Effect of A-site cation size mismatch on charge ordering and colossal magnetoresistance properties of perovskite manganites

A. Sundaresan, A. Maignan, and B. Raveau

Laboratoire CRISMAT, ISMRA, 6 Bd du Maréchal Juin 14050, Caen Cedex, France

Resistivity and ac-susceptibility measurements demonstrate that the cation size mismatch at the A site in perovskite manganites influences greatly the electrical and magnetic properties which are associated with colossal magnetoresistance. It has been reported that the $Pr_{1-x}Ca_xMnO_3$ system does not exhibit an insulator-metal transition and remains insulating at all temperatures because of charge ordering at high temperatures. We show that the cation size mismatch at the A site, introduced by replacing the Pr^{3+} ions by larger La^{3+} and smaller Y^{3+} ions with constant average A-site ionic radius $\langle r_A \rangle = 1.18$ Å, suppresses charge ordering and the samples with $x = 0.25$ and 0.3 undergo insulator-metal transitions at 130 and 60 K, respectively, without applying a magnetic field. For $0.30 \leq x \leq 0.5$, they all show a spin-glass behavior. [S0163-1829(97)00734-0]

The ferromagnetic metal transition, T_{fm}, in distorted perovskite manganites, $R_{1-x}M_xMnO_3$ (where $R =$ trivalent lanthanides and $M =$ divalent alkaline earths), is controlled by the amount of hole doping, x, and the average radius, $\langle r_A \rangle$, of A-site cations and occurs at a maximum $T = 360$ K for $x = 0.3$ with $\langle r_A \rangle = 1.23$ Å. With decreasing $\langle r_A \rangle$, T_{fm} decreases monotonically.[1–4] Below $\langle r_A \rangle \sim 1.19$ Å, the system becomes a spin-glass insulator[5] because of the competion between ferromagnetic and antiferromagnetic interactions. Due to the large differences in ionic size between R^{3+} and M^{2+} cations, it has not been possible to study the effect of hole concentration, x, alone, (i.e., with constant $\langle r_A \rangle$ and without introducing ionic size mismatch) on the magnetic and electrical properties of these perovskites. However, there exists a system $Pr_{1-x}Ca_xMnO_3$ where the Pr^{3+} and Ca^{2+} ions have almost the same ionic radius (1.179 Å and 1.180 Å, respectively[6]) but, unfortunately, this system is an insulator[7] because the $\langle r_A \rangle (= 1.18$ Å) is just lower than that reported for a ferromagnetic metal.[2] On the other hand, it shows the colossal magnetoresistance (CMR) effect under an applied magnetic field for $0.3 \leq x \leq 0.5$.[8] Several studies have shown that the absence of an insulator-metal transition is due to charge ordering and accompanying antiferromagnetic ordering at high temperatures.[7,9,10] Recently, it has been shown from low-field ac-χ measurements that the system $Pr_{1-x}Ca_xMnO_3$ ($0.25 \leq x \leq 0.5$) has a complicated magnetic behavior.[11] For $0.35 \leq x \leq 0.5$, the resistivity and susceptibility measurements show that charge and antiferromagnetic ordering occur simultaneously in the temperature range $220 – 250$ K. At low temperatures and for $x = 0.25, 0.3$ they show a spin-glass behavior.

It is known that disorder due to ionic size mismatch between various ions at the same crystallographic site influences the transport properties of materials. In the case of doped manganites, since the conductivity and magnetism are strongly correlated, it is particularly important to consider the effect of A-site ionic size mismatch on the CMR properties, in addition to other lattice effects such as random potential fluctuation due to R^{3+} and M^{2+} cations and Jahn-Teller distortions associated with Mn^{3+} ion with a $3d^4$

configuration. Recently, it has been shown[12] that the increase of ionic size mismatch at the A site of $R_{0.7}M_{0.3}MnO_3$ system, with a fixed doping level decreases both T_{fm} and magnetoresistance ratio.

In the present study, we have investigated the effect of cationic size mismatch at the A site on the electrical and magnetic properties in $R_{1-x}M_xMnO_3$ with constant $\langle r_A \rangle = 1.18$ Å and different x to compare the results with those of $Pr_{1-x}Ca_xMnO_3$ which can be considered as a system having no or least mismatch due to similar size of the Pr^{3+} and Ca^{2+} ions. In this system, we have introduced size mismatch at the A site by replacing the Pr^{3+} ion by larger La^{3+} ($r = 1.216$ Å) and smaller Y^{+3} ($r = 1.075$ Å) ions without changing the $\langle r_A \rangle = 1.18$ Å. We use the *variance* ($\sigma^2 = \Sigma y_i r_i^2 - \langle r_A \rangle^2$) to measure the ionic size mismatch[12] (Table I). Our study shows that the charge ordering in the $Pr_{1-x}Ca_xMnO_3$ system is suppressed by the ionic size mismatch at the A site and samples with $x = 0.25$ and 0.3 undergo insulator-metal transitions even at zero applied magnetic field.

Polycrystalline samples of $(La,Y)_{1-x}Ca_xMnO_3$ with various values of x were prepared by the solid-state reaction method described elsewhere.[13] The ratio of La/Y for a given x with constant $\langle r_A \rangle = 1.18$ Å was calculated and is given in Table I. X-ray-diffraction patterns of all the samples confirmed that the samples are single phase and orthorhombic with the space group $Pbnm$. Lattice parameters obtained from the Rietveld analysis of the x-ray data are also given in Table I. Oxygen content for various samples determined by redox titrations involving Fe^{3+}/Fe^{2+} redox couple suggested that the oxygen is stoichiometric. Low-field ac-susceptibility (χ') and magnetoresistance measurements were made with a Lake shore 7000 susceptometer and a physical property measuring system (PPMS, Quantum Design), respectively.

Temperature dependence of resistivity $\rho(T)$ at zero applied magnetic field for $(La,Y)_{1-x}Ca_xMnO_3$ with various x are shown in Fig. 1. The $\rho(T)$ behavior of this system should be compared with the $Pr_{1-x}Ca_xMnO_3$ system[11] with negligible A-site ionic size mismatch. The room-temperature

TABLE I. Variation of lattice parameters, resistivity at room temperature ρ_{RT}, activation energy E_a (see text), and the *variance* σ^2 of A-site cation size mismatch with x in $(La,Y)_{1-x}Ca_xMnO_3$ with $\langle r_{(La,Y)} \rangle = \langle r_{Pr} \rangle = 1.18$ Å. σ^2 for (Pr,Ca) is $\sim 2 \times 10^{-7}$.

Composition	σ^2	a (Å)	b (Å)	c (Å)	ρ_{RT} (Ω cm)	E_a (eV)
$(La_{0.56}Y_{0.19})Ca_{0.25}MnO_3$	0.00282	5.4460(2)	5.4974(2)	7.6950(3)	1.05	0.136
$(La_{0.49}Y_{0.21})Ca_{0.3}MnO_3$	0.00298	5.4289(2)	5.4806(2)	7.6746(3)	0.92	0.128
$(La_{0.485}Y_{0.165})Ca_{0.35}MnO_3$	0.00245	5.4292(2)	5.4599(2)	7.6722(3)	0.37	0.123
$(La_{0.445}Y_{0.155})Ca_{0.4}MnO_3$	0.00293	5.4184(3)	5.4426(2)	7.6565(4)	0.24	0.120
$(La_{0.375}Y_{0.125})Ca_{0.5}MnO_3$	0.002285	5.3991(3)	5.4255(2)	7.6191(4)	0.06	0.116
$(Tb_{1/2}La_{2/3})_{2/3}Ca_{1/3}MnO_3$ [a]	0.00243	5.4273(11)	5.4603(11)	7.6662(17)		

[a] Reference 5.

resistivity, ρ_{RT}, in both systems decreases with increasing hole concentration, x, which is in agreement with the fact that the conductivity increases with increasing of hole concentration. However, there are remarkable differences in the $\rho(T)$ behavior of these two systems which reveal the role of ionic size mismatch. First, the ρ_{RT} for various x in the former is higher than that for the corresponding x in the latter which is in agreement with the fact that the disorder localizes the charge carriers. Second, in contrast to the $Pr_{1-x}Ca_xMnO_3$ system, there is no anomaly in the present system that can be linked to the charge ordering. This indicates that the charge/antiferromagnetic ordering is suppressed by the ionic size mismatch. The third important observation is that the samples with $x=0.25$ and 0.3 undergo insulator-metal transitions at about 130 and 60 K, respectively, even without applying a magnetic field. Below 50 K, for both the samples, the resistivity increases with decrease of temperature which suggests the presence of antiferromagnetic correlation at low temperatures. Similar behavior has been reported for the $La_{0.5}Y_{0.2}Ca_{0.3}MnO_3$ system[13] which has La/Y ratio very close to the one investigated in the present study (see Table I). However, this behavior is different from that observed for $Pr_{1-x}Ca_xMnO_3$ where the system is an insulator with an anomaly only for $0.35 \leq x \leq 0.5$ at temperatures between 200 and 250 K.[11] These results further

support the suggestion[7,9,10] that the low-temperature ferromagnetism in $Pr_{1-x}Ca_xMnO_3$ is masked by the charge/antiferromagnetic ordering at high temperatures as reported earlier.[7,9–11] In the present system, with the ionic size mismatch at the A site, the charge/antiferromagnetic ordering is suppressed and the ferromagnetic interaction becomes predominant for the samples with $x=0.25$ and 0.3.

At temperatures above 150 K, the $\rho(T)$ behavior could be best fitted with the relation $\rho \sim T \exp(E_a/kT)$, predicted by Emin and Holstein[14] for small polaron hopping in the adiabatic approximation. Values for E_a obtained from the fit are given in Table I. E_a decreases with increase of x, implying the increased motion of polarons with hole concentration which is consistent with the decrease of ρ_{RT} with increase of x.

We now comment upon the results of low field ac-$\chi'(T)$ measurements (see Fig. 2) and compare them with those of the $Pr_{1-x}Ca_xMnO_3$ system.[11] It can be seen that the $\chi'(T)$ of all the samples shows a maximum in χ' (χ'_{max}) at a temperature T_{max}. The χ'_{max} decreases with increase of x. On the other hand, the T_{max} first decreases with increase of x until $x=0.35$ and then it does not change significantly. The decrease of both χ'_{max} and T_{max} suggest that the strength of the ferromagnetic interaction decreases with increase of x. This is consistent with the $\rho(T)$ measurements which show that the samples ($x=0.25$ and 0.3) with the higher χ' undergo insulator-metal transitions with $T_{fm}=130$ and 60 K, respectively, while the other samples with lower χ' remain insulating at all temperatures. Further, for $x=0.25$ and 0.3, the decrease of χ' below χ'_{max} explains the increase of resistivity below T_{fm}. A sample with $x=0.5$ shows a small anomaly at the temperature around 240 K which can be attributed to charge/antiferromagnetic ordering since the Coulomb interactions are more predominant than the kinetic energy of the charge carriers for such a commensurate value of x. However, the resistivity does not show any anomaly at that temperature, indicating that the charge ordering occurs to a smaller extent. This behavior is different to that observed for the $Pr_{1-x}Ca_xMnO_3$ system[11] where, for samples with $0.35 \leq x \leq 0.5$, the χ' shows a sharp peak at the temperature around 250 K indicating charge ordering. For $x=0.30$ and 0.25, it shows no anomaly at high temperatures and the frequency dependence of χ' suggested a spin-glass behavior as mentioned in the Introduction.

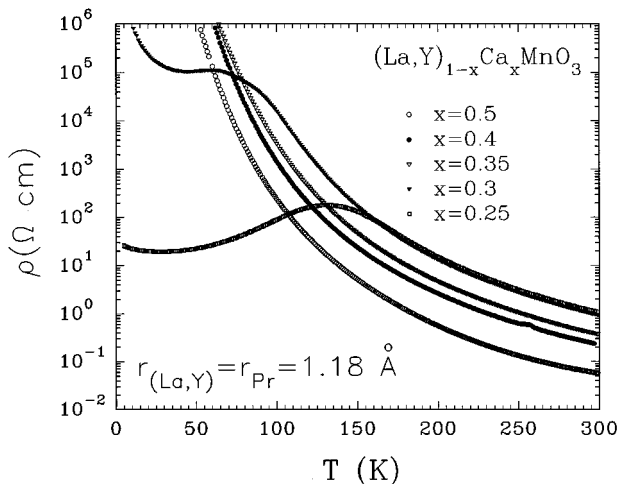Spin-glass states arise due to a strong competition between ferromagnetic and antiferromagnetic interactions. In

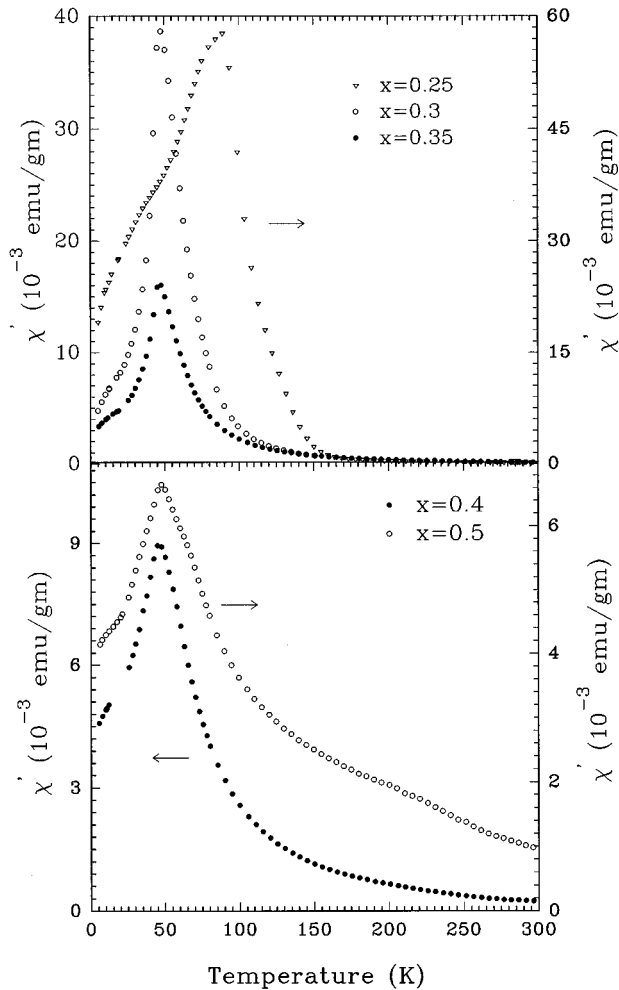FIG. 1. Temperature dependence of resistivity of $(La,Y)_{1-x}Ca_xMnO_3$. An insulator-metal transition is clearly seen for $x=0.25$.

FIG. 2. Variation of ac$-\chi'$ as a function of temperature for $(La,Y)_{1-x}Ca_xMnO_3$.

the system with smaller $\langle r_A \rangle$ and for x near the commensurate value ($x=0.5$), the dominant interaction is antiferromagnetic; for the composition around $x=0.3$ a spin-glass behavior occurs due to competition between ferromagnetic and antiferromagnetic interactions. We have studied the frequency dependence of the susceptibility $\chi'(f)$ of all the samples. For $0.30 \leq x \leq 0.5$, all the samples showed spin-glass behavior with a freezing temperature T_g in the range 40–55 K. For example, the ac-$\chi'(T)$ plot for $x=0.4$ measured at various frequencies is shown in Fig. 3. It can be seen that the T_{max} increases with frequency suggesting spin-glass behavior. Further support for such spin-glass behavior comes from the power-law dependence of the dynamical slowing down of the spin fluctuations near T_g. The data were fitted to the relation,

$$T_g = T_c[1 + (\tau_0 f)^{(1/z\nu)}],$$

where τ_0 is usually taken as 10^{-13} and $z\nu$ are critical exponents. Values for $z\nu$ and T_c obtained from the above fit are 7.4 and 45 K, respectively. These values for $z\nu$ are similar to those observed for spin-glass manganese oxides with a pyrochlore-type structure.[15] The observation of spin-glass behavior with no anomaly in $\rho(T)$ associated with charge ordering for the $(Tb_{1/3}La_{2/3})_{2/3}Ca_{1/3}MnO_3$ system[5] with
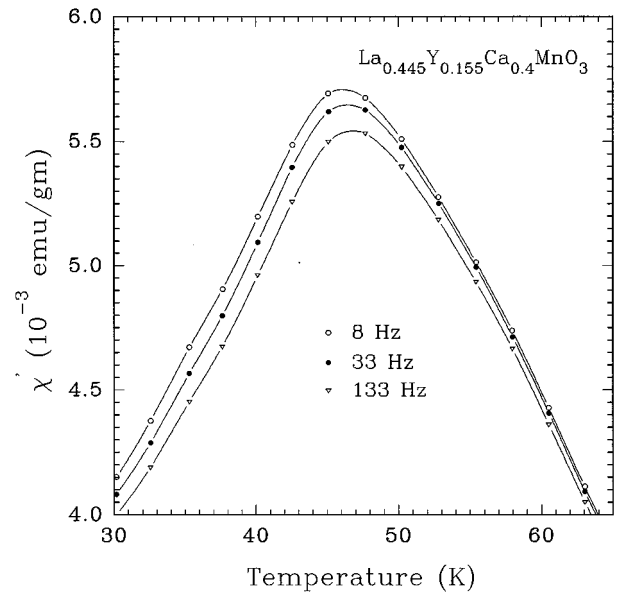

FIG. 3. Temperature dependence of the real part of the ac susceptibility at different frequencies for $(La_{0.445}Y_{0.155})Ca_{0.4}MnO_3$, showing a spin-glass behavior.

similar $\langle r_A \rangle (=1.177$ Å$)$ and ionic size mismatch at the A site ($\sigma^2 = 0.00243$) is consistent with our finding that the charge ordering is suppressed by ionic size mismatch at the A site.

The $\rho(T)$ for $x=0.25$ measured under various applied magnetic fields are shown in Fig. 4. It can be seen that although there is a negative magnetoresistance effect, the T_{fm} does not seem to increase with magnetic field. This is different from the other CMR materials where the T_{fm} increases with magnetic field. This may be due to ionic size mismatch at the A site. It should be noticed that the low-temperature antiferromagnetic state persists even at 5 T. Other samples
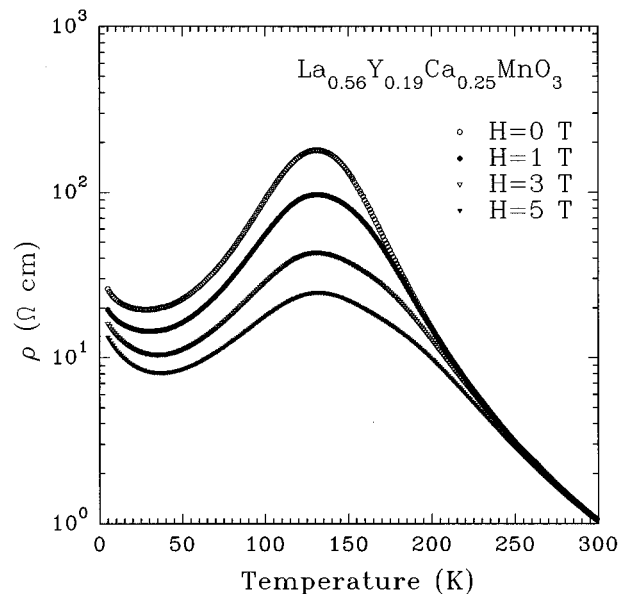

FIG. 4. Temperature dependence of resistivity under different applied magnetic fields, 0, 1, 3, and 5 T.

show insulator-metal-insulator transitions similar to those observed for the spin-glass $Eu_{0.58}Sr_{0.42}MnO_3$ system having large $\langle r_A \rangle = 1.199$ Å and high disorder due to ionic size mismatch ($\sigma^2 = 0.00879$).[16]

In conclusion, we have shown that the charge/antiferromagnetic ordering in $Pr_{1-x}Ca_xMnO_3$ is suppressed by introducing ionic size mismatch at the A site by replacing the Pr^{3+} ions by the bigger La^{3+} and smaller Y^{3+} ions with constant $\langle r_A \rangle = 1.18$ Å. Consequently, the samples with $x = 0.25$ and 0.3 undergo insulator-metal transitions at 130 and 60 K, respectively, at zero applied magnetic field. Samples with $x \geqslant 0.3$ show a spin-glass behavior.

[1] B. Raveau, A. Maignan, and V. Caignaert, J. Solid State Chem. **117**, 424 (1995).

[2] H. Y. Hwang *et al.*, Phys. Rev. Lett. **74**, 914 (1995).

[3] A. Maignan *et al.*, Z. Phys. B **99**, 305 (1996).

[4] F. Damay *et al.*, Solid State Commun. **98**, 997 (1996).

[5] J. M. De Teresa *et al.*, Phys. Rev. Lett. **76**, 3392 (1996).

[6] R. D. Shannon, Acta Crystallogr. Sec. A **32**, 751 (1976).

[7] Z. Jirak *et al.*, J. Magn. Magn. Mater. **53**, 153 (1985).

[8] Y. Tomioka *et al.*, Phys. Rev. B **53**, R1689 (1996).

[9] H. Yoshizawa *et al.*, J. Phys. Soc. Jpn. **65**, 1043 (1996).

[10] J. M. De Teresa *et al.*, Phys. Rev. B **54**, R12 689 (1996).

[11] A. Maignan *et al.*, Z. Phys. B (to be published).

[12] L. M. Rodriguez-Martinez, and J. P. Attfield, Phys. Rev. B **54**, R15 622 (1996).

[13] A. Maignan *et al.*, J. Appl. Phys. **79**, 7891 (1996).

[14] D. Emin and T. Holstein, Ann. Phys. (N.Y.) **53**, 439 (1969).

[15] J. E. Greedan *et al.*, Phys. Rev. B **54**, 7189 (1996).

[16] A. Sundaresan, A. Maignan, and B. Raveau, Phys. Rev. B **55**, 5596 (1997).