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Phase transition in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ perovskites

I O Troyanchuk†, D A Efimov†, N V Samsonenko†, E F Shapovalova† and H Szymczak‡

† Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, P Brovki Street 17, 220072 Minsk, Belarus

‡ Institute of Physics, Polish Academy of Sciences, Al. Lotnikow, 32146, 02-668 Warsaw, Poland

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Abstract. Transport and magnetic properties of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \leq 0.55$) have been studied to construct the magnetic phase diagram. $\text{NdMnO}_{2.99}$ is found to be a weak ferromagnet with $T_N = 88$ K. Anomalous magnetic behaviour of $x = 0$ and $x = 0.1$ compositions is attributed to the Nd-sublattice magnetic contribution. Materials with $x \leq 0.15$ and $0.25 \leq x \leq 0.35$ are suggested to be mixtures of antiferromagnetic and ferromagnetic states. The inhomogeneous ferromagnets $0.2 \leq x \leq 0.25$ exhibit the giant magnetoresistance effect without the temperature-induced metal–insulator transition. The results are discussed in terms of the superexchange interaction model proposed by Goodenough.

1. Introduction

Since the discovery of colossal magnetoresistance (CMR) the study of perovskite-type manganese oxides has been revived [1]. Recent experimental and theoretical investigations have revealed many discrepancies within the simple double-exchange model and pointed out the importance of the strong electron–lattice interaction and the orbital order [2, 3]. The lattice distortions depend strongly on the lanthanoid ion size and increase with decreasing lanthanoid ionic radius. It was found that lattice distortions and 3d bandwidth correlate with each other. It is worth noting that numerous investigations have been made on $\text{A}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\text{A} = \text{La}, \text{Pr}$) with the largest A cations among lanthanoids. The $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solution with a relatively smaller A-cation in comparison with $\text{A} = \text{Pr}$ has not been studied well at present. Therefore in order to study the relative importance of double-exchange and other mechanisms we have chosen the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ system. According to [4, 5] these compounds exhibit charge ordering over a large composition range of $0.30 \leq x \leq 0.80$. For $0.3 < x < 0.5$ a magnetic field induces a first-order antiferromagnetic semiconductor to ferromagnetic metal transition [5]. The magnetic structure of the NdMnO_3 compound was studied by the neutron diffraction technique [6] and it has turned out that this material has a layer A-type antiferromagnetic structure as found earlier for LaMnO_3 [7].

The present paper reports further investigation aimed at better understanding of the role of lattice distortions as well as 3d bandwidth in the formation of different magnetic states in manganites.

2. Experiment

The $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions used in this experiment were prepared by the standard ceramic route in air. The final synthesis temperature was 1450°C . The samples were cooled slowly down to room temperature with a furnace. The $\text{NdMnO}_{2.99}$ was received in evacuated quartz tube. The oxygen content in $\text{NdMnO}_{3+\lambda}$ samples was established by reduction in high vacuum. The crystal structure as well as phase purity of the samples were checked by x-ray analysis.

The magnetization has been measured using a Foner vibrating sample magnetometer. Resistivity measurements were performed on $2 \times 2 \times 10 \text{ mm}^3$ bars by means of a four-probe method.

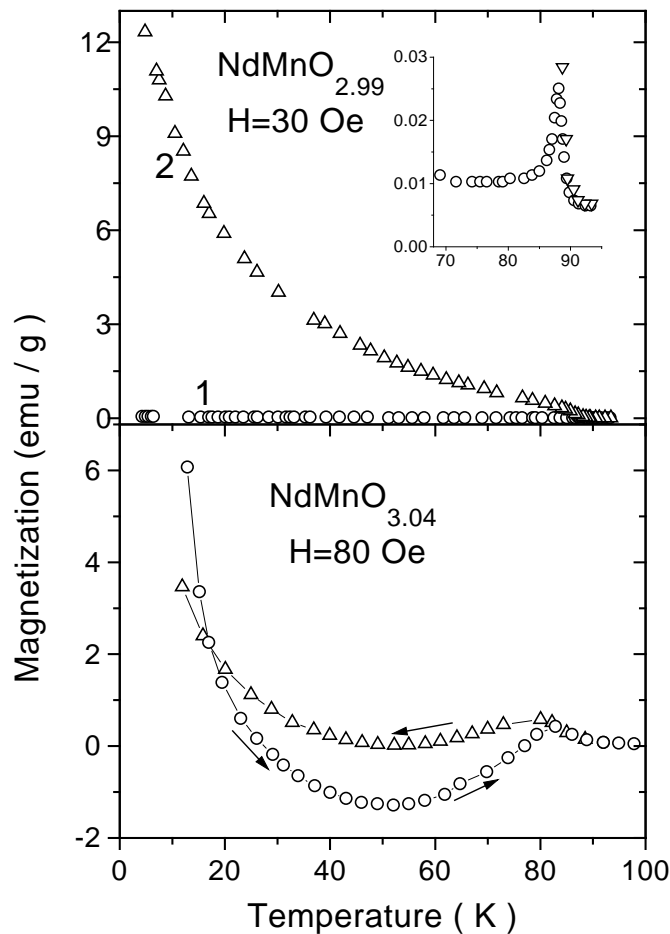


Figure 1. ZFC (1) and FC (2) magnetization against temperature for $\text{NdMnO}_{2.99}$ in a field of 30 Oe (top panel). The inset shows the magnetization behaviour around the Néel temperature. The bottom panel shows magnetization against temperature for $\text{NdMnO}_{3.04}$ in a field of 80 Oe. The data received on heating were collected after cooling in a field of 11 kOe.

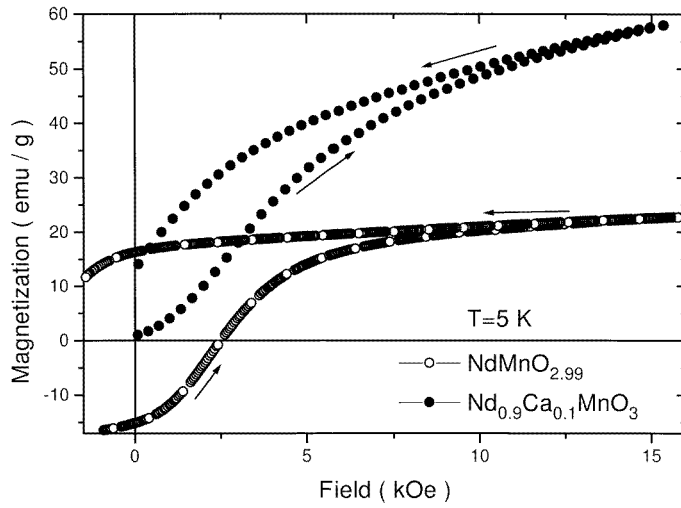


Figure 2. Magnetization against field for $NdMnO_{2.99}$ and $Nd_{0.9}Ca_{0.1}MnO_3$ at 5 K.

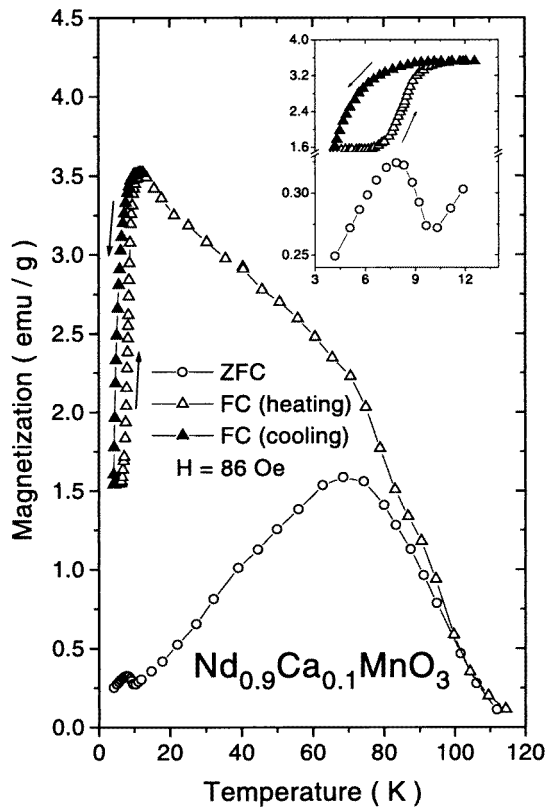


Figure 3. Magnetization against temperature for $Nd_{0.9}Ca_{0.1}MnO_3$. The inset shows the magnetization behaviour at low temperature.

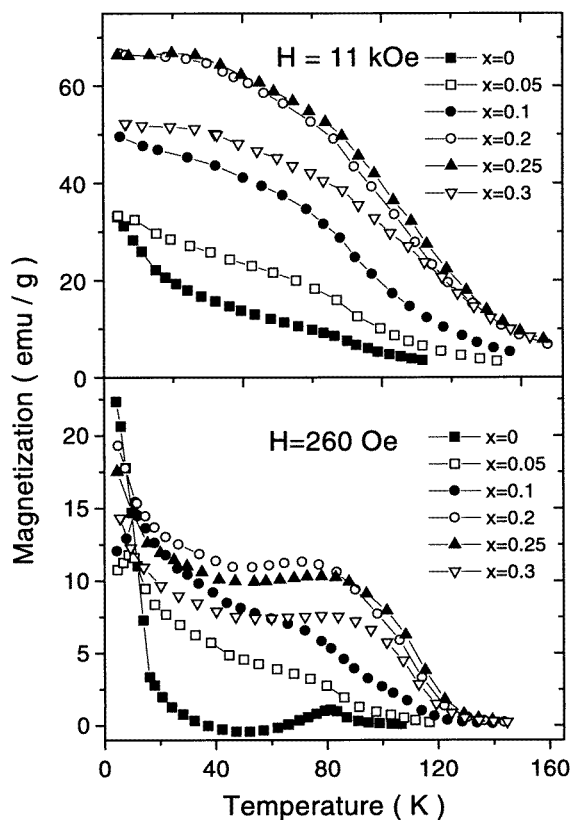


Figure 4. Magnetization against temperature for $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ in a field of 11 kOe (top panel) and in a field of 260 Oe after cooling in a field of 11 kOe.

3. Results

All the samples were found to crystallize in an orthorhombic structure (space group $Pnma$) without extra diffraction peaks indicative of impurities. The obtained unit cell parameters are very close to those reported in [4]. The crystal structure distortions decrease strongly with increasing calcium concentration. The samples with $x \leq 0.1$ have so-called O' -orthorhombic structure whereas samples with $x \geq 0.15$ are characterized by the O -orthorhombic one with relatively small unit cell distortions. According to [8] the O' -orthorhombic structure results from d_{z^2} -orbital ordering.

In figure 1 we show the temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization at a magnetic field of 30 Oe for the parent $\text{NdMnO}_{2.99}$ compound. The peak of ZFC magnetization at 86 K results from antiferromagnetic ordering of magnetic moments whereas enhancement of FC magnetization at low temperature can be attributed to the Nd-sublattice contribution. According to [4] the NdMnO_3 compound is an antiferromagnet with two Néel temperatures, 14 and 60 K. However, the oxygen content in NdMnO_3 studied in [4] is not determined. We think that the NdMnO_3 studied in [4] contains an oxygen excess due to oxidative condition of synthesis. It is known that LaMnO_3 and EuMnO_3 with nonmagnetic (the ground state of Eu^{3+} is characterized by $J = 0$) large cations are weak ferromagnets with spontaneous magnetization around 2 emu g^{-1} at 4.2 K

[9]. Therefore the strong increase of magnetization at low temperature in $NdMnO_3$ arises apparently from f–d exchange interaction between manganese and neodymium sublattices. This exchange interaction is relatively strong and negative as seen clearly from figure 1 (bottom panel) where $M(T)$ data for $NdMnO_{3.04}$ are presented. The negative magnetization observed in $NdMnO_{3.04}$ results from strong magnetic anisotropy associated with Mn^{3+} ions occupying Jahn–Teller distorted MnO_6 octahedra. In accordance with $M-H$ data (figure 2) the spontaneous magnetization of $NdMnO_{2.99}$ at 5 K is 17 emu g^{-1} . The increase of the oxygen content in the parent $NdMnO_3$ compound leads to increasing magnetization whereas the Néel temperature decreases slightly (figure 1).

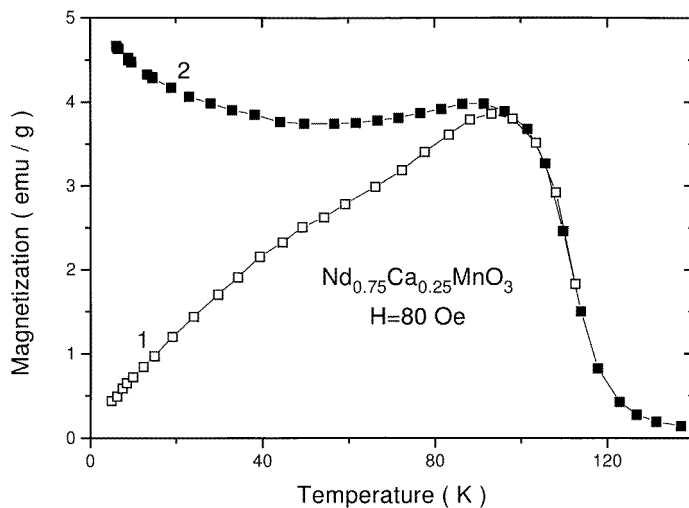


Figure 5. ZFC (1) and FC (2) magnetization for $Nd_{0.75}Ca_{0.25}MnO_3$ in a field of 80 Oe.

Rather interesting results have been obtained for $Nd_{0.9}Ca_{0.1}MnO_3$. This composition undergoes phase transitions at 110 K and 7 K on heating (figure 3). The transition at 110 K results obviously from Mn^{3+} magnetic moment ordering whereas the nature of the first order transition at 7 K is difficult to understand at the moment. This transition may be the result of Nd sublattice magnetic ordering or the changing magnetic structure of the manganese sublattice. The magnetic behaviour near the Curie temperature is also complicated. The peak of ZFC magnetization has been observed at 72 K, sufficiently below the Curie temperature. Therefore $Nd_{0.9}Ca_{0.1}MnO_3$ exhibits properties of an inhomogeneous soft magnetic material in the temperature interval 72–110 K.

The magnetization–temperature behaviour of $Nd_{1-x}Ca_xMnO_3$ in a high field region is displayed in figure 4. The most pronounced ferromagnetic component has been observed for $Nd_{0.8}Ca_{0.2}MnO_3$ and $Nd_{0.75}Ca_{0.25}MnO_3$ compositions. However, their magnetization (68 emu g^{-1} or $2.8 \mu_B$ per formula unit) is less (approximately by 20%) than the value expected for the pure ferromagnetic state ($3.5 \mu_B$ per formula unit). Furthermore these compounds exhibit the rise of FC magnetization with increasing temperature. Both $x = 0.2$ and $x = 0.25$ show a peak of ZFC magnetization at a temperature 15 K below the onset of magnetic ordering (figure 5). Such a behaviour indicates an inhomogeneous magnetic state. The spontaneous magnetization of $Nd_{0.7}Ca_{0.3}MnO_3$ composition is much less than that for the $x = 0.25$ one; however the onsets of the ferromagnetic transition coincide for both

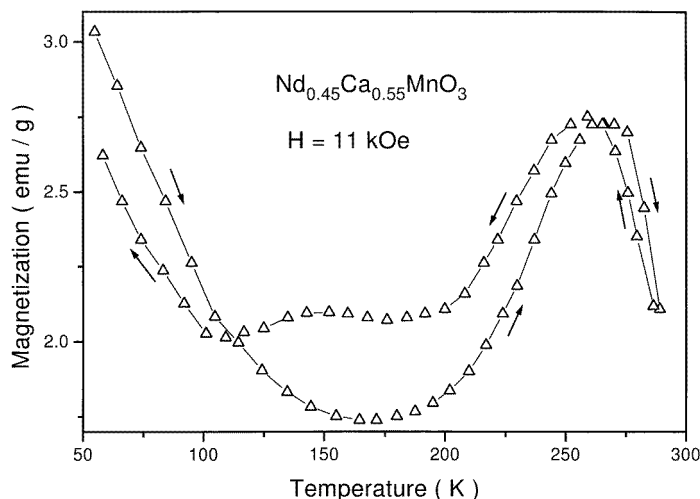


Figure 6. Field cooled magnetization against temperature for $\text{Nd}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$ measured on heating and on cooling.

compounds (figure 4). All $0.3 < x < 0.55$ compositions exhibit peaks of magnetization slightly below room temperature (figure 6). Large temperature hysteresis is associated with a first order phase transition which could be attributed to charge ordering [5]. The anomalous behaviour associated with antiferromagnetic ordering is far less pronounced.

The magnetotransport behaviour in the magnetic field of 10 kOe is presented in figure 7. The $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds are semiconductors over a wide concentrational range $0 \leq x \leq 0.3$. The ferromagnetic ordering affects slightly the electrical resistivity of these compounds (figure 7) in contrast to $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ where magnetic ordering causes an insulator–metal transition. However, the magnetoresistance ratio $[R(0) - R(10 \text{ kOe})]/R(0)$ is relatively large and reaches 45% in a field of 10 kOe for the $x = 0.25$ composition. This is a typical magnitude for bulk polycrystalline samples of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ series around the metal–insulator transition. The electrical resistivity for $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ decreases gradually with increasing calcium content independent of the magnetic state type. This behaviour correlates with removing unit cell distortion due to Ca doping. The $x = 0.3$ composition is dominantly antiferromagnetic and does not show appreciable magnetoresistance in a field up to 10 kOe. Apparently this field is too low to induce the metamagnetic transition in this compound [5].

4. Discussion

The crystal structure phase diagram of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) is sketched in figure 8. The temperatures of $O-O'$ (orbital order–disorder) transition were quoted from the literature [9]. This transition occurs in a wide temperature range through the two-phase state. The substitution of Nd by Ca leads to decreasing temperature of phase transition. The compositions with $x \geq 0.2$ do not exhibit the $O'-O$ transition. However, compositions in the interval $0.3 < x \leq 0.5$ undergo transition into a charge ordered low temperature phase. The temperature of charge ordering depends slightly on composition in a relatively wide range of Ca concentrations.

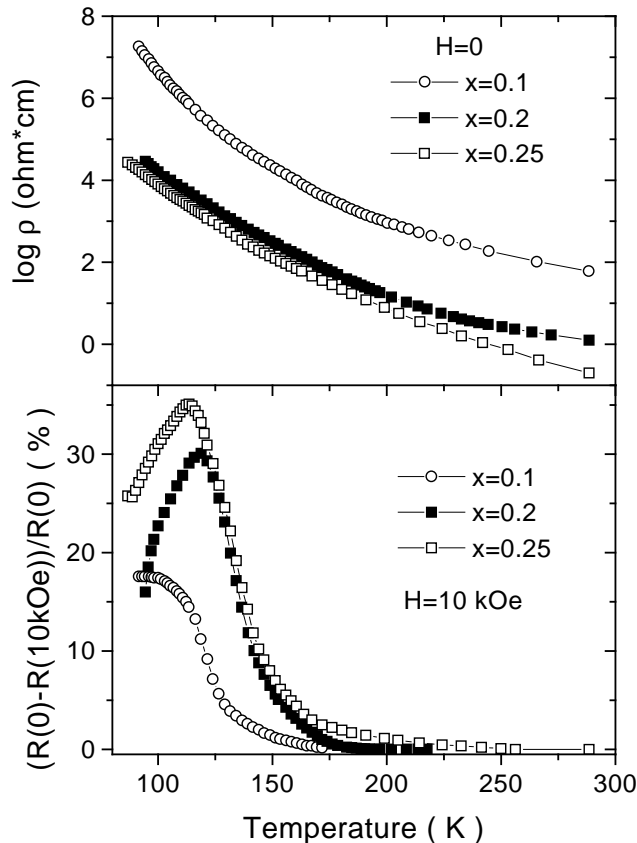


Figure 7. Resistivity (top panel) and magnetoresistance (bottom panel) against temperature for $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$.

As one can see clearly from the magnetic phase diagram (figure 8, bottom panel) the magnetic properties correlate strongly with crystal structure changes. The stoichiometric NdMnO_3 is a weak ferromagnet. Assuming the manganese sublattice moment to be the same as for LaMnO_3 and EuMnO_3 ($0.1 \mu_B$ per formula unit) we can estimate the Nd-sublattice contribution as being $0.8 \mu_B$ which is received taking into account the opposite alignment of Nd and Mn ions. The low spontaneous manganese sublattice magnetic moment is related to the weak ferromagnetic exchange interaction of Dzialoshinsky–Moriya type because there are no Mn^{4+} ions interacting ferromagnetically with Mn^{3+} ones. It is well known that the ABO_3 perovskites ($A = \text{lanthanoid}$, $B = \text{Fe, Cr, V}$) exhibit weak ferromagnetism of Dzialoshinsky–Moriya type. Both increasing oxygen content and substitution of Nd by Ca ions lead to enhancement of spontaneous magnetization. This effect could be attributed to formation of canting magnetic structure in the double exchange model [10] or appearance of clusters enriched by Mn^{4+} ions with dominant ferromagnetic interaction between manganese ions. In the case of phase separation the Néel point of the antiferromagnetic phase must decrease whereas the Curie point of the ferromagnetic phase must increase with enhancement of Ca content. The magnetic properties of $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ seem to be in agreement with a two phase model. At 110 K the domains of the sample with relatively high content of Mn^{4+} ions are ferromagnetically ordered. The peak of ZFC magnetization at 72 K may be

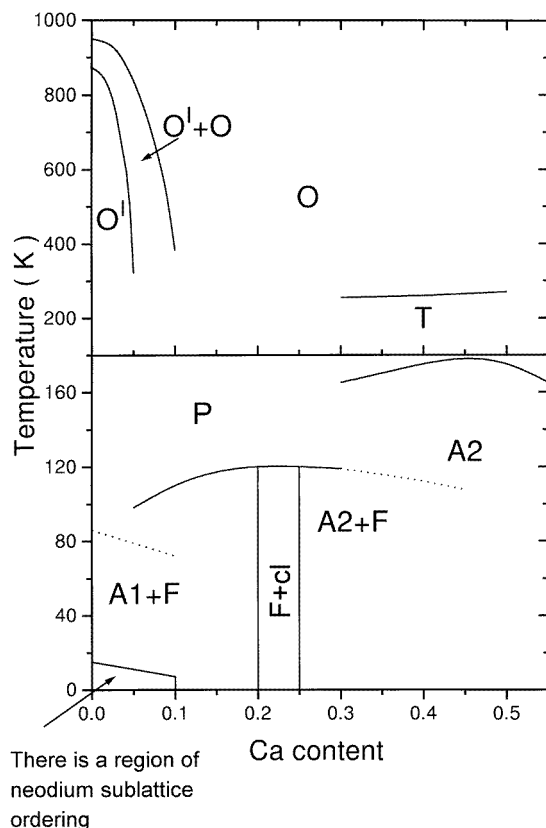


Figure 8. Crystal structure (top panel) and magnetic phase diagrams (bottom panel) for $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$. A1—magnetic state with antiferromagnetic structure of A-type, F—ferromagnetic state, cl—magnetic clusters with antiferromagnetic local structure, A2—magnetic state with antiferromagnetic structure of CE type.

the result of antiferromagnetic ordering in the domains with relatively low content of Mn^{4+} ions. These domains are apparently orbitally ordered in the manner of the parent compound NdMnO_3 . The low temperature magnetic properties of $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ differ markedly from those of the $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ and $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ analogous compositions [7, 11]. The latter compounds do not show any magnetic phase transitions below 10 K. Therefore we think the anomalous magnetic properties of $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ at low temperature are the result of the changing magnetic state in the Nd sublattice. Apparently the Nd sublattice is antiferromagnetically ordered below 7 K in some domains of the sample. Further neutron diffraction experiments are needed to understand this phenomenon.

The spontaneous magnetization reaches maximal magnitude around $0.2 \leq x \leq 0.25$; however, the expected value for pure ferromagnetic state ($3.5 \mu_B$ per formula unit, taking into account only the manganese sublattice because the neodymium sublattice is paramagnetic in this region) is larger than the observed one $2.8 \mu_B$. So we believe that even for $x = 0.2$ and $x = 0.25$ compositions an inhomogeneous magnetic state is realized. In contrast to the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.2$ and $x = 0.25$) are semiconductors below T_C with large resistivity $\rho \sim 10^4 \Omega \text{ cm}$ at 77 K. These compounds exhibit a large magnetoresistance effect at T_C , comparable with that for La-

based manganites. The electrical resistivity decreases monotonically with increasing content independent of magnetic state. Therefore the electrical conductivity and ferromagnetic state are not connected directly with each other in the $Nd_{1-x}Ca_xMnO_3$ series. The spontaneous magnetization of the compositions in the range $0.25 < x \leq 0.35$ decreases strongly with increasing calcium content. However, the temperature at which spontaneous magnetization appears does not depend practically on Ca concentration. Such a behaviour could be attributed to phase separation. These compositions exhibit both charge and antiferromagnetic ordering. The temperatures of these phase transitions also depend slightly on composition as expected in the two phase model.

From our experimental findings one can conclude that the antiferromagnetic state shows an orbitally or charge ordered phase whereas disordered phases $0.15 < x < 0.25$ (where static cooperative Jahn–Teller deformations are suppressed) exhibit predominantly ferromagnetic behaviour.

The truly ferromagnetic state has been observed in a number of insulating orthomanganites without Mn^{4+} ions such as $La_{1-x}Ba_x(Mn_{1-x}^{3+}Ti_x^{4+})O_3$ [12], $Bi^{3+}Mn^{3+}O_3$ [13] and $La(Mn_{1-x}Ga_x)O_3$ [8]. Furthermore, it was found that substitution of Bi^{3+} by divalent Ca^{2+} or Sr^{2+} leads to collapse of long-range ferromagnetic order in spite of Mn^{4+} ion appearance [13, 14]. The double exchange theory does not explain these data.

In order to account for the ferromagnetism found in the single-valent system $LaMn_{1-x}Ga_xO_3$ Goodenough [8] pointed out that the cooperative oxygen vibrations of a dynamic J–T coupling would coordinate empty and half-filled Mn^{3+} σ -bonding orbitals alternating on opposite sides of an oxygen atom to give an isotropic ferromagnetic superexchange interaction. The ferromagnetic Mn^{3+} – Mn^{3+} exchange interaction in perovskite manganites can be successfully interpreted in terms of the above-mentioned phonon-assisted superexchange. In contrast to double exchange this mechanism does not involve a real charge transfer within Mn^{3+} –O– Mn^{4+} pairs. In the frame of the superexchange model static Jahn–Teller deformations lead to antiferromagnetism whereas dynamic Jahn–Teller coupling gives rise to ferromagnetic interaction. The decrease of lanthanoid ionic size leads to enhancement of crystal structure distortions thus stabilizing static Jahn–Teller deformations. Hence, the concentrational range of ferromagnetic compositions becomes narrower. For $Nd_{1-x}Ca_xMnO_3$ $0.2 < x \leq 0.25$ compositions the 3d bandwidth is sufficient for appearance of the ferromagnetic state whereas the 3d bandwidth is too small for realization of metallic-like behaviour below T_C in spite of the parallel spin alignment. In the superexchange model the colossal magnetoresistance around T_C results from the spin-dependent scattering of charge carriers on magnetization fluctuations around T_C as found for single-valent $Tl_2Mn_2O_7$ pyrochlore [15], and $CdCr_2Se_4$ spinel [16].

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