

LETTER TO THE EDITOR

Charge Order–Disorder Transition in the $\text{Nd}_{0.6}(\text{Ca}_{0.4-x}\text{Cd}_x)\text{MnO}_3$ Perovskites

I. O. Troyanchuk,¹ D. D. Khalyavin, N. V. Kasper, and L. S. Lobanovsky

Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, P. Brovki str. 17, 220072 Minsk, Belarus

and

H. Szymczak and A. Nabialek

Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

Communicated by J. B. Goodenough October 2, 1997; accepted October 12, 1997

In this paper it is shown that the substitution of Ca^{2+} ions by Cd^{2+} in $\text{Nd}_{0.6}(\text{Ca}_{0.4-x}\text{Cd}_x)\text{MnO}_3$ leads to a transition from an antiferromagnetic charge-ordered state to a nonhomogeneous ferromagnetic state without changes in the electrical conductivity. The charge-ordering temperature decreases with increasing cadmium content whereas the critical field inducing the charge order–disorder transition increases. © 1997 Academic Press

INTRODUCTION

The discovery (1–5) of a magnetic-field-induced electronic phase transition in $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($\text{Ln} = \text{Pr}, \text{Nd}$) and $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}; 0.3 \leq x \leq 0.5$) has attracted great attention. These materials with the perovskite crystal structure undergo a transition from a charge-ordered antiferromagnetic state to a ferromagnetic metallic state. This transition can be induced by both temperature and magnetic field in the $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ series. $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) in zero field does not show a transition from the charge-ordered antiferromagnetic state to a ferromagnetic metallic state. Such a transition was observed in external magnetic fields above 3 T. The charge order–disorder transition is believed to be first-order and shows a large hysteresis accompanying the increase and decrease of the external magnetic field. The charge-ordering phenomenon has not been observed in manganites doped with Ba^{2+} and Pb^{2+} ions apparently due to the large ionic

radii of these ions. It is well known that the Cd^{2+} ion has an ionic radius very close to that of Ca^{2+} . In order to achieve a deeper understanding of the charge-ordering phenomenon, we have investigated the effect of Cd^{2+} substitution for Ca^{2+} . It was found that the incorporation of Cd ions into the crystal lattice leads to the stabilization of an insulating ferromagnetic state in the manganites.

EXPERIMENTAL

$\text{Nd}_{0.6}(\text{Ca}_{0.4-x}\text{Cd}_x)\text{MnO}_3$ ($0 \leq x \leq 0.25$) solid solutions have been prepared in air by solid-state reaction from a mixture of Nd_2O_3 , CaCO_3 , Mn_2O_3 , MnO_2 , and CdO at 1173 K for 2 h followed by sintering at 1693 K ($x = 0$) and 1493 K ($0.1 \leq x \leq 0.25$); 5% weight excess of CdO was added to compensate for the evaporation of Cd ions during synthesis. The $\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_3$ was prepared at 1493 K following the procedure described above. All the samples were cooled slowly with a furnace. A decreased weight of the samples after synthesis corresponds to the loss of the excess cadmium in the starting materials. X-ray patterns of the samples showed them to be nominally single-phase with either orthorhombic (Nd-containing samples) or rhombohedral ($\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_3$) distortions of the unit cells. The chemical analysis was made only for the $\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_3$ nominal composition. It was found that the true chemical formula is $\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_{2.96}$. The magnetization was measured with a vibrating sample magnetometer. The magnetostriction measurements were made with a strain-gauge technique. The magnetoresistance was measured by a standard four-probe method. The magnetic field was provided by a 12 T superconducting coil.

¹To whom correspondence should be addressed.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of field-cooled (FC) magnetization for $\text{Nd}_{0.6}(\text{Ca}_{0.4-x}\text{Cd}_x)\text{MnO}_3$ compounds. Peaks of magnetization were observed in the vicinity of 250 K ($x = 0$) and 160 K ($x = 0.10$). There are no peaks of magnetization for compounds with a large content of Cd ions. By analogy with the detailed earlier studied $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (3), these anomalies can be associated with a charge ordering. The increasing Cd content leads to an increase of magnetization at low temperature. However, the magnetization of the sample with $x = 0.25$ is slightly less than that which could be expected in the case of a pure ferromagnetic state. The resistivity vs temperature data show that all the samples are semiconductors with similar resistivity over a wide range of temperature (Fig. 2).

For the specimens showing a peak of magnetization, the magnetization measurements reveal significant changes in magnetic ordering with increasing magnetic field. M - H data for the $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample ($x = 0$) cooled to 4.2 K in $H = 0.02$ T are shown in Fig. 3. A metamagnetic transition from an antiferromagnetic to a ferromagnetic state is observed in fields above 4 T. The saturation moments correspond to $3.7 \mu_B$ per formula unit. This is close to the spin value for Mn ions in the case of ferromagnetic ordering in the Mn sublattice. Applying an external magnetic field at 4.2 K leads to a fall of resistivity from $10^7 \Omega \cdot \text{cm}$ ($H = 4$ T) to $10^{-2} \Omega \cdot \text{cm}$ ($H = 12$ T). The transition is irreversible at low temperatures. The magnetization vs field curves for $\text{Nd}_{0.6}(\text{Ca}_{0.3}\text{Cd}_{0.1})\text{MnO}_3$ at 4.2 K are similar to those obtained for the $x = 0$ sample.

The magnetostriction isotherms of $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at 4.2 K are shown in Fig. 4. The 4.2 K isotherm shows a value of parallel magnetostriction approximately of 3×10^{-4} at

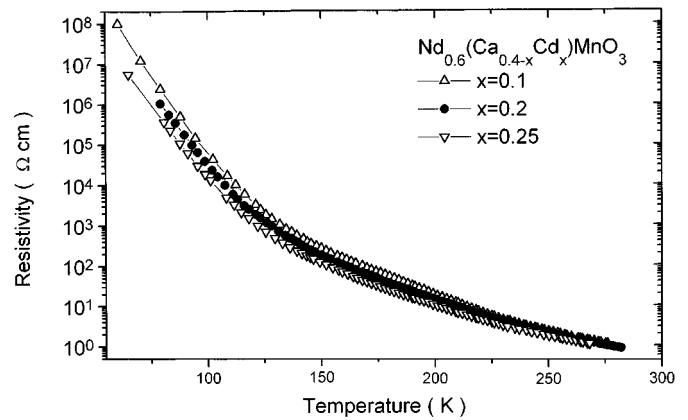


FIG. 2. The temperature dependence of the resistivity for $\text{Nd}_{0.6}(\text{Ca}_{1-x}\text{Cd}_x)\text{MnO}_3$ ($x = 0.1, 0.2, 0.25$).

12 T or a volume magnetostriction $\sim 10^{-3}$ ($\Delta V/V = 3\Delta l/l$). In the first cycle of measurement, the changes in the magnetization, magnetostriction, and magnetoresistance with applied field H are mainly due to the metamagnetic transition, whereas in the second cycle the material is ferromagnetic over the whole range of the magnetic field.

The temperature variation of the ratio $R(H)/R(12 \text{ T})$ for $\text{Nd}_{0.6}(\text{Ca}_{0.3}\text{Cd}_{0.1})\text{MnO}_3$ is shown in Fig. 5a. All the data were collected after a zero field procedure. As one can clearly see from Fig. 5, a sharp decrease of resistivity occurs above 7 T at 90 K. This phenomenon is accompanied by large hysteresis when the field decreases. The critical field at which the transition starts decreases slightly with decreasing temperature. Unfortunately we cannot carry out the measurement in the low-field regime below 60 K due to the saturation of our experimental setup. The transition becomes irreversible at 53 K. After the measurement cycle is

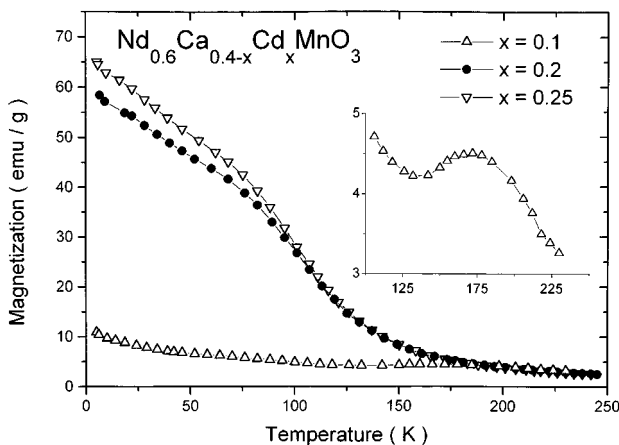


FIG. 1. The temperature dependence of the FC magnetization for $\text{Nd}_{0.6}(\text{Ca}_{0.4-x}\text{Cd}_x)\text{MnO}_3$ ($x = 0.1, 0.2, 0.25$) in a field of 1 T.

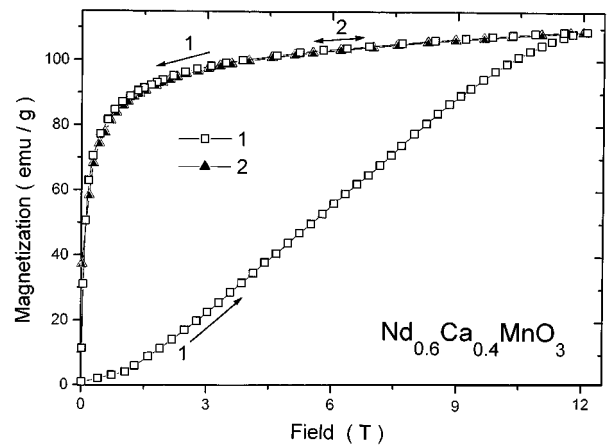


FIG. 3. Magnetization vs field dependence for $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at 4.2 K (1, first cycle of measurements; 2, second cycle).

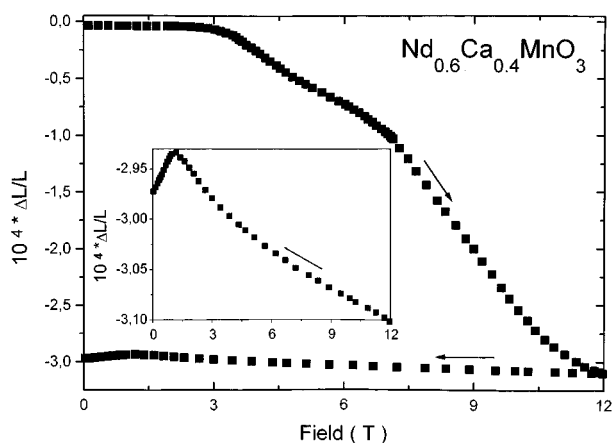


FIG. 4. Magnetostriction of $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at 4.2 K.

finished, the sample relaxes into the insulating state without an external field. At 4.2 K the relaxation occurs very slowly.

The magnetoresistance data for the $\text{Nd}_{0.6}(\text{Ca}_{0.15}\text{Cd}_{0.25})\text{MnO}_3$ sample resembles those obtained for the $x = 0.1$ compound; however, the magnetoresistance is much less than that for $x = 0.1$ (Fig. 5b). Therefore one can assume that the $x = 0.25$ nominal composition appears to behave like a mixture of two materials, i.e., a material with high content of cadmium ions and a material resembling the $\text{Nd}_{0.6}(\text{Ca}_{0.3}\text{Cd}_{0.1})\text{MnO}_3$ sample. The microdomains with low Cd content undergo a field induced phase transition from the insulating antiferromagnetic state to the ferromagnetic fairly conductive state. We were not able to obtain a completely single-phase sample of $\text{Nd}_{0.6}\text{Cd}_{0.4}\text{MnO}_3$. The single-phase sample of $\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_3$ exhibits ferromagnetic behavior with $T_C = 160$ K and a magnetic moment per formula unit of $3.3 \mu_B$ at 4.2 K. This sample is poorly conductive below T_C and shows a large

magnetoresistance ratio (Fig. 6) comparable to that for the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Ca}, \text{Ba}$) series.

Traditionally the interplay between magnetic and transport properties in the manganites is explained in terms of the double-exchange model. In this model (6), the ferromagnetism results from electron hopping between Mn^{3+} and Mn^{4+} ions. However, the properties of manganites could also be explained with a superexchange model (7–10).

In the superexchange model, the ferromagnetic fraction of the exchange will be determined by electron transfer from the half-filled e_g orbitals of the Mn^{3+} ion to the empty ones. The antiferromagnetic part of the exchange is the result of transfers between the half-filled t_{2g} orbitals of the Mn ions (7). In the case of a relatively broad $3d$ band, the contribution of the first type of transfer should dominate, thus leading to ferromagnetism.

According to (7), the ferromagnetic $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ superexchange interactions are directional, depending on a coupling of occupied and empty e -orbitals on either side of the oxygen atom. Where the orbitals are ordered by static, cooperative Jahn–Teller deformations as in LaMnO_3 , the magnetic interactions are strongly anisotropic; however, where the local Jahn–Teller deformations are dynamic, an isotropic ferromagnetic superexchange interaction may be encountered. Fast charge transfer between Mn^{3+} and Mn^{4+} ions in a $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ pair leads to strong double-exchange ferromagnetic coupling within the pair; this interaction is also anisotropic where static orbital ordering occurs.

Truly ferromagnetic ordering has been observed in many insulating orthomanganites without Mn^{4+} ions (for example, $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ (8), $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}^{3+}\text{Ti}_x^{4+})\text{O}_3$ (9), $\text{Bi}^{3+}\text{Mn}^{3+}\text{O}_3$ (11)). The T_C value for $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}^{3+}\text{Ti}_x^{4+})\text{O}_3$ is smaller than that for conductive $\text{La}_{1-x}\text{Ba}_x(\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+})\text{O}_3$ because Ti^{4+} ions are diamagnetic and do not participate in exchange interactions. The

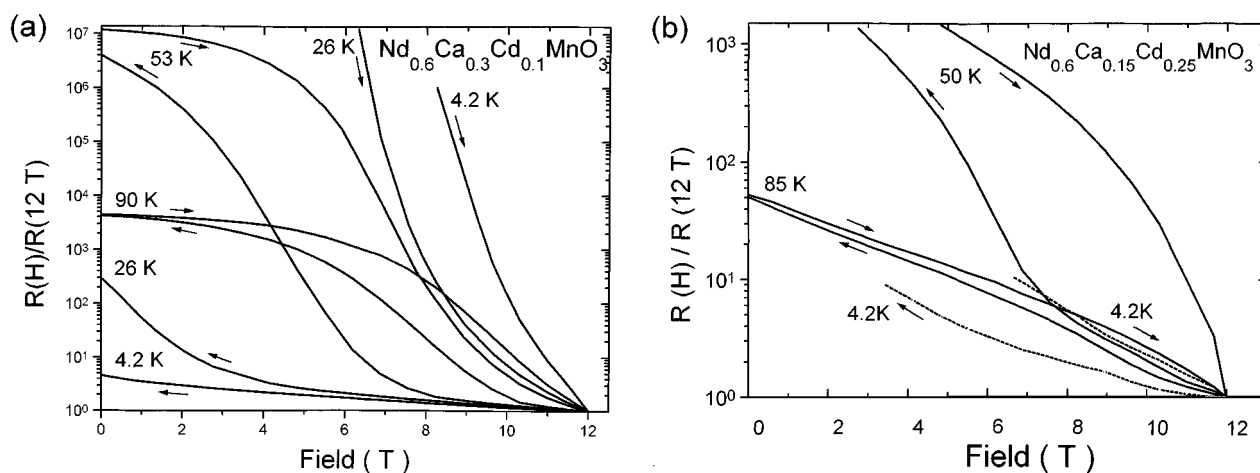


FIG. 5. The magnetoresistance of $\text{Nd}_{0.6}(\text{Ca}_{0.3}\text{Cd}_{0.1})\text{MnO}_3$ (a) and $\text{Nd}_{0.6}(\text{Ca}_{0.15}\text{Cd}_{0.25})\text{MnO}_3$ (b) at various temperatures.

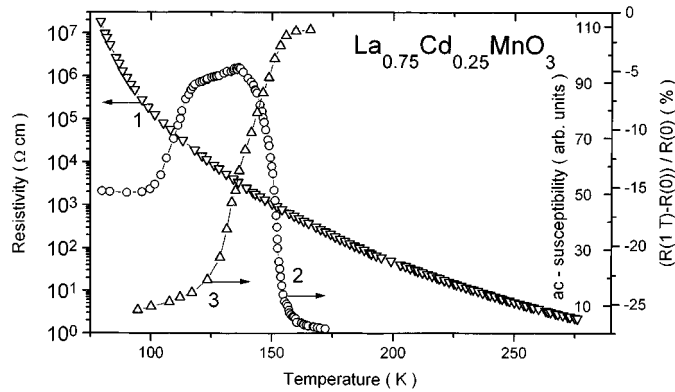


FIG. 6. The temperature variation of resistivity (1), ac magnetic susceptibility (2), and magnetoresistance at $H = 1$ T (3) for $\text{La}_{0.75}\text{Cd}_{0.25}\text{MnO}_3$.

temperature of ferromagnetic and antiferromagnetic ordering (being comparable to each other) is correlated with crystal structure distortions and practically independent of the specific resistivity of the compounds.

The properties of Cd-containing samples seem to agree with the superexchange via anions model. The incorporation of Cd ions into A -sites of the manganites AMnO_3 leads to destruction of the charge ordering and to the antiferromagnet–ferromagnet transition without changes in the electrical properties. Such behavior arises apparently from a strong hybridization of $3d$ orbitals of manganese ions and sp orbitals of Cd ions. Upon replacement of Ca ions with Cd, the samples are divided into domains with different Cd content and different magnetic properties. There are a number of facts in favor of the realization of a nonhomogeneous

magnetic state in the concentration interval of the antiferromagnet–ferromagnet transition in the orthomanganites (10, 12), whereas the double-exchange theory (13) predicts a homogeneous noncollinear magnetic structure in the intermediate compositions.

ACKNOWLEDGMENTS

The work was partly supported by the Belarus Fund for Fundamental Research (Grant F96-135) and the Polish State Committee for Scientific Research (Grant 2 P03B 095 12).

REFERENCES

1. Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Phys. Rev. Lett.* **74**, 5108 (1995).
2. H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Science* **270**, 961 (1995).
3. M. R. Lees, J. Barrat, G. Balakrishnan, D. Mck Paul, and M. Yethiraj, *Phys. Rev. B* **52**, R14303 (1995).
4. H. Y. Hwang, S. W. Cheong, P. G. Radaelli, M. Merezio, and B. Batlogg, *Phys. Rev. Lett.* **75**, 914 (1995).
5. R. Mahendiran, R. Manesh, R. Gundakaram, A. K. Raychaudhuri, and C. N. Rao, *J. Phys. Condens. Matter* **8**, L455 (1996).
6. C. Zener, *Phys. Rev.* **82**, 403 (1955).
7. J. B. Goodenough, "Magnetism and the Chemical Bond." Interscience, New York/London, 1963.
8. J. B. Goodenough, A. Wold, R. J. Arnett, and N. Menyuk, *Phys. Rev.* **124**, 373 (1961).
9. E. E. Havinga, *Philips Res. Rep.* **21**, 432 (1966).
10. I. O. Troyanchuk, *Sov. Phys. JETP* **75**, 132 (1992).
11. F. Sugawara, S. Iida, Y. Suoko, and S. Akimoto, *J. Phys. Soc. Jpn.* **25**, 1553 (1965).
12. E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).
13. P. S. de Gennes, *Phys. Rev.* **118**, 141 (1960).