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Insulator–metal transition in $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{(1-x)}\text{Co}_x\text{O}_3$ perovskites

E. Pollert,^{a,*} J. Hejtmánek,^a K. Knížek,^a M. Maryško,^a J.P. Doumerc,^b
J.C. Grenier,^b and J. Etourneau^b

^aInstitute of Physics, ASCR, 162 53 Praha 6, Czech Republic

^bInstitut de Chimie de la Matière Condensée de Bordeaux, CNRS, 33608 Pessac, France

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Abstract

The electric and magnetic properties of the perovskites $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{(1-x)}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.2$) prepared by the usual ceramic procedure were investigated. The insulator-to-metal-like (IM) transition, closely related to a ferromagnetic arrangement, was revealed for the composition of $x = 0.04$ and a similar tendency was detected for $x = 0$. The insulating behavior persists down to low temperatures for higher contents of cobalt ions in spite of the transition to the bulk ferromagnetism. The properties are interpreted in terms of the steric distortion, tilting of the $\text{Mn}(\text{Co})\text{O}_6$ octahedra and the double-exchange interactions of the type $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ and $\text{Mn}^{3.5+\delta}-\text{O}^{2-}-\text{Co}^{2+}$, respectively. Presence of antiferromagnetic domains in the ferromagnetic matrix for the most of cobalt-substituted samples is supposed.

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1. Introduction

The extended studies of the manganites $\text{Re}_{1-x}\text{M}_x\text{MnO}_3$, stimulated by the discovery of colossal magnetoresistance (CMR), showed unambiguously the importance of the antagonistic correlation effects on their behavior. Actually, the charge ordering giving rise to an antiferromagnetic arrangement and electron itinerancy inducing via double-exchange mechanism, ferromagnetic metallic-type state should be distinguished. The resulting behavior is strongly influenced by the variation of the chemical composition, substitution of trivalent rare earth for bivalent alkaline earth or alkaline metal ions and there are two basic factors decisive for the resulting ordering, the variation of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and geometry of the Mn–O–Mn bonds.

Thus, a tendency to the charge ordering promoted by buckling of the MnO_6 octahedra exists in the series $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($T_{\text{CO}} \sim 250$ K, $T_{\text{N}} \sim 175$ K for $x \sim 0.5$) and $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($T_{\text{CO}} \sim 240$ K, $T_{\text{N}} \sim 160$ K, for $x = 0.35$), whereas ferromagnetic double exchange is

favoured for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($T_{\text{C}} \sim 270$ K, $T_{\text{CO}} \equiv T_{\text{N}} \sim 175$ K) where the Mn–O–Mn angles become close to the ideal 180° arrangement [1–4].

Recently, it was found that the charge ordering can be suppressed by suitable substitutions (e.g. Co, Ni ions) on the manganese sites. An example is provided by the series $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ where, for $0.03 \leq x \leq 0.05$, an insulator–metal transition occurs in the temperature range from 80 to 60 K [5]. Evidently, in these materials, a problem of the cobalt and nickel formal valency and the character of the Co/Ni(3d)–O(2p)–Mn(3d) interactions arises. Original idea suggests the charge distribution of the type $\text{LaMn}_{0.5}^3+\text{Co}_{0.5}^3+\text{O}_3$ with the trivalent cobalt and nickel ions in the low-spin state and the ferromagnetic superexchange interactions (Co^{3+} , Ni^{3+})– O^{2-} – Mn^{3+} [6]. In contrast the combination (Co^{2+} , Ni^{2+}) and Mn^{4+} was found more stable in the double perovskites $\text{La}_2\text{Mn}(\text{Co},\text{Ni})\text{O}_6$ [7]. The recent X-ray absorption spectroscopic studies carried out on $\text{LnMn}_{0.85}\text{Co}_{0.15}\text{O}_3$ and $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{B}_x\text{O}_3$ manganites, where $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ and $\text{B} = \text{Co}, \text{Ni}$ ($0 < x \leq 0.1$) confirm the charge distribution giving rise to ferromagnetic double-exchange interactions of the type $\text{Mn}^{3.5+\delta}-\text{O}^{2-}-\text{Co}^{2+}$, Ni^{2+}) [8–10]. Further, the stability of $\text{Co}^{2+} + \text{Mn}^{4+}$ couples was evidenced by

*Corresponding author. Fax: +420-2-3123-184.

E-mail address: pollert@fzu.cz (E. Pollert).

NMR [11] and follows from the magnetic studies of the $\text{La}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_3$ system [12].

Beside the current investigations of systems where the mean valence of the manganese ions is controlled by a mutual replacing of trivalent rare earth ions by bivalent alkaline earth ions, we focused in the past years our attention on novel series with monovalent ion substitutions of the type $\text{Re}_{1-x}^{3+}\text{M}^+\text{Mn}_{1-2x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_3$, where $\text{Re} = \text{La}, \text{Pr}$ and $\text{M} = \text{Na}, \text{K}$ [13–15].

The solid solutions exist in the range of $0 \leq x \leq 0.2$, i.e. up to a maximum content of 40% Mn^{4+} and their structural and magnetic properties depend on the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in a similar way as for divalent substitution. Particularly, let us mention the evolution from the antiferromagnetic ordering of the layered A type for $x = 0$ to the ferromagnetic one for $x = 0.1$ and a commensurate charge and orbital ordering of the kind (1:1) below $T_{\text{CO}} = 215 \text{ K}$, followed by the transition to the antiferromagnetic arrangement of pseudo-CE type at $T_{\text{N}} = 175 \text{ K}$, evidenced recently by electron and neutron diffraction for $\text{Pr}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ [16]. That is analogous to the pseudo-CE magnetic structure described previously in the calcium system $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ for $x \sim 0.3\text{--}0.4$ [17–19]. Now, by analogy with the divalent alkaline earth manganites, we attempted to destroy the charge ordering and induce the insulator–metal transition by a suitable substitution in the “monovalent systems”. The solid solutions of the general formula $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ were selected for this purpose.

2. Experimental

The samples of the compositions $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.2$) were prepared by the usual ceramic procedure starting from commercially available chemicals. The analyzed materials, were homogenized in the appropriate ratios and heated at 900°C in air for 24 h. Then the mixtures were pressed into pellets, sintered at 1100°C under oxygen atmosphere for 96 h and subsequently quenched or cooled down by switching off the furnace. Preliminary experiments, carried out in order to select the optimum heating conditions, showed that it was nearly impossible to complete the reaction in a reasonable time at lower temperatures while a tendency to a phase separation caused by an increased oxygen deficiency in the samples was observed at higher temperatures.

The phase composition was checked by EPMA and SEM combined with X-ray analysis and the oxygen stoichiometry of the studied samples was determined by a redox cerimetric method. The structural refinement was performed by a profile analysis using the program FULLPROF [20].

The four-probe method was used for the study of the electrical conductivity in the temperature range of 4.2–300 K and the thermoelectric power in the range of 10–300 K was measured by a method described elsewhere [21]. The AC magnetic susceptibility (field amplitude of 3.9 Oe, frequency of 100 Hz) and the DC magnetization in fields up to 50 kOe were measured by means of a SQUID magnetometer.

3. Results

The studied samples were found to be single phase and no deviations from the nominal ratios of the cations were detected.

An increase of the oxygen deficiency with increasing content of cobalt ions was determined by the redox analysis. A particular attention was devoted to the composition of $x = 0.04$ where two samples of slightly different oxygen stoichiometries, denoted as 0.04a (quenched down) and 0.04b (slowly cooled down), were prepared. Employing the determined oxygen stoichiometries and presumption of the stability of the $\text{Mn}^{4+}\text{--}\text{Co}^{2+}$ couples the occupancy of the octahedral sites by cations of the respective formal valencies were calculated, see Table 1. The actual contents of Mn^{4+} are lower than for the ideal oxygen stoichiometry ($\gamma = 0$).

The variation of the lattice parameters and the cell volume with composition plotted in Fig. 1 shows a sudden depression of both the orthorhombic distortion and cell volume for $x = 0.04$ sample and a subsequent increase for $x = 0.1$ and 0.2. An influence of the oxygen stoichiometry is demonstrated by the comparison of the respective data for the samples 0.04a and 0.04b. The plotted dependences of $(\text{Mn}\text{--}\text{O}1)_{\text{apical}}$, $(\text{Mn}\text{--}\text{O}2)_{\text{equatorial}}$ distances and $(\text{Mn}\text{--}\text{O}1\text{--}\text{Mn})_{\text{apical}}$, $(\text{Mn}\text{--}\text{O}2\text{--}\text{Mn})_{\text{equatorial}}$ angles (samples $x = 0, 0.04\text{b}, 0.1, 0.2$) suggest a similar evolution, see Figs. 2 and 3.

The electrical conductivities plotted in Fig. 4 show that a tendency to IM transition is traced already for $x = 0$ but the residual resistivity remains very high. The transition is however clearly evidenced for both the $x = 0.04\text{a}$ and 0.04b samples. Further increase of the cobalt

Table 1
Oxygen stoichiometry and occupancy of the octahedral sites for $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\gamma}$

x	$3-\gamma$	% of cation in octahedral sites		
		Mn^{3+}	Mn^{4+}	Co^{2+}
0	2.950	70	30	0
0.04a	2.960	60	36	4
0.04b	2.975	57	39	4
0.1	2.950	50	40	10
0.2	2.915	37	43	20

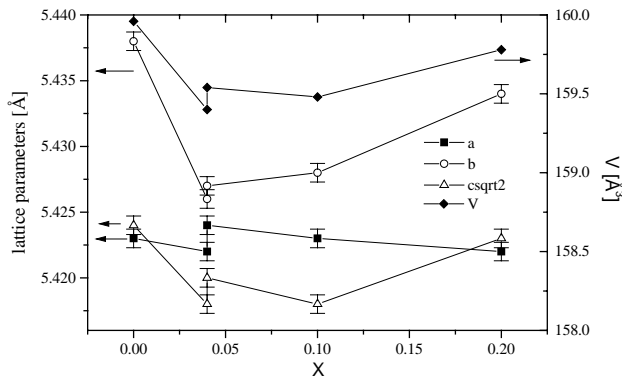


Fig. 1. Compositional dependence of the lattice parameters of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series.

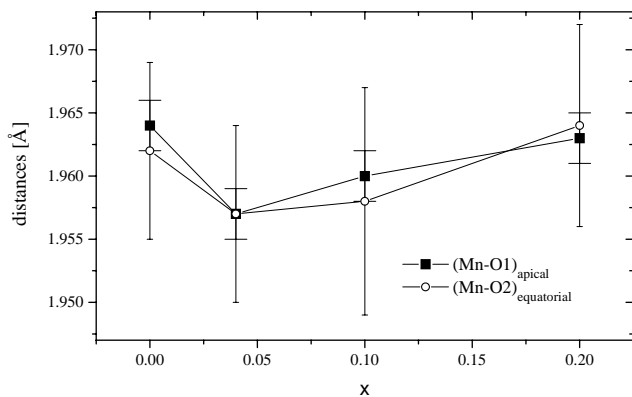


Fig. 2. Compositional dependences of the distances $(\text{Mn-O1})_{\text{apical}}$ and $(\text{Mn-O2})_{\text{equatorial}}$.

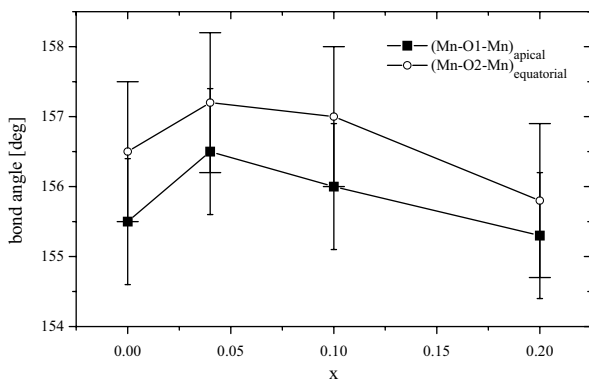


Fig. 3. Compositional dependences of the angles $(\text{Mn-O1-Mn})_{\text{apical}}$ and $(\text{Mn-O2-Mn})_{\text{equatorial}}$.

concentration ($x = 0.1$ and 0.2) leads to an insulating behavior in the whole temperature range. The thermoelectric power measurements undoubtedly confirm the IM transition for the sample $x = 0.04b$ (Fig. 5). The measurements carried out on the samples with $x = 0.0$ and 0.2 were limited to a temperature of ~ 60 K due to their high resistivity. The slight change in the slope of the thermal dependence of the thermoelectric power at

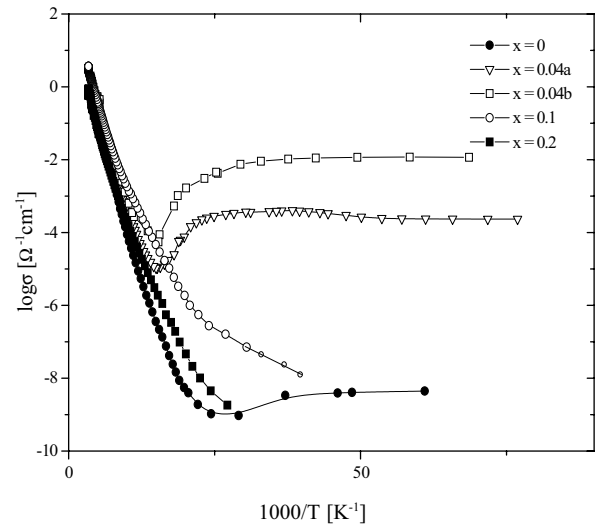


Fig. 4. Temperature dependences of the electric conductivity of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series.

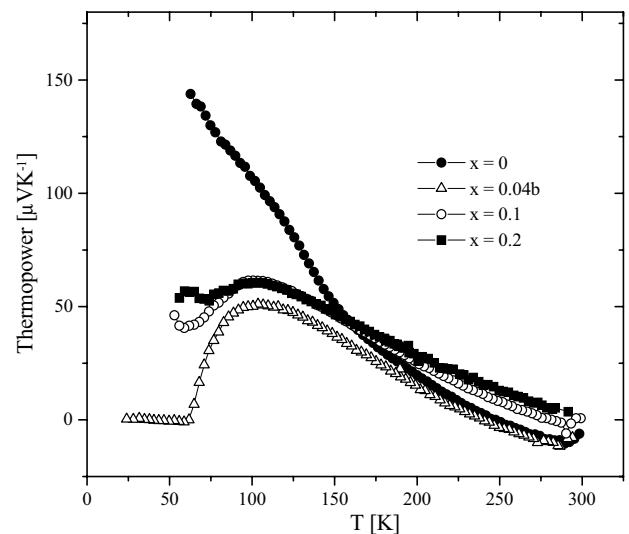


Fig. 5. Temperature dependences of the thermoelectric power of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series.

~ 150 K for $x = 0$ can probably be ascribed to the charge ordering. In contrast to the conductivity measurements, no IM transition can be evidenced for $x = 0$, but such a tendency is suggested for $x = 0.1$ and 0.2 (Fig. 5). The contents of Mn^{4+} deduced on the base of the model described elsewhere [14] agree qualitatively with the values determined independently by the chemical analysis. The non-linear behavior of the $1/\chi$ vs. T dependencies in the paramagnetic region, see Fig. 6, made difficult to evaluate accurately the paramagnetic Curie temperature and Curie constants. This behavior indicates probably the existence of short-range magnetic interactions persisting above the critical temperature of the long range magnetic ordering. One

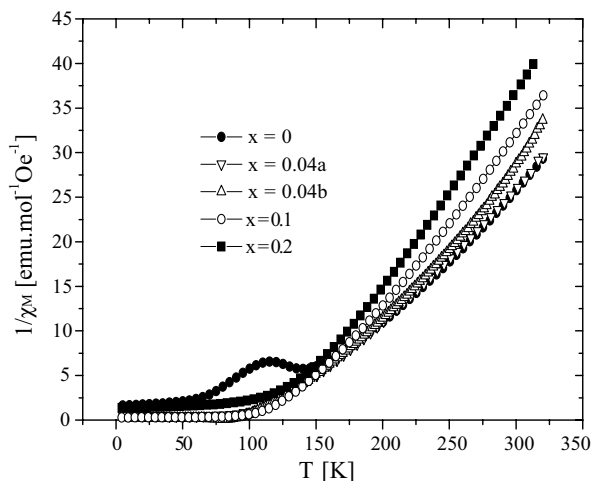


Fig. 6. Temperature dependences of the reciprocal magnetic susceptibility of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series, for $T < T_c$, the plots correspond to M/H for $H = 3 \text{ kOe}$.

can observe a small “hump” on the $1/\chi$ vs. T and M_s vs. T dependencies of $x = 0$ at $\sim 150 \text{ K}$ (see Figs. 6 and 7) and a weak ferromagnetic contribution is detectable below $T \approx 75 \text{ K}$ enhanced under an influence of the magnetic field above $\sim 35 \text{ kOe}$, see Fig. 8. The compositions of $0.04 \leq x \leq 0.2$ arrange ferromagnetically at $T < T_c$.

Some data yielded from the conductivity and magnetic measurements are summarized in Table 2.

4. Discussion

There are two principal effects influencing the resulting behavior of the studied series, namely

- macroscopic cooperative distortions, tilting of the octahedra, giving rise to deviations of the Mn–O–Mn/Co bonds from the ideal 180° arrangement due to variation of the mean dimension of the octahedral cations, $r(\text{Me}_B)$.
- acting of the cobalt ions as point defects to disturb the antiferromagnetic and charge ordering.

Both these effects depend on the Mn/Co ratio and the valencies of the present cations and an interplay of their mutual acting is decisive for the resulting properties.

An unusual course of the structural distortion, see Figs. 1–3, seems to be better comprehensible from a comparison of the compositional dependences of the B-site cations mean dimension, calculated from the occupancy of these sites and the mean structural distortion D calculated from the independently measured lattice parameters, see Fig. 9.

An exceptional conformity of both these dependences seems to confirm the influence of the oxygen stoichiometry on the resulting tilting, evident also from a

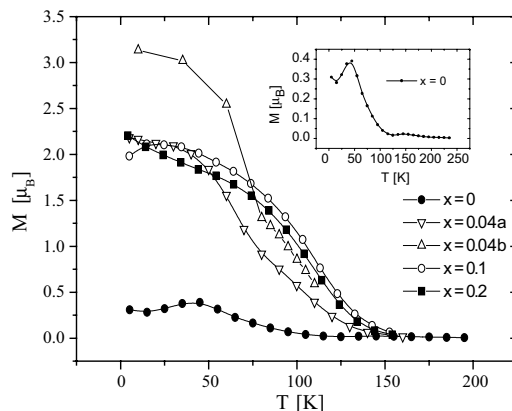


Fig. 7. Temperature dependences of the spontaneous magnetization under 20 kOe of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series.

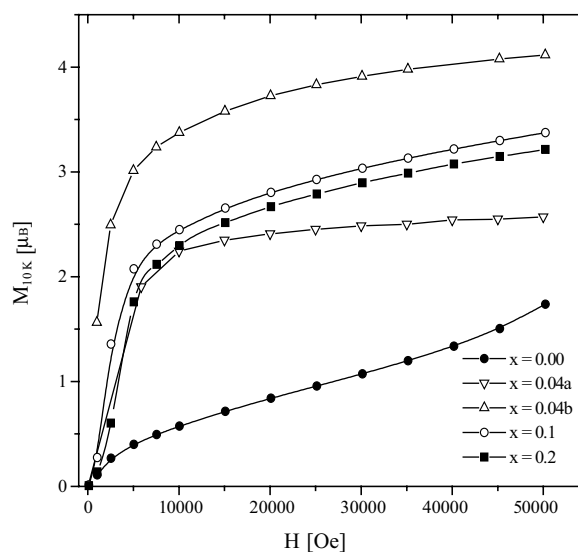


Fig. 8. Magnetic field dependences of the magnetization at 10 K of $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series.

comparison of the samples $x = 0.04a$ ($\tilde{\gamma} = 0.04$) and $x = 0.04b$ ($\tilde{\gamma} = 0.025$). In order to elucidate better the observed behavior, the dependence $r(\text{Me}_B)$ vs. x , calculated for the ideal oxygen stoichiometry ($\gamma = 0$), is plotted too. Thus, one can observe for our samples an abrupt decrease of the tilting for $x = 0.04$ due to a decrease of the mean dimension of the B-site octahedral cations and its subsequent increase for $x = 0.1$ and 0.2 , where the deviations from the ideal oxygen stoichiometry become more important.

The sample of $x = 0$ exhibits a relatively important tilting and the determined $30\% \text{ Mn}^{4+}$ is close to the value of $36\% \text{ Mn}^{4+}$ found in the recently studied composition $\text{Pr}_{0.8}\text{Na}_{0.2}\text{MnO}_3$. Thus in analogy, it seems to be reasonable to attribute the small “hump” on $1/\chi$ vs. T and M_s vs. T dependences in a vicinity of 150 K found for $\text{Nd}_{0.8}\text{Na}_{0.2}\text{MnO}_3$, see Figs. 4 and 5, to the

Table 2
Electric and magnetic data of the series $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{(1-x)}\text{Co}_x\text{O}_3$

Sample	Thermoelectric power ^a	Electrical conductivity	Magnetic constants			
x	Mn^{4+} (%)	T_{I-M} onset (K)	M_s (5 K) (μ_B)	T_c^b (K)	T_{CO} onset (K)	T_N (K)
0.0	29	77	0.29	≈ 75	150	≤ 150
0.04a		91	2.2	88	—	—
0.04b	32	97	3.2	85	—	—
0.1	35	—	1.97	100	—	—
0.2	36	—	2.2	106	—	—

^a $\alpha = (k_B/e)E_S/k_B T + \ln(1-c)/c$, where E_S is energy gap (-0.02 eV) and $c = \text{Mn}^{3+}/\text{Mn}_{\text{total}}$.

^b Arrot plot, $H/\sigma = a(T - T_c) + b\sigma^2$.

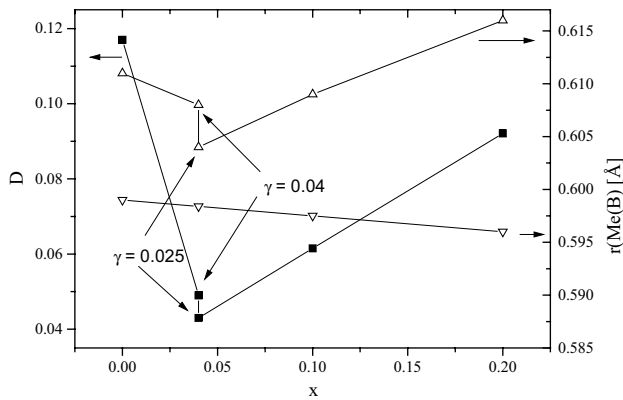


Fig. 9. Compositional dependences of the B-site cations mean dimension $r(\text{Me(B)}) = [(\% \text{Mn}^{3+})r(\text{Mn}^{3+}) + (\% \text{Mn}^{4+})r(\text{Mn}^{4+}) + (\% \text{Co}^{2+})r(\text{Co}^{2+})]/100$, ∇ —for ideal oxygen stoichiometry ($\gamma = 0$), Δ —for measured oxygen stoichiometry, see Table 2, \blacksquare —mean structural distortion $D = \frac{1}{3} \sum |(a_i - \bar{a})/a_i| \times 100$, where $\bar{a} = (abc/\sqrt{2})^{1/3}$, $a_1 = a$, $a_2 = b$, $a_3 = c/\sqrt{2}$.

charge and orbital ordering accompanied by the antiferromagnetic arrangement and insulating behavior. [16,17]. A weak ferromagnetic contribution below 75 K should be probably related to the presence of small domains exhibiting ferromagnetic double-exchange $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ interactions in a matrix with prevailing antiferromagnetic superexchange interactions. Such coexistence areas, giving rise in some cases canted structures, were evidenced by the neutron diffraction scattering in several studies [22,23].

For a low concentration of cobalt ions ($x = 0.04$) the steric distortion becomes nearly negligible and the ferromagnetic metallic-type state related to $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ double-exchange interactions prevails at low temperatures. In contrast an increase of the concentration of Co^{2+} ions ($x = 0.1$ and 0.2) leads to a simultaneous acting of both the double-exchange interactions $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ and $\text{Mn}^{3.5+\delta}-\text{O}^{2-}-\text{Co}^{2+}$, respectively. Nevertheless, because of the local character of the latter interactions and restored tilting of the $\text{Mn}(\text{Co})\text{O}_6$ octahedra the transport of the charge carriers becomes blocked and the insulating behavior even persists in the ferromagnetic state for $T < T_c$. The

determined values of spontaneous magnetization are substantially lower than the expected ones ($\sim 3.6 \mu_B$) for most of the cobalt-substituted samples. This result can be attributed to a presence of antiferromagnetic domains in the ferromagnetic matrix. The comparison of the samples 0.04a and 0.04b reveals a large sensibility to the oxygen stoichiometry. A relatively subtle increase of the Mn^{4+} content, see Table 2, probably strongly decreases the amount of the antiferromagnetic phase and the experimental value of the spontaneous magnetization approaches the ideal ferromagnetic value (Fig. 6). This conclusion seems to be further confirmed by the evolution of the conductivity assuming a percolation process. A gradual disappearance of the antiferromagnetic phase accompanied by an increase of the FM phase volume fraction seems to be conspicuous in the series $x = 0.00 \rightarrow x = 0.04a \rightarrow x = 0.04b$ where a substantial increase of the conductivity at temperatures below the IM transition is observed.

5. Conclusion

- The properties of the $\text{Nd}_{0.8}\text{Na}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ series can be apparently related to an interplay of the steric distortion, double-exchange interactions of the type $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ and $\text{Mn}^{3.5+\delta}-\text{O}^{2-}-\text{Co}^{2+}$ and superexchange interactions of the type $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$ and $\text{Mn}^{4+}-\text{O}^{2-}-\text{Mn}^{4+}$, respectively. Besides the Co^{2+} ions, acting as local defects, a particular importance should be attributed to the deviations of the oxygen stoichiometry from the ideal one influencing tilting of the $\text{Mn}(\text{Co})\text{O}_6$ octahedra and hence the character of the interactions.
- The $I-M$ transition observed for $x = 0.04$ is conditioned by suppression of a tendency of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions to the charge and orbital ordering; $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ double-exchange interactions play a decisive role.
- In contrast, the insulating behavior observed even in the ferromagnetic state for $T < T_c$ for higher

concentration of Co^{2+} ions ($x = 0.1$ and 0.2) is a consequence of both, the restored tilting and local character of the $\text{Mn}^{3.5+\delta}\text{-O}^{2-}\text{-Co}^{2+}$ interactions.

Acknowledgments

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