

# Ferromagnetism in lacunar perovskite manganites $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$ and $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$

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**Abstract.** Deficiency effects in the A site upon the structural, magnetic and electrical properties in the lacunar perovskite manganite oxides  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  ( $0 \leq x \leq 0.3$ ) and  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  ( $0 \leq x \leq 0.23$ ) have been investigated. This study focuses on the different parameters which govern the magnetic and electrical properties in such samples. The powder X-ray diffraction patterns for all samples could be indexed either with a rhombohedral perovskite structure and  $R\bar{3}c$  space group for  $x \leq 0.2$  in strontium deficient samples and for  $x \leq 0.1$  for praseodymium deficient ones. For other values of  $x$  the samples could be indexed in the orthorhombic structure with  $Pbnm$  space group. Magnetic and electrical investigations show that praseodymium and strontium vacancies do not have similar effects on the lacunar compounds. Magnetization measurements *versus* temperature show that all our samples exhibit a magnetic transition when the temperature decreases. All the praseodymium deficient samples exhibit a paramagnetic-ferromagnetic transition when the temperature decreases while the strontium deficient ones exhibit this transition only for low  $x$  values. The magnetic transition temperature shifts to lower values as the strontium deficiency increases (from 265 K for  $x = 0$  to 90 K for  $x = 0.3$ ) and to higher values with the praseodymium deficiency increase (from 265 K for  $x = 0$  to 315 K for  $x = 0.23$ ). Resistivity measurements as a function of temperature show a semiconducting-metallic transition for all  $x$  values in the praseodymium lacunar samples and only for low  $x$  values ( $0 \leq x \leq 0.1$ ) in the strontium lacunar ones when the temperature decreases.

**PACS.** 71.20.Ps Other inorganic compounds – 71.30.+h Metal-insulator transitions and other electronic transitions – 75.50.-y Studies of specific magnetic materials

## 1 Introduction

The perovskite-type manganite oxides of general formula  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  where Ln is a trivalent rare-earth and A is a divalent alkaline-earth or a monovalent alkali metal have been investigated extensively since the discovery of colossal magnetoresistance effects in such materials [1–10]. Different substitutions in these systems lead to different crystal structures, spin states and transport properties. The substitutional replacement of the trivalent element by divalent or monovalent elements produces an inhomogeneous distribution of mixed valence  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$  ions to maintain charge neutrality and subsequently a modification of both of the magnetic and transport properties. Such modifications can be understood on the basis of double-exchange interactions between the spins of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. However, there are many other interactions which compete with the double-exchange such as

super-exchange, orbital ordering, charge ordering, Jahn-Teller interactions, mismatch effects, etc.

Previous studies [11,12] showed that  $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$  samples with  $0.2 \leq x < 0.5$  exhibit a ferromagnetic-paramagnetic transition at  $T_c$  and a metallic-semiconducting one with a resistivity peak at  $T_\rho \approx T_c$ . Furthermore, these effects ( $T_c$ , magnetoresistance,...) are most prominent at the typical composition  $x$  of about 0.3.

In order to study the vacancy effects in the A site of  $(\text{Pr,Sr})\text{MnO}_3$  manganites, we investigate the structural, magnetic and electrical properties in the lacunar samples  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  with  $x = 0$  up to 0.23 and  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  with  $x = 0$  up to 0.3.

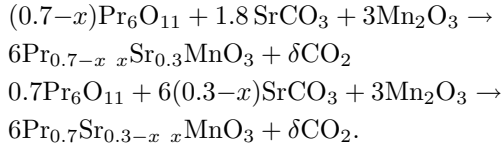
## 2 Experimental

Powdered samples of  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  ( $0 \leq x \leq 0.23$ ) and  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  ( $0 \leq x \leq 0.3$ ) were prepared by mixing  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{SrCO}_3$  (up to 99.9% pure) in the desired proportion according to the

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following reactions:



The starting materials are intimately mixed in an agate mortar and then heated in air at 1000 °C for 60 hours. A systematic annealing at high temperature is necessary to ensure a complete reaction, the powders are pressed into pellets (of about 1 mm thickness) and sintered at 1400 °C in air for 60 hours with intermediate regrinding and repelling. Finally these pellets are rapidly quenched in water. This step was taken in order to freeze the structure at the annealed temperature.

Phase purity, homogeneity, and cell dimensions are determined by powder X-ray diffraction at room temperature (diffractometer using Fe radiation for praseodymium deficiency samples and Guinier-Hägg cameras using  $\text{CrK}\alpha_1$  radiation for strontium deficiency compounds and Si powder as internal standard). Unit cell dimensions were obtained by least-squares calculations.

Magnetization measurements *versus* temperature were recorded by a vibrating sample magnetometer in the temperature range 10–350 K, using an applied field of 500 Oe. Resistivity measurements *versus* temperature, in the earth magnetic field, were performed on dense ceramic pellets using the conventional four-probe method.

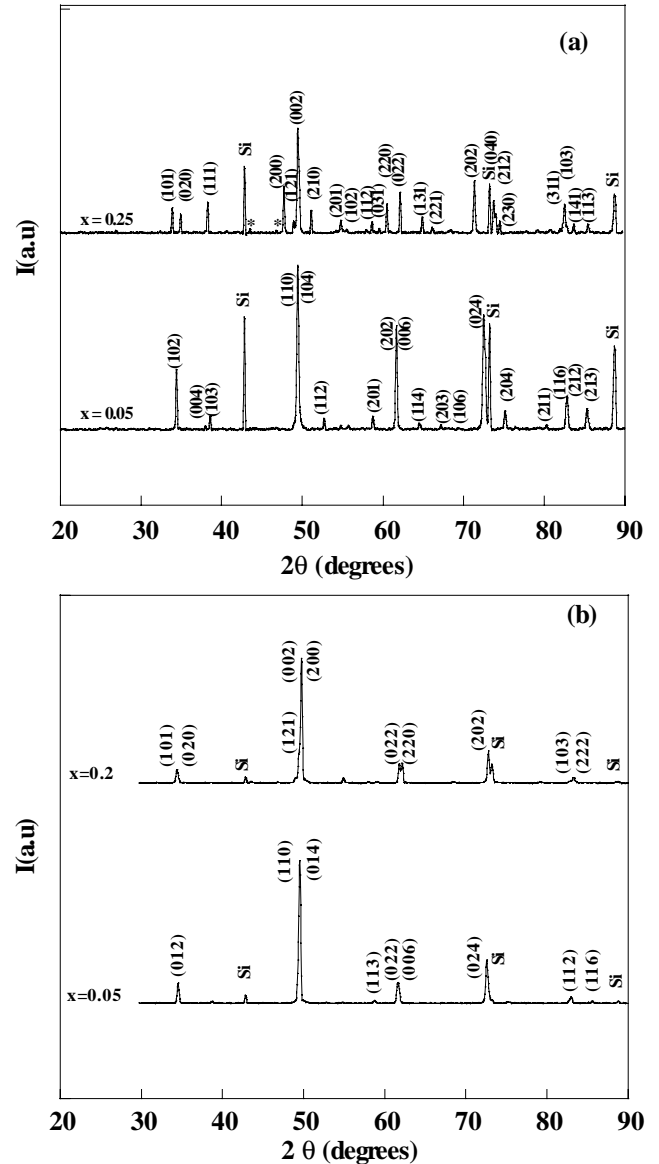
## 3 Results and discussion

### 3.1 X-ray diffraction analysis

A vacancy in the A site implies a partial conversion of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and surely a change in the average ionic radius ( $r_A$ ) of this site. According to the general formula, the Mn tetravalent and the Mn trivalent contents are respectively  $(0.3+2x)$  and  $(0.7-2x)$  in the strontium lacunar samples and  $(0.3+3x)$  and  $(0.7-3x)$  in the praseodymium lacunar samples. The  $\text{Mn}^{4+}$  contents in these two series vary nominally from 30% up to 90% in the first one and up to 99% in the second one.

Structural studies show that all of the lacunar samples have a perovskite structure but with different degrees of distortion. We show, in Figure 1, X-ray diffraction patterns at room temperature of some samples with low and high vacancies content (in Fig. 1b, we rescaled the  $x$ -axis using Cr radiation). The X-ray patterns showed that our samples are single phase. However for the high vacancies contents ( $x > 0.15$ ), we noticed the presence of diffraction peaks with very small intensities, in the X-ray diffraction spectra which can be attributed to traces of  $\text{Mn}_3\text{O}_4$ .

In Tables 1 and 2, we list crystallographic data for both series. For the strontium deficient series, samples crystallized in a rhombohedral structure with  $\text{R}\bar{3}\text{c}$  space group for  $0 \leq x \leq 0.2$  and in the orthorhombic symmetry with  $\text{Pbnm}$  space group for  $x > 0.2$ ; while in the praseodymium



**Fig. 1.** X-ray diffraction patterns at room temperature for some lacunar samples:  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  (a) and  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  (b), ( $x$ -axis had been rescaled using Cr radiation) attributed to  $\text{Mn}_3\text{O}_4$ .

deficient samples, the rhombohedral to orthorhombic transition occurs for  $x > 0.1$ . Both praseodymium and strontium deficiencies lead to a change in the average ionic radius ( $r_A$ ) and an increase of the  $\text{Mn}^{4+}$  content with smaller ionic radius ( $r(\text{Mn}^{3+}) = 0.785 \text{ \AA}$ ;  $r(\text{Mn}^{4+}) = 0.68 \text{ \AA}$  [13]). These two effects imply a decrease in the unit cell volume.

The orthorhombic phase in both of the two series presents a ratio  $c/a < \sqrt{2}$  characteristic of a cooperative Jahn-Teller deformation.

In the orthorhombic phase, the lattice parameters of all the deficient strontium samples and the deficient praseodymium sample corresponding to  $x = 0.15$ , fulfill  $c/\sqrt{2} < a < b$  which corresponds to the O'-type

**Table 1.** Crystallographic data for  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  samples.

$x$	Symmetry	$a_r(\text{\AA})$	$\alpha_r(^{\circ})$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
0.00	R	5.468(5)	60.09(3)	---	---	---	232.15
0.05	R	5.466(7)	60.12(5)	---	---	---	231.97
0.10	R	5.465(3)	60.15(2)	---	---	---	231.86
0.15	R	5.460(2)	60.17(5)	---	---	---	231.41
0.20	R	5.455(7)	60.18(5)	---	---	---	230.95
0.25	O	---	---	5.4540(4)	5.7179(4)	7.6090(6)	237.29
0.30	O	---	---	5.4299(5)	5.7444(7)	7.6052(9)	237.10

O: orthorhombic, R: rhombohedral.

**Table 2.** Crystallographic data for  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  samples.

$x$	Symmetry	$a_r(\text{\AA})$	$\alpha_r(^{\circ})$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
0.00	R	5.468(5)	60.09(3)	---	---	---	232.15
0.05	R	5.464(7)	60.12(4)	---	---	---	231.614
0.10	R	5.461(5)	60.15(3)	---	---	---	231.342
0.15	O	---	---	5.4542(7)	5.4670(7)	7.7114(6)	229.939
0.20	O	---	---	5.4822(5)	5.4430(6)	7.6944(5)	229.602
0.23	O	---	---	5.4586(3)	5.4433(4)	7.6729(3)	227.980

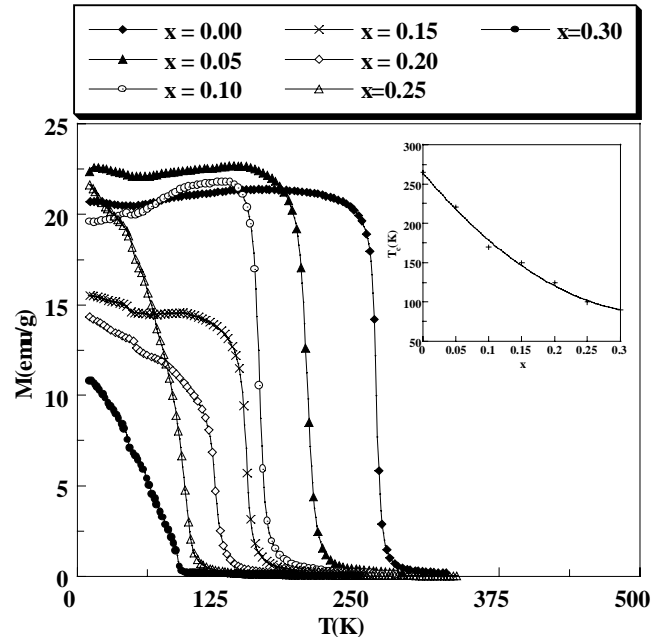
O: orthorhombic, R: rhombohedral.

structure. However, in the deficient praseodymium samples, these parameters correspond to  $x = 0.2$  and  $0.23$ ,  $c/\sqrt{2} < b < a$ . Such a result where  $a$  and  $b$  are found to reverse ( $a > b$ ) has been mentioned by Knizek *et al.* for  $x \geq 0.3$  in  $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$  system [14], Dabrowski *et al.* in  $\text{La}_{0.87}\text{Sr}_{0.13}\text{MnO}_3$  as a function of temperature [15]. It has also been observed by Ritter *et al.* in  $\text{LaMnO}_{3+\delta}$  as a function of oxygen content [16].

The influence of the A-site cation size can be explained by its ability to modify the Mn-Mn distance and the Mn-O-Mn angle and consequently the distortion of the ideal perovskite structure in which Mn-O-Mn angle is equal to  $180^{\circ}$ .

### 3.2 Magnetic properties

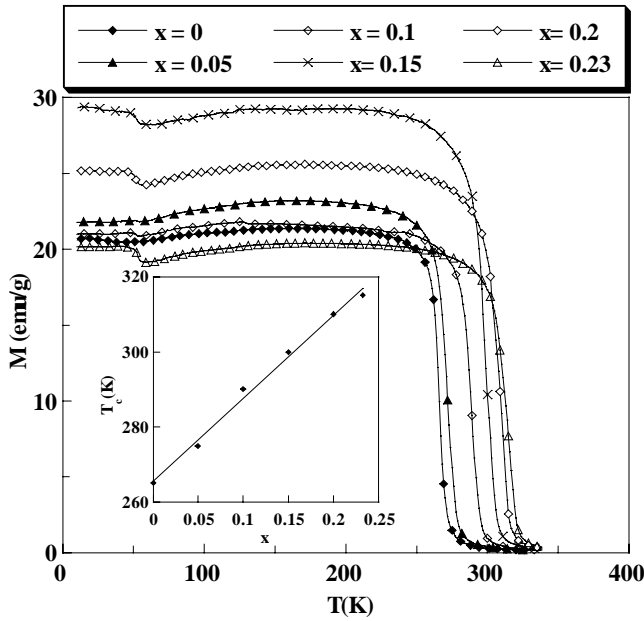
The stoichiometric sample  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (30%  $\text{Mn}^{4+}$ ) is ferromagnetic below  $T_c = 265$  K. In order to study the A site deficiency effects on this magnetic transition and its temperature, we performed magnetization measurements *versus* temperature in an applied field of 500 Oe. Figures 2 and 3 show the magnetization evolution *versus* temperature for  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  and  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  systems. These curves show that all the praseodymium deficient samples exhibit a paramagnetic to ferromagnetic transition when the temperature decreases while this transition persists in the strontium deficient samples only up to  $x = 0.15$ . For higher  $x$  values, the magnetic behavior depends strongly on the deficiency content. The samples corresponding to  $0.2 \leq x \leq 0.3$  exhibit a paramagnetic to a spin canted ferromagnetic state with temperature decrease while the paramagnetic-ferromagnetic transition in



**Fig. 2.** Magnetization of  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  samples as a function of temperature at  $H = 500$  Oe, (in set Curie temperature evolution *versus*  $x$ ).

the  $\text{Pr}_{0.7}\text{Sr}_{0.2}\text{MnO}_3$  sample is followed by a decrease of the magnetization. This result would be due to a spin-canted state. It could also be attributed to a structural transition or eventually to anisotropy effects.

Deficiency effects on the Curie temperature are very spectacular. In fact, in the strontium deficient samples,



**Fig. 3.** Magnetization of  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  samples as a function of temperature at  $H = 500$  Oe, (in set Curie temperature evolution *versus*  $x$ ).

the ferromagnetic transition temperature  $T_C$  is observed to shift to lower values with increasing  $x$ . It is found to decrease from 265 K for  $x = 0$  to 90 K for  $x = 0.3$ . Such a result has been observed by Laroussi *et al.* [17] in the lacunar  $\text{La}_{0.67}\text{Sr}_{0.33-x}\text{MnO}_3$ . However, in the praseodymium deficient samples, this temperature  $T_C$  increases with increasing  $x$  from 265 K for  $x = 0$  to 315 K for  $x = 0.23$  (Figs. 2 and 3).

If the decrease of the magnetic transition  $T_C$  in the strontium deficient samples can be explained by the increase of the  $\text{Mn}^{4+}$  content which leads to a decrease of the double exchange interactions (such a result is in concordance with previous work on  $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$  which shows a parabolic behaviour of  $T_C$  *versus*  $\text{Mn}^{4+}$  content with a maximum obtained at about 30%  $\text{Mn}^{4+}$  content corresponding to the maximum of the double exchange interactions [11,12,14]); The increase of  $T_C$  with the  $\text{Mn}^{4+}$  content beyond 30%, in the praseodymium deficient compounds, can not be explained by the same phenomenon (the increase in the  $\text{Mn}^{4+}$  content). Such a result has never been observed in praseodymium perovskite manganites. Indeed until now, the highest known  $T_C$  in these compounds was about of 280 K obtained for 33%  $\text{Mn}^{4+}$  [11,12], while our magnetic measurements show that some lacunar samples are ferromagnetic at room temperature ( $T_C = 315$  K for  $x = 0.23$  which corresponds to a  $\text{Mn}^{4+}$  content of about 99%). It is important to specify that the ferromagnetism in these compounds with  $\text{Mn}^{4+}$  content beyond 50% is not governed only by the  $\text{Mn}^{4+} / \text{Mn}^{3+}$  ratio. There are surely other parameters which lead to the  $T_C$  increase. The tolerance factor effect studied by Hwang *et al.* [18] may explain such results. In fact, as a vacancy must have an average radius  $\langle r_V \rangle \neq 0$ , the  $T_C$  decrease with increasing strontium deficient in the lacu-

nar  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  samples and the  $T_C$  increase with increasing praseodymium deficient in the lacunar  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  samples can be explained if we attribute to the vacancy a radius  $\langle r_V \rangle$  smaller than  $\text{Sr}^{2+}$  (1.31 Å) and larger than  $\text{Pr}^{3+}$  (1.179 Å).

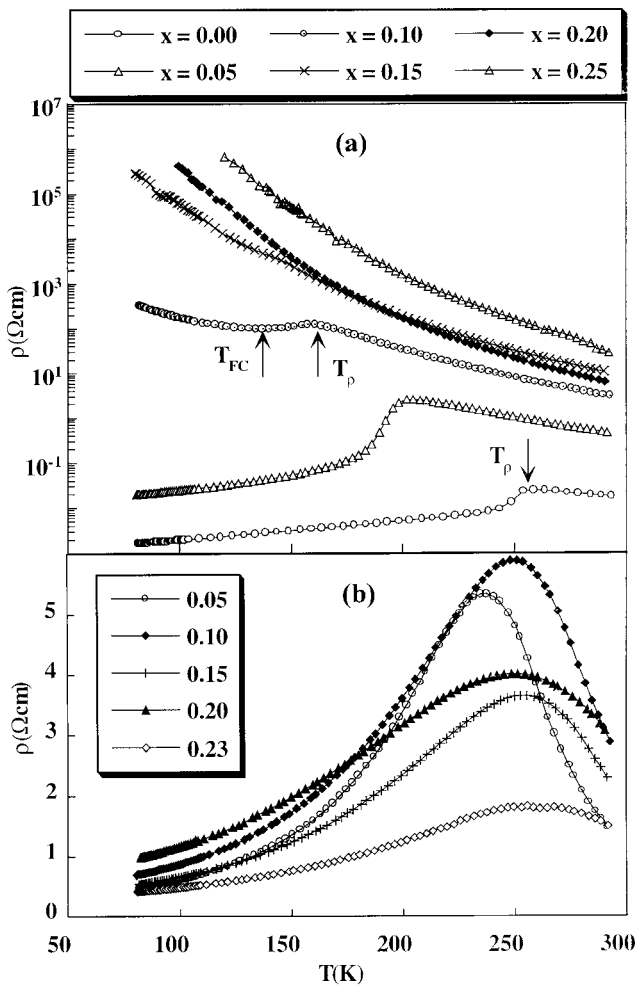
### 3.3 Electrical properties

Deficiency effects on the electrical properties are also spectacular. Both the praseodymium and the strontium vacancies in the A site induce an increase in the  $\text{Mn}^{4+}$  content in our samples. However, while the semiconducting-metallic transition decreases with temperature, as observed in the stoichiometric sample  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , is maintained for all  $x$  values in the praseodymium deficient samples, the strontium deficient compounds exhibit three types of behavior. For low  $x$  values ( $x < 0.1$ ), we observe a semiconducting-metallic transition which decreases with temperature, while for high  $x$  values ( $x \geq 0.15$ ), the samples exhibit a semiconducting behavior over the whole temperature range (70 K–300 K). However we observe unique behaviour for  $x = 0.1$ . This sample, which is semiconducting at high temperature is metallic and ferromagnetic between  $T_\rho$  and  $T_{FC}$ . Below  $T_{FC}$  the sample becomes a canted ferromagnetic insulator. As a consequence of the canted ferromagnetic order charge transfer between neighbouring sites becomes difficult in agreement with the double exchange theory.

We have reproduced in Figure 4 the temperature dependence of the resistivity  $\rho(T)$  in the polycrystalline samples in the earth magnetic field.

As observed in Figure 4, it is important to note that the evolution of the resistivity peak temperature  $T_\rho$  *versus*  $\text{Mn}^{4+}$  content is not similar. In fact with increasing deficient content *i.e.* with increasing  $\text{Mn}^{4+}$ , we observe a  $T_\rho$  decrease in the strontium deficient samples and a  $T_\rho$  increase in the praseodymium deficient ones. Furthermore, the  $\text{Mn}^{4+}$  content increase has different effects on the resistivity in the two samples series. The resistivity value at a fixed temperature in the ferromagnetic region ( $T = T_\rho$ ), is about  $10^2$  higher in the praseodymium deficient compounds compared to the stoichiometric sample  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and about  $10^3$  to  $10^6$  higher in the strontium deficient samples. This increase in resistivity value with the  $\text{Mn}^{4+}$  content is in concordance with previous work on some lanthanum [19] and praseodymium [11,12] stoichiometric manganites.

Magnetisation and resistivity curves *versus* temperature for strontium deficient samples corresponding to  $x \leq 0.1$  and for all praseodymium deficient samples (Figs. 2, 3 and 4) show a steep decrease of the resistivity in agreement with the onset of the ferromagnetic magnetisation. Thus the resistivity temperature dependence can be interpreted in terms of the carrier scattering by thermal spin fluctuation as well as the decrease of the hole-carrier concentration [20–24]. The electron (hole) transfer ( $t_{ij}$ ) between the neighbouring sites depends on the relative angle ( $\Delta\theta_{ij}$ ) of the local spins such as  $t_{ij} = t_0 \cos(\Delta\theta_{ij}/2)$  [23]. The



**Fig. 4.** Resistivity of  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  (a) and  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  (b) samples as a function of temperature.

ferromagnetic spin arrangement reduces the randomness of the transfer.

We also remark that in the stoichiometric sample, the metallic-semiconducting transition occurs at the same temperature as the ferromagnetic-paramagnetic transition indicating a strong correlation between magnetic and electrical properties in this sample. However, in lacunar samples,  $T_c$  and  $T_p$  evolutions as a function of the  $\text{Mn}^{4+}$  content exhibit similar behavior with little difference in their values (which increases with increasing  $\text{Mn}^{4+}$  content): both of them decrease in the strontium deficiency samples and increase in the praseodymium ones. This result confirms the strong correlation between magnetic and electrical properties in the lacunar compounds. However both properties are not solely governed by the manganese mixed valence.

## 4 Conclusion

In this work we present a comparative study of the effects of praseodymium and strontium deficiencies upon the structural and physical properties of both series

$\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$  and  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$ . With increasing vacancies content *i.e.* increasing  $\text{Mn}^{4+}$  content magnetization, resistivity and Curie temperature exhibit different behavior depending on the vacancy nature. Curie temperature decreases from 265 K to 90 K as  $x$  increases from 0 to 0.3 in  $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_3$  and increases from 265 K to 315 K for  $x$  increasing from 0 to 0.23 in  $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$ .

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