reported for $La_{1-x}Sr_xCoO_3$ perovskites for which a maximum of 40% is reached at 50 K in 6 T for $La_{0.93}Sr_{0.07}CoO_3$ [28,29]. It is remarkable that the resistance ratios R_0/R_{7T} of these 112 phases are significantly larger than that of $La_{1-x}Sr_xCoO_3$ (greater than 10 against less than 2), although both compounds exhibit quite similar MR percentages.

The magnetotransport properties of these phases are in fact related to the existence of two types of magnetic transitions; antiferromagnetic to ferromagnetic, and ferromagnetic to paramagnetic, that appear at 250 K and 360 K respectively.

5.2. The 1201-type $Tl_{0.94}Sr_2Cu_{0.4}Co_{0.6}O_{5-\delta}$

This phase exhibits a 1201 structure built up of single octahedral perovskite layers $[SrCu_{0.4}Co_{0.6}O_3]_\infty$ intergrown with distorted rock salt type layers $[Tl_{0.94}SrO_2]_\infty$.

The $R(T)$ curve of this phase and its $\chi(T)$ dependence show that its behaviour is characteristic of a spin glass

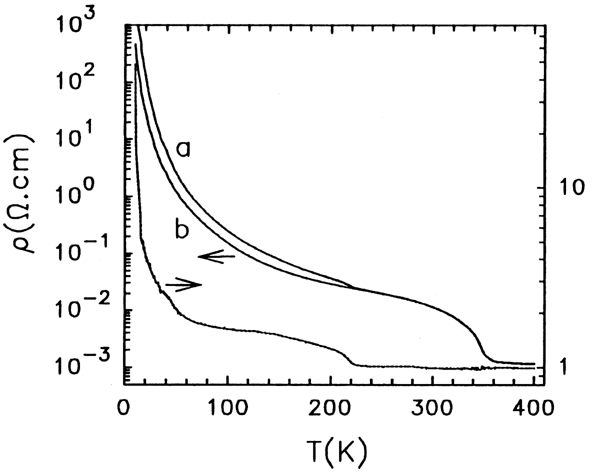


Fig. 9. $\rho(T)$ curves registered during cooling in zero field (a) and in 7 T (b) (left y-axis, solid lines), and corresponding $\rho_0(T)/\rho_{7T}$ curve (right y-axis) for $GdBaCo_2O_{5.4}$.

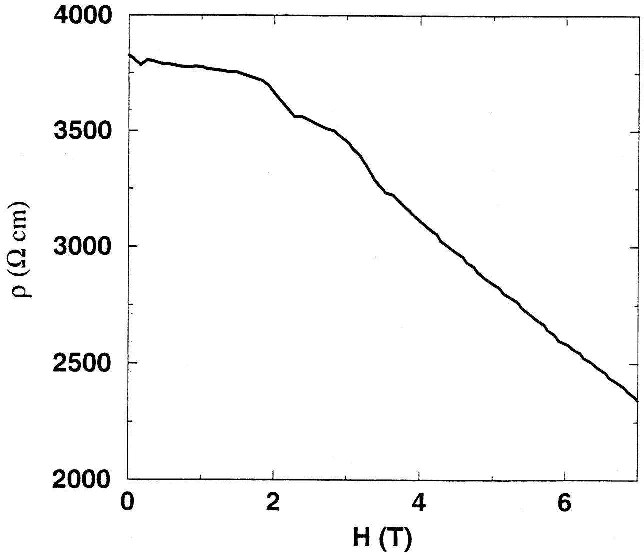


Fig. 10. Resistivity of $Tl_{0.94}Sr_2Cu_{0.4}Co_{0.6}O_{5-\delta}$ sample at 5 K as a function of an increasing applied magnetic field.

insulator [36]. This property is confirmed by the significant shifting of the susceptibility peak to higher temperature on applying higher frequencies.

The application of a magnetic field of 5 T lowers significantly the resistivity, but the magnetoresistance ratio R_0/R_{5T} remains rather small, reaching 1.2 at low temperature. The exploration of the magnetic field dependence of the resistivity, acquired on raising the field from 0 to 7 T at a rate of 0.025 $T\,s^{-1}$, the sample being held at 5 K, confirms the magnetoresistance effect (Fig. 10). It is seen that the resistivity of the sample falls slowly initially, before rapidly decreasing from about 3700 Ω cm at 0 T to 2400 Ω cm under 7 T. This magnetoresistance effect, although much weaker than that observed in $Ln_{1-x}A_xMnO_3$ perovskites, is of great interest since it may be ubiquitous across a variety of transition metal oxides.

6. Concluding remarks

The doping of Mn sites with various elements in manganites represents a very promising field for the investigation of CMR properties of these materials.

Although the mechanisms are so far not understood, several features can be emphasized which can be used as a guideline for further investigations. The most important result concerns the possibility to induce a MI transition and consequently CMR properties by chemical doping of the Mn site of the insulating phases $Ln_{0.5}Ca_{0.5}MnO_3$. In all cases, the doping with various M elements, M=Mg, Al, Fe, Ga, Ti, Sn, Co, Ni, Cr suppresses charge ordering. Such a phenomenon is not unexpected if one considers that this doping changes the Mn(III)/Mn(IV) ratio. But, more important is the fact that the behaviour is different for the series M=Mg, Al, Fe, Ga, Ti, Sn than for M=Co, Ni, Cr. The first series keeps in the insulating properties of the undoped phase $Ln_{0.5}Ca_{0.5}MnO_3$, whereas the second one induces a MI transition. This shows that the suppression of charge ordering is not sufficient to generate a ferromagnetic metallic state under zero magnetic field. The different behaviour of cobalt, nickel and chromium suggests that the presence of such elements as doping agents induces a significant variation of the crystal field for manganese, or at least may create a narrow band very close to the conduction band of manganese. Then, this different property of chromium, cobalt, and nickel may be due to the ability of these elements to exhibit itinerant carriers in oxides with high valence states; this is indeed known, for instance, in CrO_2 which is a ferromagnetic metal, in $La_{2-x}Sr_xNiO_4$ that is also a semi metal, and in $La_{1-x}Sr_xCrO_3$ which is a good metal. It is also remarkable that the doped phases $Ln_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ exhibit CMR properties whatever M, even if they remain insulating. Nevertheless, the appearance of such an effect is favoured by a MI transition. We note finally, with the study of the $Ln_{0.5}Ca_{0.5}Mn_{1-x}Ni_xO_3$ series that the ability of the dopant (Ni) to suppress charge ordering decreases with the size of the lanthanide. In any case, the doping of the Mn sites with foreign elements, and especially with Cr, Co or Ni, modifies considerably the magnetic phase diagrams that have been established previously by different authors for the undoped manganites on the only basis of the size of the interpolated cations. The latter property is of capital importance for the optimisation of the CMR properties of these materials.

The doping of the manganese sites in manganites, such as $Ln_{0.7}(Sr, Ca)_{0.3}$ MnO_3 is also interesting, although it generally decreases T_C. The possibility of increasing the CMR effect by several orders of magnitude, by doping with iron or magnesium, may be useful for applications. Further investigations will have to be made to understand these properties.

The synthesis of new CMR oxides without manganese, such as the cobaltites $LnBaCo_2O_{5.4}$ (Ln=Eu, Gd) and the phase $Tl_{0.94}Sr_2Cu_{0.4}Co_{0.6}O_{5-\delta}$ is also a very important route for the research of new CMR oxides, in spite of the fact that these materials exhibit much smaller resistance ratios.

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