

LETTER TO THE EDITOR

Increase of T_N up to 190 K in the Type II CMR Manganite $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$

J. Wolfman, Ch. Simon, M. Hervieu, A. Maignan, and B. Raveau

Laboratoire CRISMAT, ISMRA et Université de Caen, URA 1318 associée au CNRS, 6 bd du Maréchal Juin, 14050 Caen Cedex, France

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Calcium doping of the type II CMR manganites $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ has allowed the transition temperature T_N to be significantly increased up to 190 K. The systematic study of the solid solution $\text{Pr}_{1/2}\text{Sr}_{1/2-x}\text{Ca}_x\text{MnO}_3$ shows that the mean size of the interpolated cation plays a prominent role in the CMR properties of these oxides: T_N increases significantly whereas T_C decreases only slightly as the mean size of the interpolated cation decreases. This behavior is fundamentally different from that observed for $\text{Pr}_{1/2-x}\text{Y}_x\text{Sr}_{1/2}\text{MnO}_3$ for which T_N increases slightly and T_C decreases dramatically as the mean size of the interpolated cation decreases. The $\rho(T)$ curves registered in a magnetic field of 7 T show a negative CMR effect characterized by a dramatic decrease of T_N and a complicated variation of the R_0/R_H ratio that reaches a maximum value of 3×10^3 at 150 K in a magnetic field of 7 T for $x = 0.09$. © 1996 Academic Press, Inc.

The recent study of the perovskite $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ by Tokura *et al.* (1) has shown its singular behavior with respect to other perovskites that exhibit colossal magnetoresistance (CMR) properties. This CMR perovskite, named here type II, shows a transition from an antiferromagnetic (AFM) nonmetal to a ferromagnetic (FM) metal as T increases, whereas other manganites such as $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, with $0.2 < x < 0.5$ (type I), exhibit a transition from a ferromagnetic (FM) metal to a paramagnetic (PM) semi-conducting state as T increases (see, for instance, Refs. 2–8). This type II effect was also observed for $\text{Nd}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ (9) and was explained in terms of charge ordering (co). The corresponding transition temperature (T_N), named T_{co} by these authors, varies from 140 K for Pr to 158 K for Nd. In a recent investigation of the solid solution $\text{Pr}_{1/2-x}\text{Y}_x\text{Sr}_{1/2}\text{MnO}_3$ (10), we demonstrated the influence of the mean size of the interpolated cation upon T_N and T_C . It was indeed shown that decreasing the mean size of the interpolated cation favors the AFM and PM semi-conducting states at the expense of the FM metallic state, so that in a first step T_N increases and correlatively T_C

decreases, as x increases. In fact, there exists an x value beyond which the two antagonist effects, type I (T_C) and type II (T_N), come near each other so that the FM state disappears. For this reason, T_N could only be increased from 136 K for $x = 0$ to 156 K for $x = 0.06$, decreasing again for higher x values.

In order to get a better understanding of this size effect of the interpolated cation upon T_N and T_C , we have studied the doping of $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ by calcium. We report herein on the study of the CMR manganites $\text{Pr}_{1/2}\text{Sr}_{1/2-x}\text{Ca}_x\text{MnO}_3$, for which T_N can be increased up to 190 K, whereas T_C decreases much more slowly than for $\text{Pr}_{1/2-x}\text{Y}_x\text{Sr}_{1/2}\text{MnO}_3$.

The manganites $\text{Pr}_{1/2}\text{Sr}_{1/2-x}\text{Ca}_x\text{MnO}_3$ were prepared by mixing Pr_6O_{11} , SrCO_3 , CaO , and MnO_2 intimately in adequate proportions. The mixtures were first heated at 950°C for 12 h, ground, heated again at 1200°C for 12 h, reground, pressed in the form of bars, and sintered at 1500°C for 12 h in air. The samples were then cooled at a rate of 5°C · mn⁻¹ down to 800°C and finally quenched to room temperature.

The resistivity was measured by a classical four-probe method in magnetic fields up to 7 T. The temperature dependence of the magnetization (M) was measured in 10⁻² T with a vibrating sample magnetometer; the samples were zero field cooled and then M was registered with T increasing.

The powder X-ray diffraction patterns of this phase and the electron diffraction study confirm its orthorhombic symmetry, with $a \approx c \approx a_p\sqrt{2}$ and $b \approx 2a_p$. Its space group is *Imma* for $0 \leq x \leq 0.10$, whereas “*Pnma*” microdomains appear as soon as $x > 0.10$. The EDS analysis shows the high homogeneity of the samples confirming their cationic composition.

The resistivity curves versus temperature (Fig. 1) registered in a zero magnetic field show a transition from a semi-conducting state at low temperature to a metallic state as T increases, whatever x , ranging from 0 to 0.12. The magnetization curves versus temperature registered

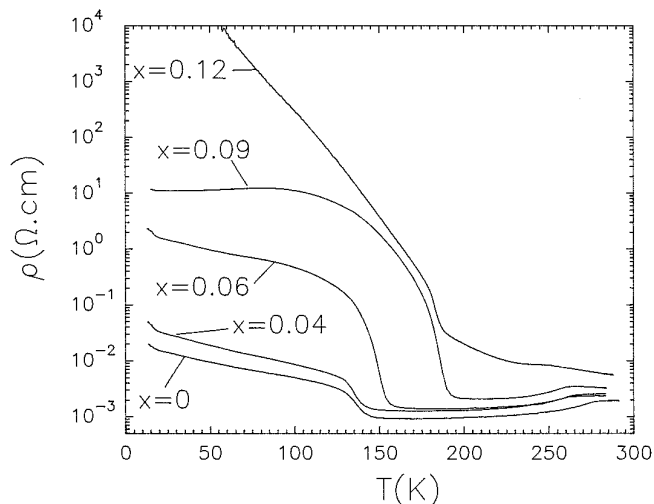


FIG. 1. Resistivity (ρ) as a function of temperature for different values of x labeled on the graph for the $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ series.

in a low magnetic field of 10^{-2} T (Fig. 2) confirm that the drop of resistivity corresponds to the AFM \rightarrow FM transition (type II). Thus, the transition temperature, T_{co} (or T_{N}) can be defined as the temperature corresponding to the inflexion point either on the $\rho(T)$ curve (Fig. 1) or on the left branch of the $M(T)$ curve (Fig. 2).

The first important result deals with the fact that T_{N} increases significantly as x increases (Fig. 3), i.e., as the mean size of the interpolated cation decreases. Although it is rather similar to that observed for $\text{Pr}_{0.5-x}\text{Y}_x\text{Sr}_{0.5}\text{MnO}_3$ [10], the increase of T_{N} is much higher for $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$, since T_{N} increases from 136 K for $x = 0$ to 190 K for $x = 0.12$. Thus, $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ with $0.09 \leq x \leq$

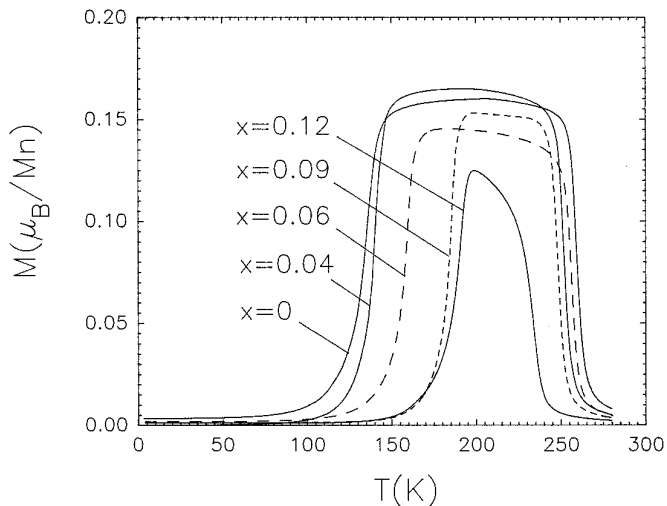


FIG. 2. Magnetization (M) as a function of temperature (10^{-2} T) for different x values in the $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ series.

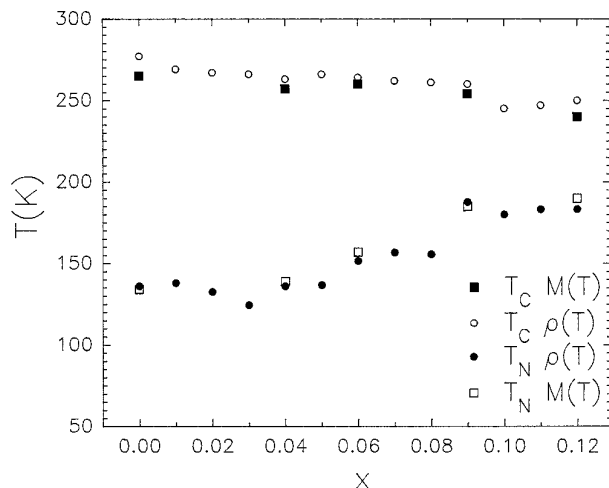


FIG. 3. x dependence of T_{C} and T_{N} deduced from resistivity and magnetization curves.

0.12 are, to date, the type II CMR manganites that exhibit the highest T_{N} , the previous records being $T_{\text{N}} = 158$ K for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (9) and $T_{\text{N}} = 156$ K for $\text{Pr}_{0.44}\text{Y}_{0.06}\text{Sr}_{0.50}\text{MnO}_3$ (10). Note also that the increase of T_{N} is not regular as for $\text{Pr}_{0.5-x}\text{Y}_x\text{Sr}_{0.5}\text{MnO}_3$ but seems to form plateaus with especially a rupture of the evolution around $x \approx 0.09$ (Fig. 3).

Like for the manganites $\text{Pr}_{0.5-x}\text{Y}_x\text{Sr}_{0.5}\text{MnO}_3$ [10], one observes a bump at higher temperature on the resistivity curves (Fig. 1), which is characteristic of the type I effect, i.e., corresponds to the FM \rightarrow PM transition in agreement with the $M(T)$ curves (Fig. 2). Nonetheless, the behavior of the manganites $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ is fundamentally different: if one considers the evolution of T_{C} deduced from the $\rho(T)$ and $M(T)$ curves (Fig. 3), one observes that T_{C} does not decrease so dramatically and so regularly as x increases; T_{C} decreases from 270 to 240 K (Fig. 3), in contrast to the manganites $\text{Pr}_{0.5-x}\text{Y}_x\text{Sr}_{0.5}\text{MnO}_3$ [10] for which T_{C} decreases dramatically and on a regular way as x increases, from 270 K for $x = 0$ to 175 K for $x = 0.10$. Moreover, the value of T_{C} deduced from the $\rho(T)$ curve is slightly higher than that deduced from the $M(T)$ curve (Fig. 3). This slight difference may be due to the high sensitivity of the magnetization of this phase to the applied magnetic field. One indeed observes that the application of a magnetic field of 1.4 T changes dramatically the shape of the $M(T)$ curve (Fig. 4) and shifts significantly T_{N} toward the low temperature side, whereas the right branch of the curve is considerably smoothed so that it is no more possible to deduce T_{C} from the curve.

The resistivity curves versus temperature registered in a magnetic field of 7 T (Fig. 5) show that a negative magnetoresistance effect is observed for all the solid solution. Whatever x , the application of a magnetic field tends to

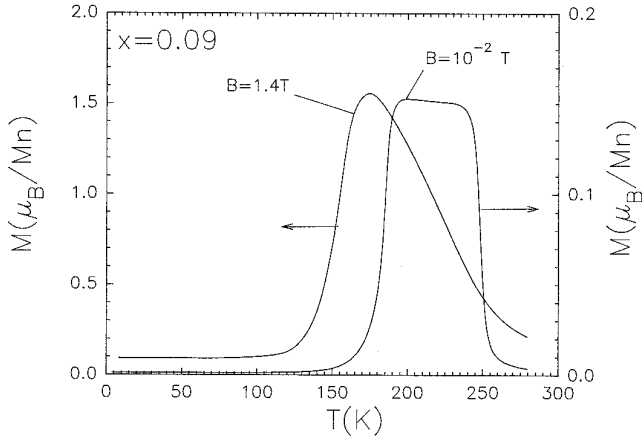


FIG. 4. T dependence of M for $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$ ($x = 0.09$) registered after zero field cooling with 10^{-2} T and 1.4 T.

decrease the $\rho(T)$ values; i.e., T_N is dramatically decreased in a magnetic field while T_C is increased. Moreover, the decrease of T_N is not regular: a variation of 100 and 140 K is observed for $x = 0.04$ (Fig. 5b) and $x = 0.06$ (Fig. 5c), respectively, whereas for $x = 0.09$ (Fig. 5d) a variation of only 60 K is observed. For higher x values, the shape of the $\rho(T)$ curve in a field of 7 T does not allow T_N to be defined as shown, for example, for $x = 0.12$ (Fig. 5e). Correlatively, the amplitude of the GMR effect does not vary regularly. The highest $R_0/R_{H=7T}$ of 3000 at 150 K is obtained for $x = 0.09$ (Fig. 5d), whereas the sample $x = 0.06$ still exhibits a ratio of 2000 but at 50 K (Fig. 5c). In contrast, much smaller $R_0/R_{H=7T}$ ratios are obtained for $x = 0.04$ and $x = 0.12$ of 25 at 60 K (Fig. 5b) and of 400 at 40 K (Fig. 5e), respectively.

Besides, one can observe a strong hysteresis of the temperature dependence of $\rho(T)$ as shown for instance in Fig. 6 for the $x = 0.09$ sample. This hysteresis also appears at 7 T where the difference between the field cooled (FC)

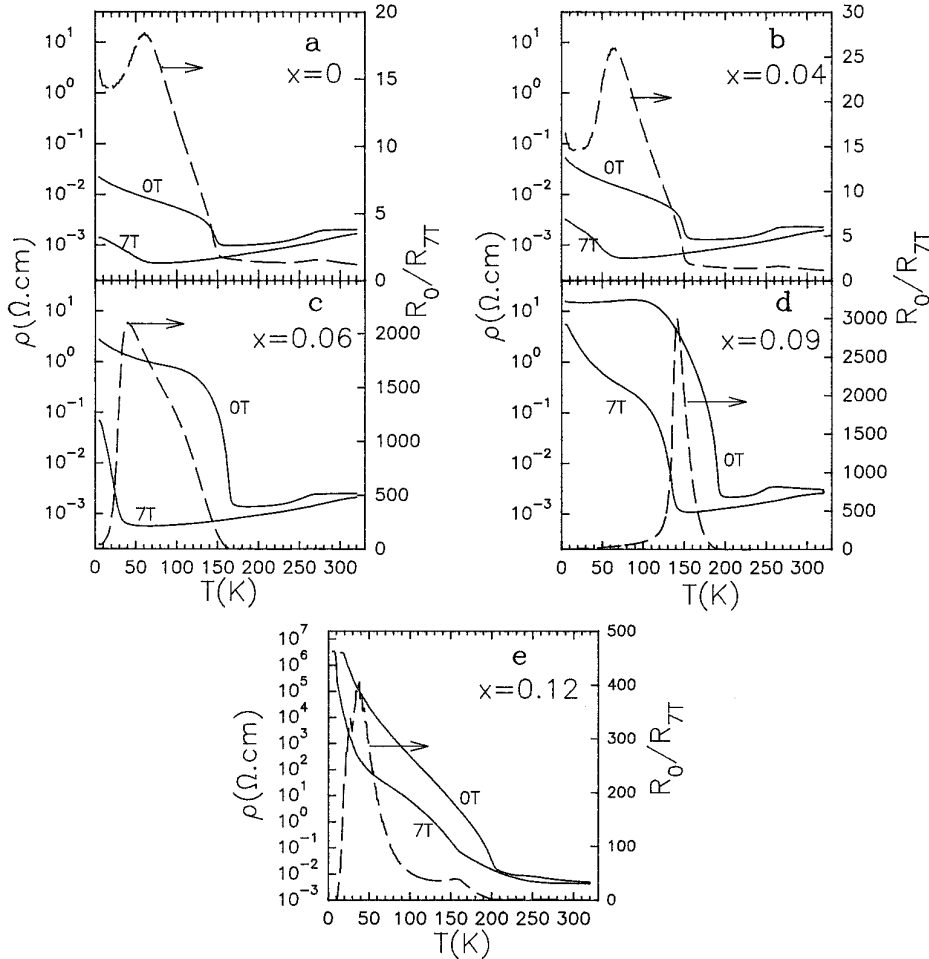


FIG. 5. T dependence of ρ at 0 and 7 T (solid lines, left y-axis). The ratio $R_0/R_{H=7T}$ is also shown (dashed lines, right y-axis). The $\rho(T)_{H=7T}$ curves registered increasing T ; after a zero field cooled process the 7-T magnetic field was applied.

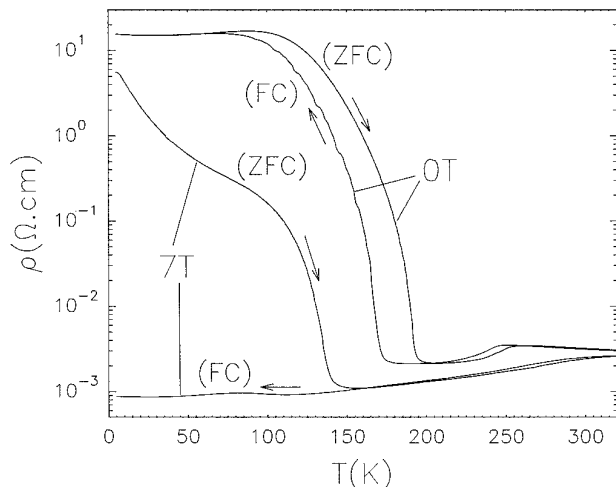


FIG. 6. T dependence of ρ for $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$ ($x = 0.09$) at 0 and 7 T, showing the hysteresis and the difference between field cooling (FC) and zero field cooling (ZFC) processes.

and the zero field cooled (ZFC) measurements is very important at low temperature: the system remains ferromagnetic when cooled under the field and presents the charge ordering state when the field is applied at low temperature. A consequence of this hysteretic behavior is that the R_0/R_H ratio is more important when measured using a FC process. For example, we have obtained in FC mode for $x = 0.09$ (Fig. 6) a $R_0/R_{H=7\text{T}}$ larger than 10^4 for temperatures ranging from 5 to 120 K. This can be compared to

that obtained under the same conditions for $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ (1) that reaches only a maximum value of 100 at 5 K.

Thus, this study has shown for the first time the possibility to increase the transition temperature T_N of the type II CMR manganite up to 190 K. It has also been demonstrated that the $R_0/R_{H=7\text{T}}$ ratio of $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ can be multiplied by 100 with calcium doping. These results strongly suggest that it should be possible to increase T_N and to optimize the R_0/R_H ratio by various substitutions on the A sites of the perovskite $\text{Pr}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$.

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