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Cadmium doping at Mn site in $Pr_{0.5}Ca_{0.5}MnO_3$

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Abstract

In this work, manganese site doping by cadmium (up to 6%) in $Pr_{0.50}Ca_{0.50}MnO_3$, has been studied. In spite of its large ionic radii, Cd^{2+} was incorporated into the manganite structure, suppressing charge-ordering, inducing ferromagnetism and CMR effects, in a similar way as other d^{10} electronic configuration ions like Sn^{4+}, Ga^{3+} and In^{3+}.

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The mixed valence manganite system $Pr_{1-x}Ca_xMnO_3$ has received considerable attention due to the richness of its phase diagram with respect to phase transitions associated with the spin, lattice, charge and orbital degrees of freedom. In particular $Pr_{0.5}Ca_{0.5}MnO_3$ presents a robust charge-ordered (CO) state for temperatures below 230 K, which can only be melted by a very high magnetic field, and an antiferromagnetic insulator state below $T_N = 180$ K [1]. Raveau et al. [2] have shown that doping at Mn sites with a few percent of transition-metal ions leads to the suppression of the CO state inducing a ferromagnetic component and, in some cases, a metallic behavior [3]. Moreover, it was recently claimed that for some doping elements (e.g. Ga, Sc) very peculiar discontinuous features were found in measurements of magnetization as a function of magnetic field [4].

In this work we study the effect of Cd substitution at the Mn site, on the electrical and magnetic properties of $Pr_{0.5}Ca_{0.5}MnO_3$. $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cd_xO_3$ samples with $x = 0$, 0.03 and 0.06 were prepared by sol gel technique allowing low sinterization temperatures and thus reducing the risk of Cd volatilization. Remark that previous studies have already shown that Cd can substitute Mn in spite of its rather large ionic radius without any evidence of Cd segregation at the grain boundaries [5].

X-ray diffractograms showed that the samples consist of a single orthorhombic (Pbmn space group) phase, and the corresponding lattice parameters were obtained from rietveld refinements. The incorporation of Cd was found to decrease the cell volume leading to a pseudocubic $(O, a<c/\sqrt{2}<b)$ structure. Magnetization measurements were performed in a commercial Quantum Design SQUID. Resistivity measurements, using the standard four contact method, were performed in an *Oxford* cryostat (1.5−300 K) equipped with a 12 T superconducting coil. The zero field cooled (ZFC), field cooled (FC) magnetization curves, measured under 50 Oe magnetic field (Fig. 1) show that Cd doping reduces drastically the charge-ordering effect, responsible for the strong maximum in the $x = 0$ sample, inducing also a ferromagnetic state which strengthens with increasing Cd content. For the Cd-doped samples, two inflection points are present at low temperature (minima in the inset of Fig. 1) pointing to the

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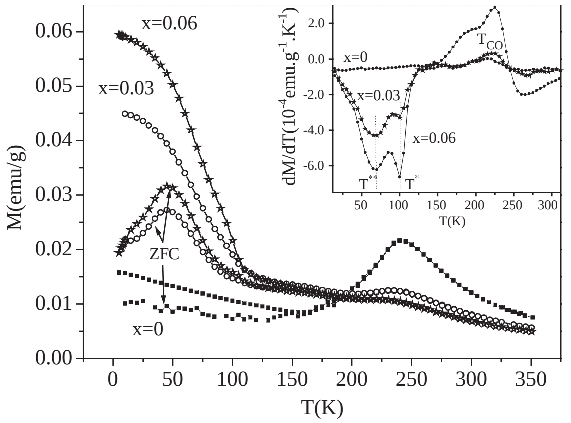

Fig. 1. ZFC and FC magnetisation measurements ($H = 50$ Oe) as a function of temperature for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cd_xO_3$ samples with $x = 0$, 0.03 and 0.06. Inset: temperature derivative of FC magnetization for the same set of samples.

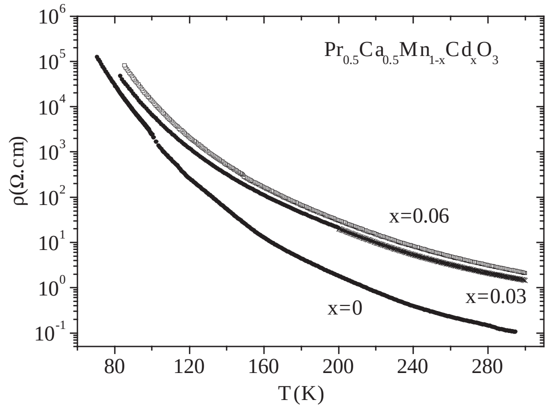

Fig. 2. Temperature dependence of zero field resistivity for $x = 0$, 0.03 and 0.06, $Pr_{0.5}Ca_{05}Mn_{1-x}Cd_xO_3$ samples.

coexistence of two ferromagnetic phases with Curie temperatures, $T^* = 100$ K, and $T^{**} = 70$ K, independently of Cd content. Moreover, the ZFC curves show spin glass features below $T_{SG} = 46$ K, similar to those found by Hébert et al. [3] for doping with other d^{10} electronic configuration cations like Sn^{4+}, Ga^{3+} and In^{3+}.

At room temperature the resistivity increases with increasing Cd content (Fig. 2), possibly due to the increase in the charge-scattering by the doping element. At low temperature the $\rho(T)$ curves (see also Fig. 2) tend to cross suggesting the effect of ferromagnetism in Cd-doped sample resistivity. In fact, we can see in Fig. 3 that such Cd-doped samples are near a ferromagnetic-metallic state and the application of a magnetic field of 4 T is sufficient to induce metallicity and CMR effects (see insets of Fig. 3), in contrast with the undoped sample, which requires 27 T to induce a similar behavior. The large thermal hysteresis patent in the curves with 4 to 6 T suggests the first-order nature of such field-induced metal–insulator transition, with coexistence of ferromagnetic metallic/insulator regions.

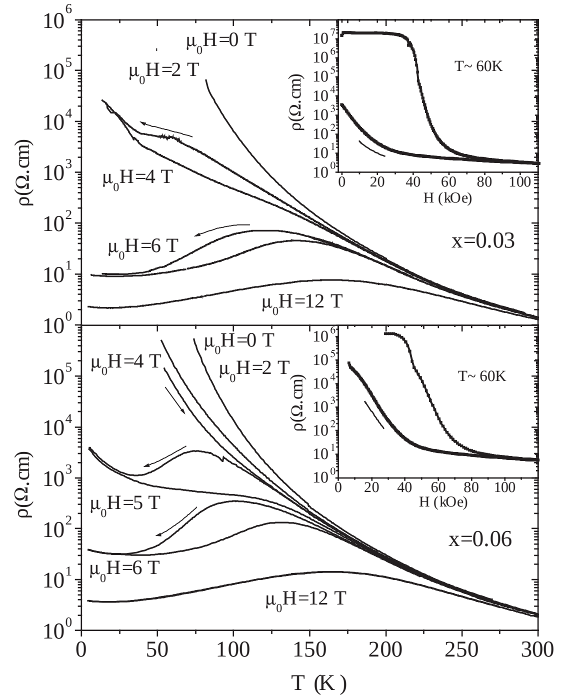

Fig. 3. Temperature dependence of resistivity for $x = 0.03$ (top) and 0.06 (bottom) $Pr_{0.5}Ca_{05}Mn_{1-x}Cd_xO_3$ samples, for several magnetic fields. Inset: Field dependence of resistivity at $T \sim 60$ K.

In conclusion, Cd^{2+} was incorporated at the Mn site in $Pr_{0.5}Ca_{0.5}MnO_3$ suppressing charge-ordering and inducing ferromagnetism and CMR effects in a similar way as other d^{10} electronic configuration ions.

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