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# Effect of Cd ions on transport properties of orthomanganites

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**Abstract.** Magnetic and magnetotransport measurements have been used to study the compositional dependence of the electronic properties of the solid solutions  $\text{La}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  and  $\text{Nd}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$ . It was found that these compounds are ferromagnets and have the rhombohedrally or orthorhombically distorted perovskite structure. The substitution of Pb ions by Cd leads to the transition from the metallic to the insulating state. The intermediate compositions exhibit two peaks of the resistivity and magnetoresistance. The high-temperature peak is associated with the Curie temperature whereas there is no magnetic anomaly in the temperature interval of the second peak. We suppose that Cd ions participate in the formation of the narrow impurity band limiting the mobility of charge carriers.

## 1. Introduction

The observation of the ‘colossal’ magnetoresistance at the Curie temperature of  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Pb}^{2+}$ ;  $0.15 \leq x \leq 0.5$ ) perovskite has attracted considerable attention [1, 2]. The effect is greatest close to  $T_C$  in these metallic oxides because the application of a magnetic field is thought to reduce the spin-disorder scattering of the charge carriers in this region. Magnetotransport properties have been traditionally explained in terms of the ‘double-exchange’ model [3]. However the validity of this model has been recently questioned [4–6] and it has been argued that Jahn–Teller coupling is a key factor [7].

It is worth noting that the most studied systems are manganites doped by  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Pb}^{2+}$ . These ions convert  $\text{Mn}^{3+}$  into  $\text{Mn}^{4+}$  thus leading to the formation of mobile charge carriers and simultaneously to ferromagnetism. It is known that the  $\text{Cd}^{2+}$  ions have ionic radii close to those of  $\text{Ca}^{2+}$ . So one can expect the formation of solid solutions of  $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$  type. In this work we are reporting the synthesis conditions and the study of transport properties of the manganites doped by Cd and Pb ions.

## 2. Experimental details

$\text{La}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  and  $\text{Nd}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  as well as  $\text{Nd}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$  and  $\text{Sm}_{0.35}\text{Nd}_{0.35}\text{MnO}_3$  were prepared by the solid state reaction of  $\text{La}_2\text{O}_3$  or  $\text{Nd}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CdO}$  and  $\text{MnO}_2$  at 1173 for 2 h followed by sintering at 1493 K for 1.5 h in air. An excess of  $\text{PbO}$  and  $\text{CdO}$  was added to compensate the evaporation of Pb and Cd ions during the synthesis. All the samples were cooled with a rate of  $100 \text{ K h}^{-1}$ . The samples as

characterized by powder x-ray diffraction at room temperature were found to be single phase and have rhombohedrally or orthorhombically distorted unit cells. Unit-cell parameters for selected samples are listed in table 1. The samples had composition close to stoichiometric as determined by the redox titration. The ac susceptibility was measured with a mutual inductance bridge. The amplitude and frequency of the driving field are 2 Oe and 1000 Hz respectively. Magnetization versus field measurements were performed on a Foner vibrating sample magnetometer at 4.2 K. Magnetotransport measurements were carried out using a standard four-terminal method.

**Table 1.** Unit-cell parameters, volume per formula unit, spontaneous magnetization per formula unit at 4.2 K and Curie temperature of manganites.

Composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$V$ (Å <sup>3</sup> )	$\sigma_s$ ( $\mu_B$ )	$T_C$ (K)
La <sub>0.7</sub> Cd <sub>0.3</sub> MnO <sub>3</sub>	7.770			90.47	58.85	3.3	160
Nd <sub>0.7</sub> Pb <sub>0.3</sub> MnO <sub>3</sub>	7.756			90.42	58.34	3.5	150
Nd <sub>0.7</sub> Cd <sub>0.3</sub> MnO <sub>3</sub>	5.407	5.522	7.661		57.19	2.5	115
La <sub>0.7</sub> (Cd <sub>0.1</sub> Pb <sub>0.2</sub> )MnO <sub>3</sub>	7.786			90.44	59.01	3.6	300
Nd <sub>0.7</sub> (Pb <sub>0.15</sub> Cd <sub>0.15</sub> )MnO <sub>3</sub>	5.452	5.547	7.713		58.32	3.3	130
Sm <sub>0.35</sub> Nd <sub>0.35</sub> Pb <sub>0.3</sub> MnO <sub>3</sub>	7.718			90.4	57.47	3.4	130

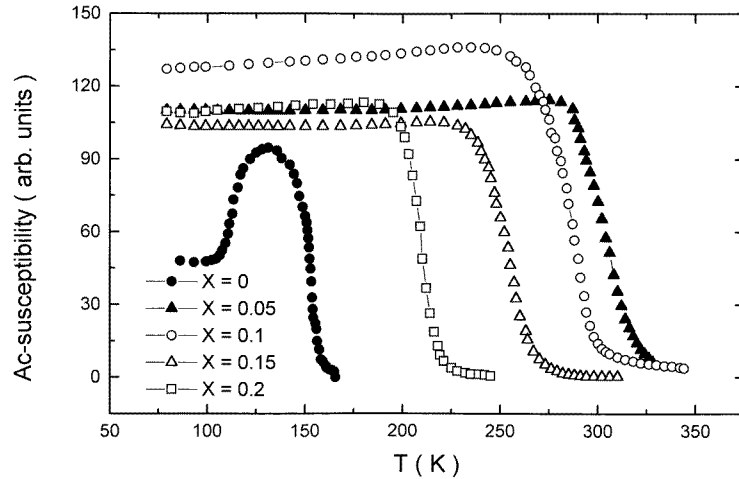
### 3. Results and discussion

Figure 1(a) shows the temperature variation of the ac susceptibility for La<sub>0.7</sub>(Pb<sub>0.3-x</sub>Cd<sub>0.3</sub>)MnO<sub>3</sub>. For all the samples ac susceptibility falls at around  $T_C$ . There is no anomalous behaviour except the temperature region around  $T_C$ . With increasing Cd content the Curie temperature decreases gradually from 350 ( $x = 0$ ) to 160 K ( $x = 0.3$ ). In accordance with the magnetization measurements all the samples are ferromagnets with the magnetic moment per chemical formula 3.3–3.6  $\mu_B$  at 4.2 K (table 1).

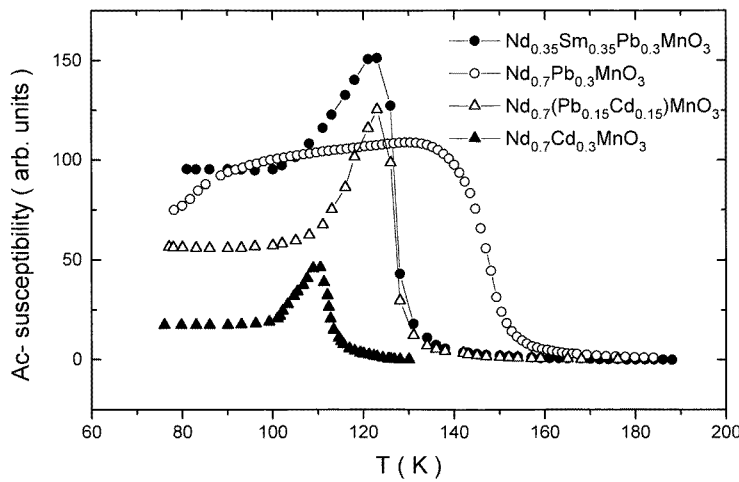
The temperature variation of electrical resistivity is displayed in figure 2(a). The substitution of Pb ions by Cd leads to the transition from the metallic to the insulating state. The resistivity of La<sub>0.7</sub>Cd<sub>0.3</sub>MnO<sub>3</sub> is higher than that of La<sub>0.7</sub>Pb<sub>0.3</sub>MnO<sub>3</sub> at 77 K by six orders of magnitude in spite of the approximately equal content of Mn<sup>4+</sup> ions, close volume of unit cells and ferromagnetic states of both compounds (table 1). La<sub>0.7</sub>Cd<sub>0.3</sub>MnO<sub>3</sub> does not show the peak of resistivity at  $T_C$ . It is worth noting that La<sub>0.6</sub>Y<sub>0.07</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> is metallic below the Curie temperature—160 K [8]. The resistivity of La<sub>0.7</sub>Cd<sub>0.2</sub>Pb<sub>0.1</sub>MnO<sub>3</sub> exhibits two peaks. The first at 225 K is associated with the Curie temperature and the second one at 130 K occurs without an anomaly of the magnetic susceptibility.

The Pb-containing samples show a peak of the magnetoresistance (defined as  $MR = \{[\rho(H) - \rho(0)]/\rho(0)\} \times 100\%$ ) at around  $T_C$  whereas the magnetoresistance of La<sub>0.7</sub>Cd<sub>0.3</sub>MnO<sub>3</sub> increases strongly with decreasing temperature below  $T_C$ . The magnetoresistance of La<sub>0.7</sub>Pb<sub>0.1</sub>Cd<sub>0.2</sub>MnO<sub>3</sub> exhibits two peaks corresponding to maxima on resistivity–temperature dependences (figure 3). Although the resistivity behaviour of Pb-containing samples differs markedly from that of La<sub>0.7</sub>Cd<sub>0.3</sub>MnO<sub>3</sub> all the samples exhibit relatively large magnetoresistance (20–40% at  $H = 1$  T).

The magnetic and transport properties of Nd-containing samples resemble those of the series based on lanthanum ions (figures 1(b), 2(b)). Nd<sub>0.6</sub>Pb<sub>0.4</sub>MnO<sub>3</sub> is metallic below  $T_C = 180$  K and shows the peak of the magnetoresistance at around  $T_C$ . The substitutions of Pb by Cd ions or Nd by Sm ones lead to insulating behaviour down to 77 K and decreasing



(a)

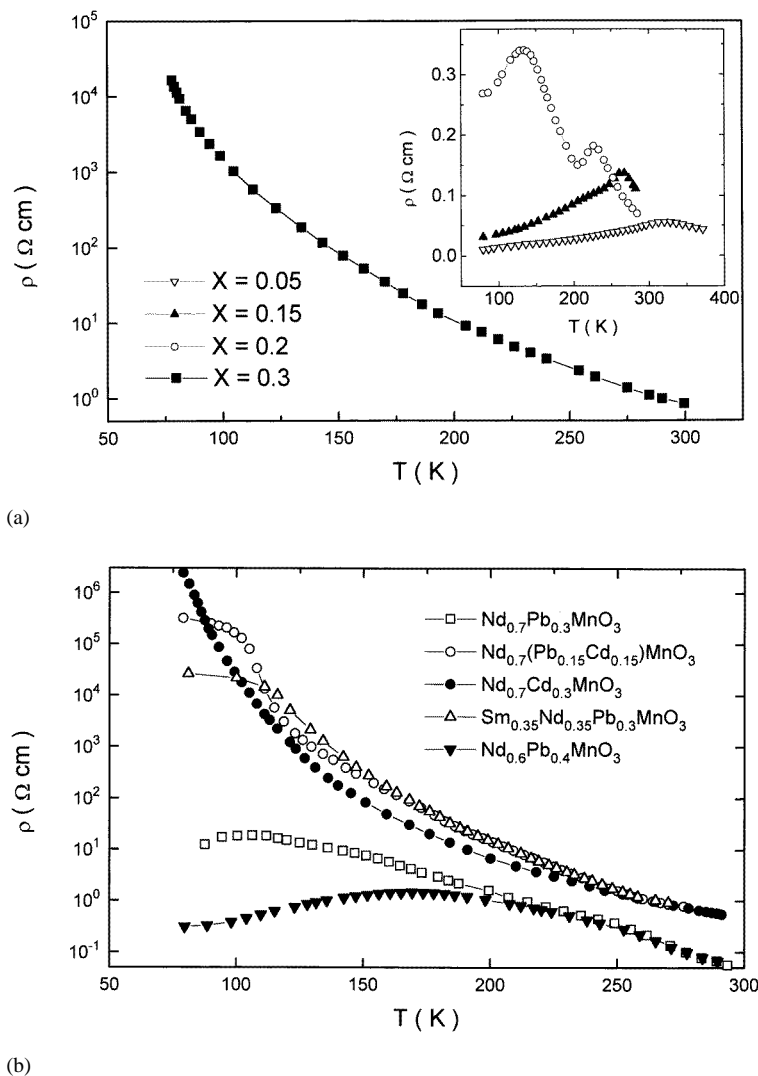


(b)

**Figure 1.** Ac susceptibility as a function of temperature for  $\text{La}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  (a),  $\text{Nd}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  and  $\text{Sm}_{0.35}\text{Nd}_{0.35}\text{Pb}_{0.3}\text{MnO}_3$  (b).

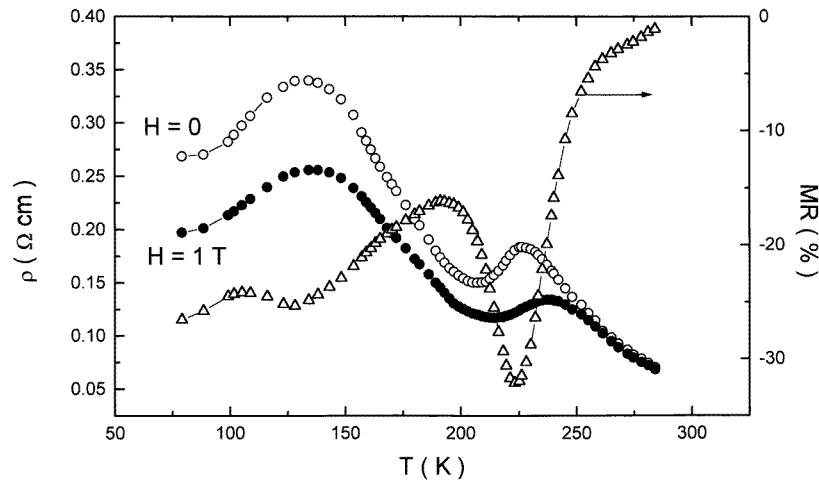
Curie temperatures (figures 1(b) and 3). It is worth noting that  $\text{Nd}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  exhibits a peak of the resistivity below  $T_C$  and an anomaly at  $T_C$  whereas  $\text{La}_{0.7}\text{Cd}_{0.3}\text{MnO}_3$  is insulating in the whole temperature range although both compounds have close Curie temperatures and concentrations of  $\text{Mn}^{4+}$  ions. The application of magnetic field produces a reduction in resistivity which is the most pronounced for compounds near the concentrational metal—insulator transition at around  $T_C$  (figure 4).

Our results show clearly that the doping by Cd ions leads to the depression of the metallic state. Apparently the  $\text{Cd}^{2+}\text{-Mn}^{4+}$  impurity centres are much more stable than those in the case of doping by Ca, Sr and Pb ions giving rise to the insulating state. We think that 3d orbitals of manganese and sp orbitals of Cd are strongly hybridized in the perovskite lattice. However the phases doped by Cd ions exhibit both ferromagnetism and large magnetoresistance increasing strongly with decreasing temperature (figure 3).

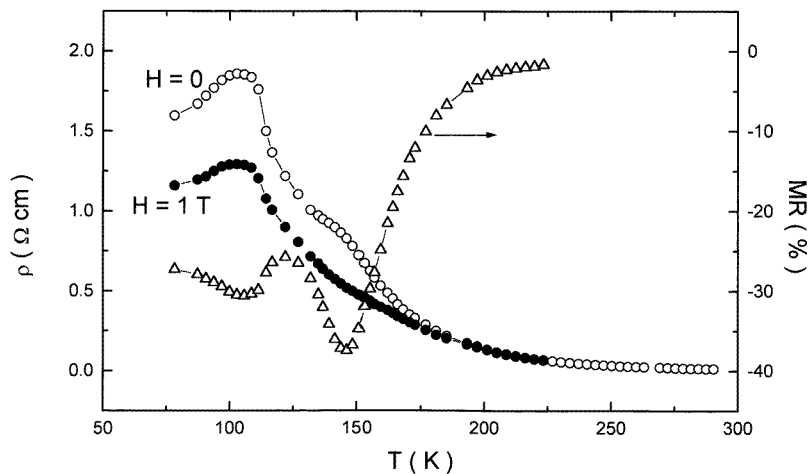


**Figure 2.** Resistivity—temperature curves for  $\text{La}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  (a),  $\text{Nd}_{0.7}(\text{Pb}_{0.3-x}\text{Cd}_x)\text{MnO}_3$  and  $\text{Nd}_{0.35}\text{Nd}_{0.35}\text{Pb}_{0.3}\text{MnO}_3$  (b).

Traditionally, the appearance of the ferromagnetic metallic state in orthomanganites is explained in terms of the double-exchange picture [3]. However the ferromagnetism of manganites could be also explained in the superexchange model [9, 10]. In this model the ferromagnetic fraction of the exchange will be determined by the electron transfer from the half-filled  $e_g$ -orbitals of the  $\text{Mn}^{3+}$  ion to the empty ones. The antiferromagnetic part of the exchange is the result of transfers between the half-filled orbitals by the  $\text{Mn}^{3+}$  ions. In the case of a relatively broad 3d band the contribution of the first type of transfer should dominate, thus leading to ferromagnetism [6, 9]. According to [9] the ferromagnetic superexchange  $\text{Mn}^{3+}\text{-O-Mn}^{3+}$  in perovskites is similar to the ferromagnetic superexchange  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ . It may be due to the dynamic correlation in the filling of  $e_g$  orbital states of the nearest manganese ions. There is a number of experimental facts in favour of the superexchange model.



**Figure 3.** Magnetoresistance and resistivity as a function of temperature for  $\text{La}_{0.7}(\text{Pb}_{0.1}\text{Cd}_{0.2})\text{MnO}_3$ .



**Figure 4.** Magnetoresistance and resistivity as a function of temperature for  $\text{Nd}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ .

(1) Truly ferromagnetic ordering has been observed in insulating orthomanganites without  $\text{Mn}^{4+}$  ions (for example  $\text{La}(\text{Mn}_{1-x}\text{Ga}_x)\text{O}_3$  [10],  $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}^{3+}\text{Ti}_x^{4+})\text{O}_3$  [11],  $\text{BiMn}^{3+}\text{O}_3$  [12]). The  $T_C$  values for the insulating  $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}\text{Ti}_x)\text{O}_3$  are smaller than those for the conductive  $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+})\text{O}_3$  [11] because  $\text{Ti}^{4+}$  ions are diamagnetic and do not participate in exchange interactions. The Curie temperatures are correlated with crystal structure distortions (3d bandwidth) and practically do not depend on the resistivity of the compounds.

(2) In contrast to  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{Ln}$  = lanthanoid;  $\text{A}$  = divalent ion) the substitution of  $\text{Bi}^{3+}$  by  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$  ions in  $\text{Bi}_{1-x}\text{A}_x\text{MnO}_3$  leads to the collapse of the ferromagnetic states whereas the electrical conductivity increases strongly [5].

(3) The properties of Cd-containing manganites (present work) seem to be in agreement

with the superexchange model.  $\text{La}_{0.7}\text{Cd}_{0.3}\text{MnO}_3$  is a ferromagnetic insulator and does not show a peak of resistivity at around  $T_C$  (figure 2(a)). It is worth pointing out that such a behaviour is observed for  $\text{Ln}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ ) ferromagnets [13] and  $\text{Sm}_{0.35}\text{Nd}_{0.35}\text{MnO}_3$  (present work). These compounds show  $\rho \sim 10^5\text{--}10^8 \Omega \text{ cm}$  at 77 K.

We think that  $\text{Mn}^{4+}$  ions (3d holes) introduced by a small number of divalent ions remain tightly bound to all the nearest-neighbour manganese ions and act as a deep acceptor level. At the higher divalent ion content (approximately 15%), the acceptor complexes interact to form an impurity band. The insulator–metal transition at around  $T_C$  in manganites can be explained in terms of the delocalization of charge carriers due to the ferromagnetic ordering. We think that in the high-temperature phase the localization of charge carriers results from the chemical (randomly distributed trivalent and divalent ions) and spin disorders (Anderson localization). With narrowing 3d impurity band (Cd-containing samples or samples with relatively small rare-earth ions) the effects of both chemical and spin disorders become more pronounced, and the transition to the metal conductivity takes place sufficiently below  $T_C$  or does not occur (figure 2). The anomalous behaviour at  $T_C$  in these compounds arises apparently from the scattering of charge carriers on critical fluctuations of the magnetization. In this model one can expect that the most pronounced magnetoresistance effect (especially in a high-field regime) will occur in compounds near the concentrational ferromagnetic–antiferromagnetic transition with a relatively small 3d bandwidth because in these compounds the external magnetic field strongly affects the magnetic order and the resistivity is rather large around  $T_C$ . The impurity bandwidth should be sufficiently large to realize the charge carriers delocalization due to the spin ordering. This picture is in good agreement with the experimental observations.

In conclusion we have observed interesting features in the magnetotransport studies of manganites doped by Cd ions which include an insulating behaviour of  $\text{A}_{0.7}\text{Cd}_{0.3}\text{MnO}_3$  ( $\text{A} = \text{La}, \text{Nd}$ ), two peaks of magnetoresistance for compositions near the concentrational metal–insulator transition and a large magnetoresistance in moderate magnetic field of both insulating and conducting phases. We are further exploring the magnetic properties of Cd-containing materials using different substitutions and methods of synthesis.

## Acknowledgment

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