

Magnetism, resistivity and magnetoresistance in $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$

H. Aliaga^a, M.T. Causa^{a,*}, B. Alascio^a, H. Salva^a, M. Tovar^a, D. Vega^b,
G. Polla^b, G. Leyva^b, P. König^b

^aCentro Atómico Bariloche and Instituto Balseiro, Universidad Nacional de Cuyo, Comisión Nacional de Energía Atómica,
8400 San Carlos de Bariloche, Río Negro, Argentina

^bCentro Atómico Constituyentes, Comisión Nacional de Energía Atómica, 1650 San Martín, Buenos Aires, Argentina

Abstract

We present magnetic and transport studies on the manganite $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ ($x \leq 0.25$). A small Y concentration produces an important decrease in the electrical resistivity and increases the magnetization but full ferromagnetic order is not achieved. The samples with $0.05 \leq x < 0.18$ show magnetoresistive effects. For $x \geq 0.18$ indications of charge order were observed in the magnetization and resistivity behaviors. © 2001 Elsevier Science B.V. All rights reserved.

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Magnetoresistance (MR) in Mn oxides was known at a very early stage of the study of the transition metal oxides. Most studies were devoted to the perovskite compounds $(A, A')\text{MnO}_3$ where A and A' are, respectively, trivalent rare-earth and divalent alkaline-earth ions producing two-valence Mn ions. Ferromagnetic (FM) double-exchange (DE) interaction between localized t_{2g} electrons, mediated by itinerant spin-polarized e_g electrons, is the basis of the MR effect. In this paper we study the series $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ in the lightly electron-doped region [1,2]. We analyze the correlation between magnetic, electric and structural properties, both in the paramagnetic (PM) and in the ordered phases.

Ceramic polycrystalline samples of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ were prepared by solid-state reaction. Room T X-rays diffractograms show that YMnO_3 crystallizes in a hexagonal $P63cm$ structure (with $a = 6.140 \text{ \AA}$ and $c = 11.398 \text{ \AA}$) and CaMnO_3 in an orthorhombic $Pnma$ structure (with $a = 5.824 \text{ \AA}$, $b = 7.453 \text{ \AA}$, and $c = 5.266 \text{ \AA}$). For $x \leq 0.8$ orthorhombic phases were sin-

tered. For $x > 0.8$ reflections corresponding to the hexagonal structure always appear indicating segregation of YMnO_3 . In the electron-doped region ($x < 0.5$) the material forms a single O-phase for $x \leq 0.25$. For $x \geq 0.5$ a single O'-phase is present. Two-phase samples (O + O') are obtained for intermediate concentrations. Here we present results obtained in the single-phase low doped region with $0 \leq x \leq 0.25$. Electrical resistivity, ρ , was measured in the range 5–300 K with magnetic fields $H \leq 0.45 \text{ T}$. The magnetization, M , was measured with a SQUID magnetometer ($T < 300 \text{ K}$) and a Faraday balance magnetometer ($T > 300 \text{ K}$).

In Fig. 1 we show $\rho(T)$ for the different samples. The highest resistivity corresponds to $x = 0$ and can be described as a thermally activated behavior $\rho(T) \propto T \exp(E_A/k_B T)$ with $E_A = 430 \text{ K}$. For $x = 0.05$ $\rho(T)$ decreases monotonically from 5 to 220 K and then increases slowly up to 300 K. This dependence corresponds to the same behavior, with $E_A = 60 \text{ K}$, in the range 70–300 K. At lower temperatures $\rho(T)$ deviates from this law and increases less rapidly and remains smaller than $1 \Omega \text{ cm}$ at 5 K. For $x = 0.10$, $\rho(T)$ shows a kink at $T \approx 105 \text{ K}$ and at lower T , $\rho(T)$ continues to increase reaching an almost constant value for $T < 25 \text{ K}$ (see Fig. 1). The sample with $x = 0.15$ presents two regions of

* Corresponding author. Fax: + 54-2944-445299.

E-mail address: causa@cab.cnea.gov.ar (M.T. Causa).

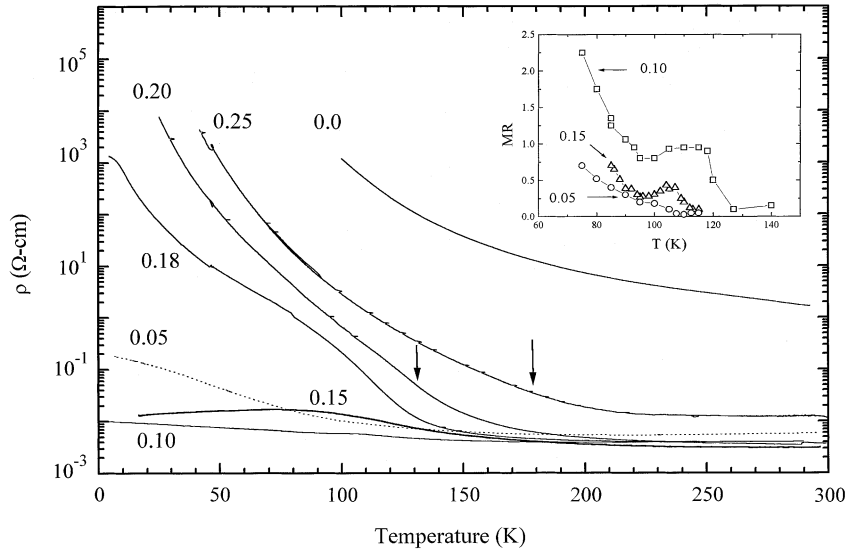


Fig. 1. $\rho(T)$ for $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$. Values for x are indicated. Inset: MR vs. T for $H = 0.25$ T.

Table 1

$\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ Curie constant (C), Curie–Weiss temperature (Θ) and transition temperatures for magnetic (T_c) and charge (T_{CO}) ordering

x	C (emu K/mol)	Θ (K)	T_c (K)	T_{CO} (K)
0.00	1.80	−350	100	—
0.05	1.90	−100	100	—
0.07	1.96	0	100	—
0.10	2.01	40	100	—
0.15	1.90	115	100	—
0.18	2.20	120	120	120
0.20	2.22	120	120	130
0.25	2.22	120	120	180

different behaviors. For high temperatures, $\rho(T)$ still resembles an activated process and a small feature in $d\rho(T)/dT$ is observed at $T \approx 110$ K. A broad maximum is reached at $T \approx 75$ K and metallic behavior is found for lower temperatures. An almost linear dependence on T is followed down to about 20 K, where $\rho(T)$ reaches a constant value. The resistivity for $x \geq 0.18$ increases monotonically for decreasing temperatures and it was not possible to fit its behavior with a single activation energy. It seems that two thermally activated mechanisms are present for $x = 0.20$ and 0.25 with transitions at $T = 130$ and 180 K, respectively (see arrows in Fig. 1), where maxima in $d(\ln \rho)/d(1/T)$ were observed. The samples with $0 < x < 0.20$ show MR effects under applied field $H \leq 0.45$ T, as shown in the inset of Fig. 1. In all cases, $\text{MR} = 100[\rho(T, 0) - \rho(T, H)]/\rho(T, 0)$ increases with de-

creasing T but, for $x = 0.10$ and 0.15 , relative maxima were observed at $T \approx 110$ K.

Antiferromagnetic (AFM) ordering driven by superexchange (SE) was found [3] in CaMnO_3 . The existence of an additional weak FM moment below T_N can be explained in terms of Dzialoshinsky–Moriya (DM) anisotropic super exchange [4]. For $x > 0$, the DC susceptibility $\chi(T)$ in the PM region was well fitted by a Curie–Weiss law whose parameters are given in Table 1. Small doping with Y causes large changes in the Curie–Weiss temperature Θ indicating an evolution from a strong AFM system, for $x = 0$, to an FM one. This behavior is accompanied by, an already mentioned, strong increase in the electrical conductivity for $x \leq 0.18$. In Fig. 2 we plot $M(T)$ measured with $H = 0.5$ T. All the samples show an FM component which defines a transition temperature $T_c \approx 100$ K, at the point of maximum negative slope for $M(T)$ vs. T . We observed the strongest magnetization for $x = 0.10$ and 0.15 , which is about $\frac{1}{3}$ of full FM ordering for $H = 5$ T. For the samples in the range $x = 0.18/0.25$, additional relative maxima in $M(T)$ were found at $T > T_c$ (see Fig. 2).

The competition between AFM–SE and FM–DE interactions is reflected in the observed changes of the magnetic behavior as a function of x : (i) For $x = 0$ the system is AFM and insulator with a DM-type weak FM component at low T . For Y-doped samples, DE generates a strong decrease in the resistivity and important variations of Θ (see Fig. 1 and Table 1). (ii) For $0.05 < x < 0.18$, the DE is dominant giving metallic-FM behavior. However, the AFM–SE interaction is not negligible and a saturated FM state is not reached. The resistivity anomalies around T_c and the MR effects give

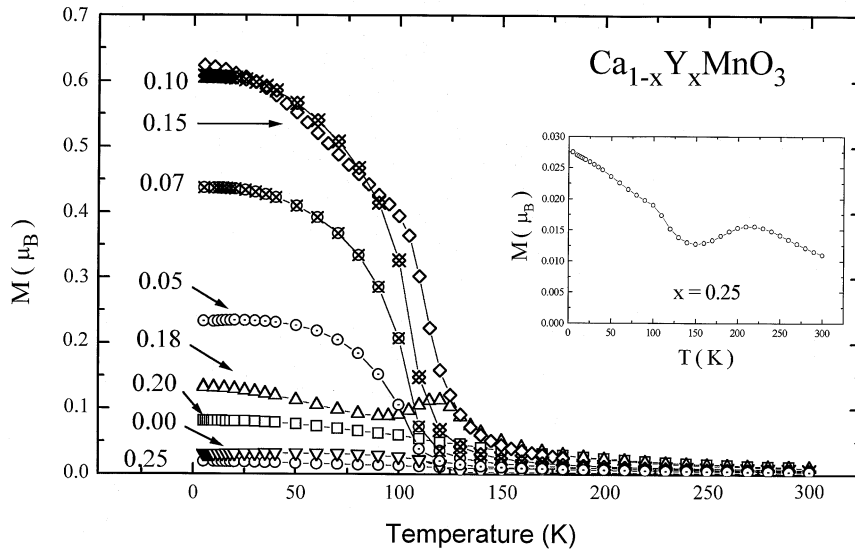


Fig. 2. $M(T)$ measured with $H = 0.5$. Corresponding values for Y concentration are indicated. Inset: $x = 0.25$ in an amplified scale.

clear evidence of the magnetic origin of these features. (iii) For $0.18 \leq x \leq 0.25$ a charge-ordered (CO) state is present at $T < T_{\text{CO}}$. A signature for the CO state is the sudden increase in $\rho(T)$, in coincidence with relative maxima in $M(T)$ above T_c (see Figs. 1 and 2).

In conclusion, the effects of double exchange are present in our electron-doped samples for $x \leq 0.18$, giving rise to a lowering of resistivity by several orders of magnitude and an increase of the magnetization reaching values comparable to the full ferromagnetic moment. In samples with higher Y concentration charge order takes place and DE is not effective below T_{CO} .

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