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Mössbauer study of partially ordered cobaltites $\text{Nd}_2\text{CoMnO}_{6+\delta}$ with perovskite structure

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Abstract

The properties of $\text{Nd}_2\text{CoMnO}_{6+\delta}$ ($\delta = 0, 0.12$) samples were investigated by Mössbauer, μSR and magnetization measurements. Our experimental data were interpreted in the following model. The samples consist mainly of clusters of cobalt and manganese ions with different degrees of order. The valence state of these ions is predominantly $\text{Co}^{2+}/\text{Mn}^{4+}$. Increasing the oxygen content leads to an enhancement of the disordered fraction of the sample which contains mainly three-valent ions. The highly ordered stoichiometric ($\delta = 0$) compound exhibits both pronounced ferromagnetic and weak spin-glass-like components. Ionic disordering leads to a partial destruction of the ferromagnetic component and to strong enhancement of the spin-glass-like one in non-stoichiometric ($\delta = 0.12$) samples. The spin-glass-like component transforms into the ferromagnetic one as a first-order metamagnetic phase transition in an external magnetic field.

1. Introduction

Mixed oxides based on both cobalt and manganese ions exhibit a large variety of magnetic properties. For example, LaCoO_3 and LaMnO_3 are paramagnetic and antiferromagnetic materials, respectively. On the other hand, $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is a ferromagnet with a Curie temperature (T_C) above 200 K [1–9]. Therefore, such compounds are of interest from both a

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theoretical point of view and in terms of their practical application. For example, they can be used as spintronic elements, magnetic media, electrode materials, oxygen membranes etc.

$\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ is one of the most studied systems from the cobalt/manganese mixed oxides. This system has been the subject of numerous crystallographic and magnetic studies. According to recent neutron diffraction and magnetization measurements, the ferromagnetism in $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ occurs because of positive exchange interactions between the Co and Mn ions. These ions are partially ordered, similar to the ion arrangement in NaCl [1–3]. This ordering leads us to use the double perovskite formula $\text{A}_2\text{B}'\text{B}''\text{O}_6$ instead of ABO_3 . Different works give different degrees of order [1–3, 10]. The data on the Co and Mn oxidative states are contradictory. Nuclear magnetic resonance (NMR) data provide evidence of Co^{2+} and Mn^{4+} valence states for $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ [7, 11]. Furthermore, it was shown that the similar compounds $\text{LaNi}_{0.5}\text{Mn}_{0.5}\text{O}_{3+\delta}$ and $\text{YCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ contain $\text{Ni}^{2+}\text{--Mn}^{4+}$ and $\text{Co}^{2+}\text{--Mn}^{4+}$ pairs, respectively [10, 12, 13]. However, according to [5] and [6] two different crystallographic and magnetic phases coexist in $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ samples heated in air between 700 and 1300 °C. Rhombohedral high- T_C and orthorhombic low- T_C phases are observed as single phase for samples prepared below 700 °C and above 1300 °C, respectively. The high- T_C phase contains the low-spin (LS) Co^{3+} ($t_{2g}^6 e_g^0$, $S = 0$) and high-spin (HS) Mn^{3+} ($t_{2g}^3 e_g^1$, $S = 2$) ions, and ferromagnetism probably arises from the superexchange $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ interactions alone as the LS Co^{3+} ions are non-magnetic. The low- T_C phase contains the HS Co^{2+} ($t_{2g}^5 e_g^2$, $S = 3/2$) and Mn^{4+} ($t_{2g}^3 e_g^0$, $S = 3/2$) ions, and the ferromagnetism results from the $\text{Co}^{2+}\text{--O--Mn}^{4+}$ interactions.

It is known, however, that the properties of compounds with the perovskite structure generally change with the replacement of the La ion by a rare-earth element with a smaller ionic radius. For instance, metamagnetic phase transitions are observed in the majority of the $\text{RE}_2\text{CoMnO}_6$ compounds, with the exception of the $\text{La}_2\text{CoMnO}_6$ system [13–17]. The magnetic properties of the RE mixed oxides also depend on the synthesis conditions. Annealing at lower temperatures in a vacuum leads to an increase in the magnetic moment and to the stabilization of the higher- T_C ferromagnetic phase [13–17].

Earlier it was suggested that the metamagnetism of the above-mentioned compounds is associated with a transformation of the magnetic structure from ferrimagnetic, where the magnetic moments of Co^{2+} and Mn^{4+} ions are antiparallel, to ferromagnetic where they are parallel [13]. However, this suggestion was based on magnetization data only. In previous work [18] we studied the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ system by a time-of-flight (TOF) neutron technique. In addition, high-resolution neutron diffraction measurements were performed [19] in order to refine precisely the crystal and magnetic structures. We considered that the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ samples contain a spin-glass-like component which transforms into a ferromagnetic one as a first-order phase transition in an applied external magnetic field. However, the exact nature of the metamagnetism in $\text{RE}_2\text{CoMnO}_{6+\delta}$ is still an open question. Therefore, studies of the systems by the different techniques can help us to prove our suggestions.

In the present paper we continue our study of one of the $\text{RE}_2\text{CoMnO}_{6+\delta}$ ($\text{RE} = \text{Nd}$) systems by means of Mössbauer, μSR and dc magnetization measurements. Our main aim was to determine the nature of the metamagnetism in the rare-earth double cobaltites $\text{RE}_2\text{CoMnO}_{6+\delta}$ ($\text{RE} \neq \text{La}$).

2. Experiment

The $\text{Nd}_2\text{CoMnO}_{6+\delta}$ compound was synthesized using the conventional ceramic method. Starting powders of Nd_2O_3 , Co_3O_4 and Mn_2O_3 were mixed in stoichiometric proportions,

pressed into pellets and sintered at 1320 °C for 24 h in air. After the synthesis the sample was slowly cooled to room temperature at a rate of 50 °C h⁻¹. To ensure a rather complete absorption of oxygen by the lattice part of the as-prepared sample was annealed at 900 °C in air for 24 h. The oxygen content of the sample was determined using thermogravimetric analysis (TGA). Estimation of the oxygen content led to the nominal chemical formula Nd₂CoMnO_{6.12} with an error of ±0.02 oxygen per formula unit. A second part of the as-prepared sample was then reduced. The reduction of Nd₂CoMnO_{6.12} was carried out in an evacuated silica tube at 1000 °C for 24 h. Metallic tantalum was used as the reducing agent. According to the TGA data, the oxygen index in the reduced compound was $x = 6.00 \pm 0.02$. Moreover, the Nd₂Co_{0.98}Mn_{0.98}Fe_{0.04}O₆ and Nd₂Co_{0.98}Mn_{0.98}Fe_{0.04}O_{6.12} samples were prepared for the Mössbauer measurements by the same procedure using the ⁵⁷Fe isotope.

The dc magnetization measurements were performed using a Quantum Design MPMS-5 SQUID magnetometer and a OI-3001 vibrating sample magnetometer. The temperature dependences of the magnetization $M(T)$ were measured on warming from 4 to 250 K in a field of 100 Oe after a field cooling (FC) or zero field cooling (ZFC) procedure. The field dependences of the magnetization $M(H)$ were measured at 4.2 K after a ZFC procedure. In order to observe the metamagnetic phase transition in the Nd₂CoMnO_{6.12} sample, $M(H)$ measurements have to be done in fields up to 50 kOe after cooling in a field of 0.5 kOe.

The Mössbauer measurements were performed using a conventional constant-acceleration spectrometer with a source of ⁵⁷Co in Rh. The spectra were recorded in a transmission geometry at temperatures ranging from 80 to 295 K. A continuous flow Oxford Instruments CF-100 cryostat was used. The temperature stability was better than ±0.5 K. The Mössbauer spectra were fitted using the NORMOS program [20]. All isomer shifts are related to the α-Fe standard.

The muon spin rotation/relaxation/resonance (μ SR) experiments were performed using a general purpose decay-channel (GPD) spectrometer in the Laboratory for Muon Spin Spectroscopy at the Paul Scherrer Institute (PSI), Switzerland. The measurements were carried out in zero field and in an external magnetic field of 100 G transverse to the direction of the muon spin. The samples had a disc shape with a diameter of 10 mm and a thickness of 5 mm. They were glued to a silver sample holder and mounted on the cold finger of a closed cycle refrigerator. The temperature of the samples was stabilized within 0.1 K in the range of 10–250 K.

3. Results

3.1. Magnetic properties

Figure 1 shows the temperature dependences of both the ZFC ($M_{ZFC}(T)$) and FC ($M_{FC}(T)$) magnetization of the Nd₂CoMnO_{6+ δ} and Nd₂Co_{0.98}Mn_{0.98}Fe_{0.04}O_{6+ δ} compounds. The field dependent magnetization ($M(H)$) is presented in figure 2. It is worth noting that the samples with Fe ions have very similar $M(T)$ and $M(H)$ curves in comparison with the Nd₂CoMnO_{6+ δ} compounds.

According to the magnetization measurements, the reduced stoichiometric samples are characterized by a sharp transition into a paramagnetic state near 180 K and a rather high spontaneous magnetization (figures 1 and 2). For the annealed non-stoichiometric compounds, the transition into a paramagnetic state occurs in a wide temperature range, indicating an inhomogeneous magnetic state. The onset of the transition into the magnetically ordered state appears near 140 K.

For these samples the $M_{ZFC}(T)$ curve deviates from $M_{FC}(T)$ slightly below T_C , passes through a maximum and then exhibits a gradual reduction with decreasing temperature. Such

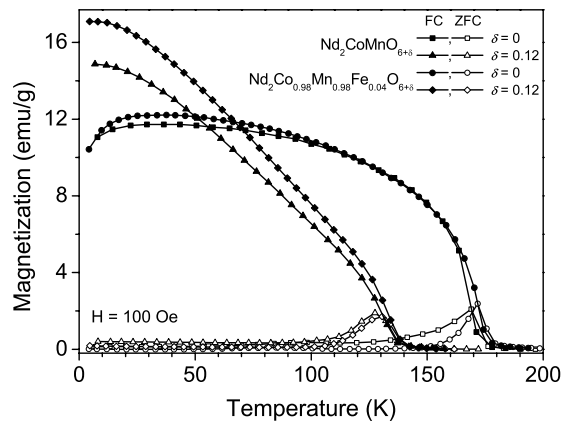


Figure 1. Temperature dependences of the dc magnetization of the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ and $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ compounds measured in a field of 100 Oe after a FC or ZFC procedure.

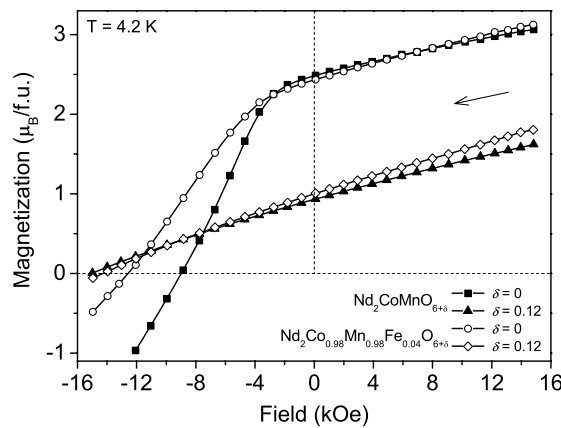


Figure 2. Field dependences of the dc magnetization of the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ and $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ compounds measured at 4.2 K. The arrow indicates the direction of the field sweep.

a behaviour of $M_{\text{ZFC}}(T)$ is characteristic of the cobaltites and lightly doped manganites and is attributed to the large magnetic anisotropy of these compounds [21]. The decrease of $M_{\text{FC}}(T)$ below ~ 30 K for the stoichiometric compounds (figure 1) most probably corresponds to an antiparallel ordering of the Nd ion's magnetic moments towards the Co/Mn ones. This suggestion is in agreement with our neutron diffraction data (see [18] for details). The magnetization measurements as a function of an applied external magnetic field have confirmed that these compounds are characterized by the large magnetic anisotropy. A very high coercivity H_C up to about 16 kOe was observed for the as-prepared sample. The reduced stoichiometric sample is characterized with a slightly smaller value of $H_C \sim 12$ kOe. Saturation of $M(H)$ is not achieved up to 15 kOe, where the magnetic moment per formula unit is about 3 and $1.6 \mu_B$ (see figure 2) for the stoichiometric and non-stoichiometric samples, respectively. Similar behaviour of the magnetization was also observed in the cobaltite $\text{La}_2\text{CoMnO}_6$ in contrast to the Ni-containing compound $\text{La}_2\text{NiMnO}_6$ [3, 12]. This is a characteristic of the

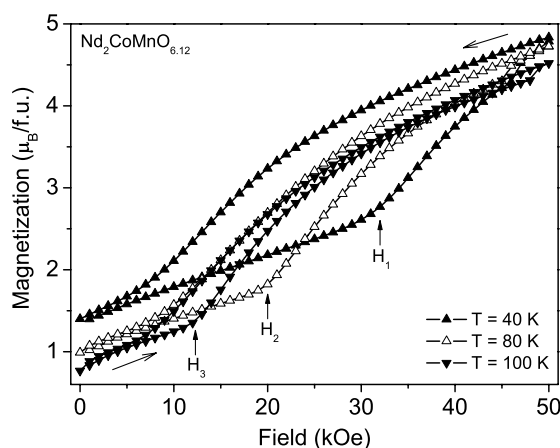


Figure 3. Field dependences of the dc magnetization of the annealed $\text{Nd}_2\text{CoMnO}_{6.12}$ compound measured at 40, 80 and 100 K. The arrows indicate the direction of the field sweep.

cobaltites, which contains Co^{2+} or Co^{3+} ions with an unquenched orbital contribution to the effective magnetic moment. The magnetic moment of the Co/Mn sublattice ($M_{\text{Co/Mn}}$) at the lowest temperature is difficult to determine as the negative f-d magnetic interaction orients the magnetic moment of the Nd sublattice (M_{Nd}) into the opposite direction.

An external magnetic field induces a metamagnetic transition in the annealed $\text{Nd}_2\text{CoMnO}_{6.12}$ sample, which is clearly revealed in the $M(H)$ dependences observed after cooling in a field of 0.5 kOe (figure 3). The metamagnetic transition starts at H_1 , H_2 and H_3 for $T = 40, 80$ and 100 K, respectively. The critical field associated with the transition decreases with increasing temperature and metamagnetic behaviour becomes more pronounced (figure 3). The large hysteresis clearly indicates a first-order phase transition. Below 20 K the metamagnetic transition becomes irreversible.

According to our neutron diffraction data [18, 19] the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ samples exhibit long-range ferromagnetic order. Ferromagnetism arises from the positive interactions between the Co and Mn ions. The valence state of the ions is predominantly $\text{Co}^{2+}/\text{Mn}^{4+}$ [18, 19]. As has already been pointed out, the total magnetic contribution consists of a sum of magnetic contributions of both the cobalt-manganese and neodymium sublattices and the vector of the magnetic moment of the Nd sublattice has an antiparallel component towards the Co/Mn moment.

From our neutron diffraction data [19] we have found that the Nd sublattice is ordered with a magnetic moment $M_{\text{Nd}} \approx 0.7 \mu_{\text{B}}$ at 2 K. Such a value of M_{Nd} per Nd ion is in agreement with data obtained from the neutron diffraction studies of $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$ [22]. We have also obtained values for the $M_{\text{Co/Mn}}$ sublattice of 5.5 and $3.7 \mu_{\text{B}}/\text{fu}$ for $\text{Nd}_2\text{CoMnO}_6$ and $\text{Nd}_2\text{CoMnO}_{6.12}$, respectively [19].

3.2. Mössbauer studies

The fitting of the Mössbauer spectra was performed assuming the coexistence of a non-magnetic fraction and a magnetic one (defined numerically using a distribution of hyperfine magnetic field $P(H)$). The non-magnetic parts of the spectra were fitted with two quadrupole doublets QS_1 and QS_2 . The results are shown in figures 4 and 5 for $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_6$ and $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6.12}$ samples, respectively. The relative magnetic fraction of both

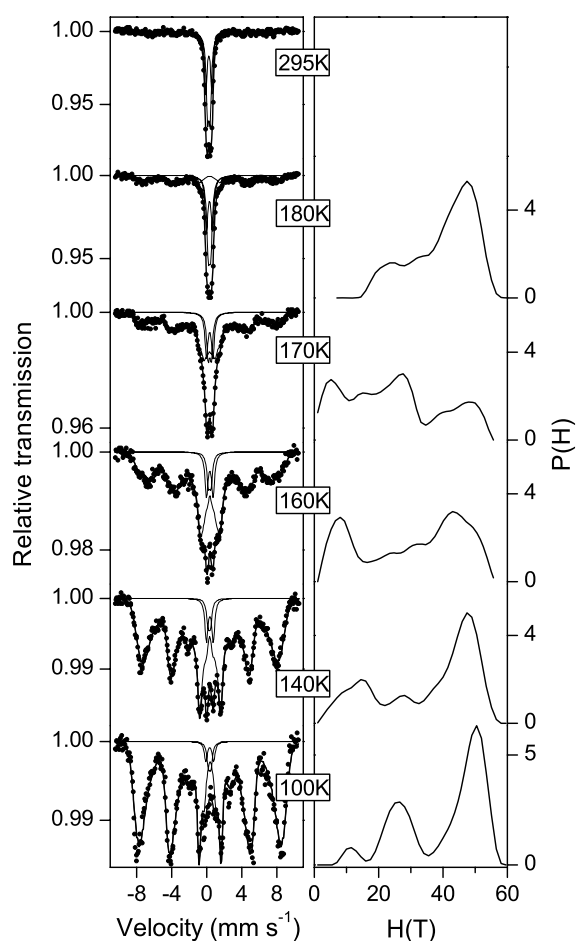


Figure 4. The Mössbauer spectra for $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_6$ measured as a function of temperature.

samples increases at decreasing temperature at the expense of the non-magnetic fraction. The hyperfine parameters are listed in table 1. The isomer shift values and the mean values $\langle H \rangle$ strongly suggest that iron is in the Fe^{3+} state and is located at, most probably, two different positions in the $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ structure, one with a larger $\text{QS}_1 \approx 0.8 \text{ mm s}^{-1}$ and the other with a smaller $\text{QS}_1 \approx 0.3 \text{ mm s}^{-1}$ quadrupole splitting (table 1), i.e. at lower-symmetry sites (larger QS) and at higher-symmetry sites (smaller QS). However, there are some differences in Mössbauer spectra for the as-prepared and stoichiometric samples to be discussed.

For the reduced $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_6$ sample the $P(H)$ distribution at 180 K shows one large peak at relatively high magnetic fields (figure 4). The mean value of the magnetic field $\langle H \rangle$ estimated from the entire distribution $P(H)$ is therefore high and equals $\sim 40 \text{ T}$. At lower temperatures (170–160 K) $P(H)$ shows a complex structure: besides the peak at high fields the peaks at lower fields are quite strong. Therefore the mean value $\langle H \rangle$ is smaller (table 1) despite the fact that the temperature is lower. Then, $\langle H \rangle$ increases with decreasing temperature. At 100 K the peaks at lower H became small and the peak at lowest H (~ 10 –

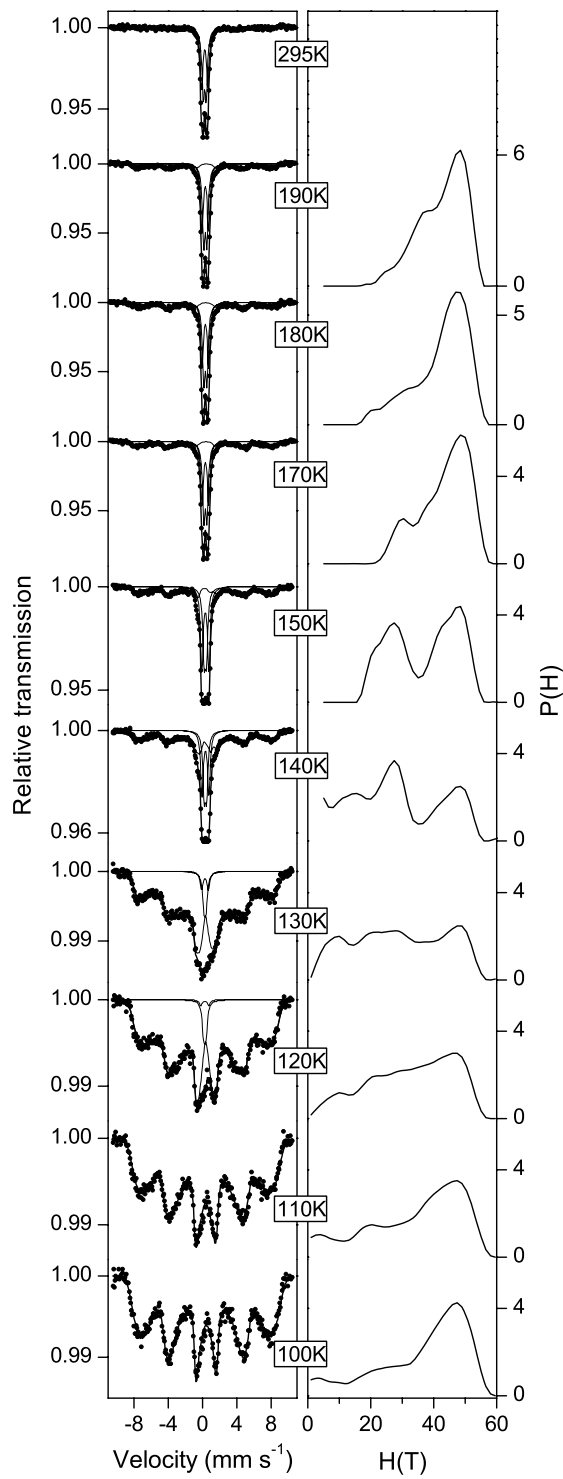


Figure 5. The Mössbauer spectra for $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6.12}$ measured as a function of temperature.

Table 1. Experimental values of the isomer shift δ , the quadrupole splitting QS and the hyperfine magnetic field H for $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ at different temperatures.

Compound	T (K)	δ (mm s ⁻¹)		QS (mm s ⁻¹)		H (T)
		Fe 1	Fe 2	Fe 1	Fe 2	
Nd ₂ CoMnO ₆	295	0.36	0.36	0.70	0.29	0
	190	0.43	0.44	0.75	0.30	0
	180	0.44	0.44	0.70	0.28	40
	170	0.45	0.46	0.73	0.36	24.5
	160	0.47	0.46	0.75	0.30	30
	140	0.46	0.40	0.78	0.26	35
	100	0.46	0.46	0.80	0.28	40
Nd ₂ CoMnO _{6.12}	295	0.36	0.36	0.73	0.36	0
	210	0.42	0.42	0.74	0.36	0
	200	0.42	0.43	0.77	0.38	47
	180	0.44	0.44	0.77	0.37	42.5
	150	0.43	0.42	0.82	0.27	37
	140	0.44	0.43	0.80	0.28	29
	80	—	—	—	—	40

15 T) almost vanishes. The non-magnetic fraction QS_1 and QS_2 coexists with the magnetic fraction in a wide temperature range from 180 to 100 K. At 100 K the spectral fraction of the magnetic component exceeds the 95% (table 1).

For the annealed $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6.12}$ sample (figure 5) the non-magnetic fraction (QS_1 and QS_2) is also the only one in the spectrum measured at room temperature. It seems, however, that the coexistence of the non-magnetic and magnetic spectral components occurs in a larger temperature range than for the previous sample, and extends up to 200 K. The shape of $P(H)$ also differs strongly depending on temperature: at 190 K the $P(H)$ distribution shows one dominant strong peak at a large field value ($\langle H \rangle \approx 42.5$ T). Then the distribution $P(H)$ also contains strong low-field components (at 150–130 K) that start decreasing at lower temperatures (below 120 K). The non-magnetic components disappear completely at 110 K, at/below which only the magnetically ordered structure remains (figure 5). The changes of relative fractions QS_1 , QS_2 and $P(H)$ versus T are shown in figure 6.

3.3. μSR studies

Figure 7 presents the temperature dependence of the asymmetry of the muon precession in a weak transverse magnetic field for both the $\text{Nd}_2\text{CoMnO}_6$ and $\text{Nd}_2\text{CoMnO}_{6.12}$ compounds. In the stoichiometric sample we observed a sharp drop in the asymmetry at the Curie temperature. In the non-stoichiometric sample we also observed a decrease in the asymmetry of the muon precession with temperature. However, the transition occurs in a wide temperature range and the decrease is not so significant, indicating that the transition into the magnetic phase takes place in a smaller fraction of the sample. Coherent muon precession in zero external magnetic field has not been observed. This fact could be explained by the inhomogeneous distribution of local magnetic moments in the bulk samples.

4. Discussion

The expected magnetic moment value of the Co/Mn sublattice, $M_{\text{Co/Mn}}$, for HS Co^{2+} ($t_{2g}^5 e_g^2$, $S = 3/2$) and Mn^{4+} ($t_{2g}^3 e_g^0$, $S = 3/2$) is $6 \mu_B$ per formula unit (Co and Mn ions) in the

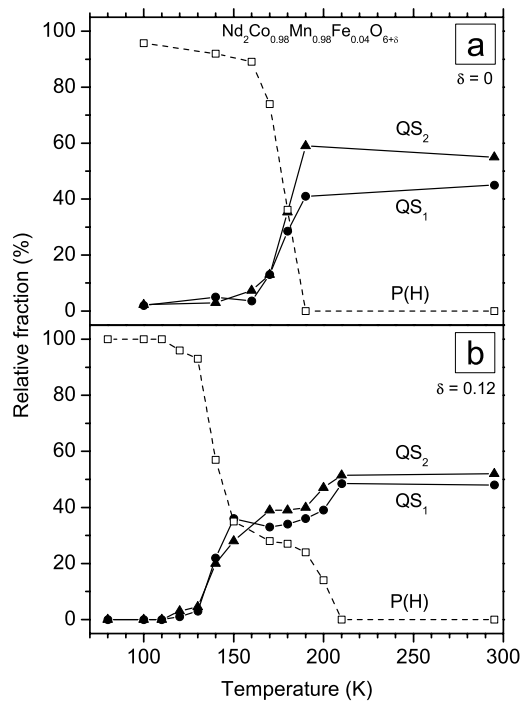


Figure 6. Relative fractions of the QS₁, QS₂ and *P(H)* components for the Nd₂Co_{0.98}Mn_{0.98}Fe_{0.04}O_{6.12} (a) and Nd₂Co_{0.98}Mn_{0.98}Fe_{0.04}O₆ (b) compounds.

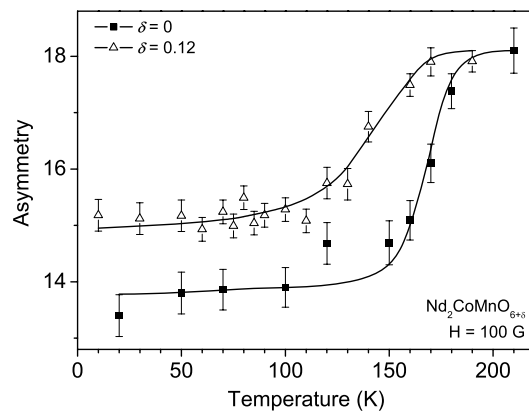


Figure 7. Temperature dependence of the muon precession asymmetry of the Nd₂CoMnO_{6+δ} compounds measured in a field of 100 G.

purely ferromagnetic model. The observed values of $M_{Co/Mn}$ from our neutron diffraction studies [18, 19] are smaller than the expected ones; this can be explained in different ways. The first model is based on the assumption about a non-collinear (or ferrimagnetic) magnetic structure, which transforms into a ferromagnetic one in an applied external magnetic field. According to the second model, a long-range ferromagnetic order coexists with a long-range antiferromagnetic one. The third model takes into account that a long-range ferromagnetic order already coexists with clusters, which have a predominantly short-range

antiferromagnetic order. All these models can explain the observed metamagnetic phase transition. However, according to our neutron diffraction data [18, 19] no coherent magnetic contribution corresponding to ferrimagnetic or antiferromagnetic long-range order in the Co/Mn sublattice was observed. Therefore, the realization of the first and second models is very questionable. Moreover, the results of our μ SR and Mössbauer studies are in agreement with the model, according to which the samples consist of the ferromagnetic phase and the antiferromagnetic (paramagnetic) clusters.

As was pointed out in section 3.2, we observed the peaks on the $P(H)$ distribution at temperatures slightly below ~ 210 and 190 K for $\text{Nd}_2\text{CoMnO}_{6.12}$ and $\text{Nd}_2\text{CoMnO}_6$, respectively. The value of hyperfine magnetic field H which corresponds to the main peaks on the $P(H)$ distribution reaches ~ 47 T (see table 1). This is unexpected, because the onset of the transition into the ferromagnetically ordered state is ~ 140 and 180 K, respectively, according to the dc magnetization (figure 1) measurements. We believe that the peaks, which correspond to large hyperfine magnetic fields at relatively high temperatures, appear mainly due to a coupling between nearest neighbour Fe–Fe ions inside the ionically disordered clusters. The ground magnetic state of these clusters in $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ should be antiferromagnetic because there is no spontaneous magnetization above the Curie temperature and the $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ exchange interactions dominate. Moreover, we suppose that there are inhomogeneous regions enriched with the three-valent Co, Mn and Fe ions. Probably, it is advantageous according to thermodynamics that the clustering of Fe is observed in the regions enriched with Co^{3+} and Mn^{3+} ions.

Moreover, according to our experimental results the Fe^{3+} ions are located at two positions with different small and large quadrupole splitting values (table 1). It is worth noting that in manganites (see for example [23]) the positions with large quadrupole splitting were connected with local distortions. Such distortions can be interpreted in terms of the cooperative orbital ordering in the system of Jahn–Teller Mn^{3+} ions. There are probably some Mn^{3+} ions also in $\text{Nd}_2\text{CoMnO}_{6+\delta}$, which leads to local distortions as in the case of LaMnO_3 , for example. Therefore, the Fe position with Mn^{3+} ions as nearest neighbours is characterized by large quadrupole splitting. On the other hand, the quadrupole splitting of the second type of Fe position is significantly lower because there are no Mn^{3+} ions as nearest neighbours.

The hyperfine magnetic field at the ^{57}Fe nuclei in manganites reaches about 45 T in the case of antiferromagnet LaMnO_3 and metallic ferromagnet $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ [23, 24]. The Fe ions in manganites present in the 3+ state and their moments are antiferromagnetically coupled to the ferromagnetic host [24, 25]. In our $\text{Nd}_2\text{Co}_{0.98}\text{Mn}_{0.98}\text{Fe}_{0.04}\text{O}_{6+\delta}$ the hyperfine magnetic field at the ^{57}Fe nuclei is about 40 T at 80–100 K. It is possible to conclude, therefore, that this field at helium temperature would be about 50 T which is comparable with manganites.

Our assumptions are in agreement with [26], according to which not only $\text{Mn}^{4+}\text{--Co}^{2+}$ pairs but also $\text{Mn}^{3+}\text{--Co}^{3+}$ ones can be stabilized in $\text{Ln}_2\text{CoMnO}_6$ samples. Co^{3+} ions seems to be in the low-spin non-magnetic state whereas $\text{Fe}^{3+}\text{--O--Fe}^{3+}$, $\text{Fe}^{3+}\text{--O--Mn}^{3+}$ and $\text{Fe}^{3+}\text{--O--Co}^{2+}$ magnetic interaction should be antiferromagnetic according to Goodenough–Kanamori rules. It was shown in [27] that the contribution from the antiferromagnetic coupling between neighbouring Fe^{3+} cations through Fe–O–Fe paths in $\text{Sr}_2\text{FeMoO}_6$ double perovskite exists at high temperatures (up to 760 K). The transition temperature into the antiferromagnetic state depends on the fraction and size of the Fe-enriched disordered regions. Thus, AFM couplings $\text{Fe}^{3+}\text{--O--Fe}^{3+}$, $\text{Fe}^{3+}\text{--O--Mn}^{3+}$ and $\text{Fe}^{3+}\text{--O--Co}^{2+}$ are probably the reason why we observed magnetic contributions at temperatures above T_C by means of Mössbauer studies but not with magnetization measurements.

As the temperature decreases further (at 170 K and below) the $P(H)$ distribution of the stoichiometric compound shows a complex structure (figure 4): besides the peak at high fields

peaks also appear at lower fields (less than 40 T). This is probably due to the appearance of long-range ferromagnetic order in the host lattice. As a result the intensity of the peaks at high fields decreases. We observed a similar behaviour for the non-stoichiometric sample, but with another critical temperature equal to about 140 K (figure 5). This is in agreement with dc magnetization (see figure 1). With a further decrease in temperature the average value of hyperfine magnetic field increases according to the $P(H)$ distribution (table 1). However, there are several peaks (without the peaks above T_C) at the Mössbauer spectra which correspond to different hyperfine fields. The peak multiplicity in the Mössbauer spectra of both samples is probably caused by the different local environments of the Fe ions in the host. We believe this is due to the existence of clusters with a different degrees of order of the Co^{2+} and Mn^{4+} ions. In other words, the samples consist of a number of clusters with different degrees of antisite defects. The component which consists of clusters with a small degree of ionic order does not give a coherent magnetic contribution. This component is spin-glass-like according to the ac susceptibility measurements [19]. The clusters enriched in Fe^{3+} ions are antiferromagnetic ones. Moreover, there are paramagnetic clusters enriched in LS Co^{3+} ions, especially in the case of the non-stoichiometric compound. The appearance of such clusters leads to a decrease of the Curie temperature and the magnetic moment. This suggestion is in agreement with the magnetization and μSR measurements, according to which the transition into the paramagnetic state becomes very broad as the degree of order decreases. Moreover, the NMR spectra of the $\text{La}_2\text{CoMnO}_6$ and $\text{La}_2\text{NiMnO}_6$ compounds were also successfully interpreted under the assumption that Mn^{4+} ions are surrounded by a different number of Co^{2+} (Ni^{2+}) ions [7, 11]. The degree of antisite defects obtained from the neutron diffraction data is an average degree of order through the sample.

As has already been pointed out, the observed value of the magnetic moment of the non-stoichiometric sample ($3.7 \mu_B$) is much lower than the expected one. That can be explained (in the model with the ferromagnetic phase and the antiferromagnetic/paramagnetic clusters) as follows. First, the disorder of Co and Mn ions should reduce the spontaneous magnetization or should even give rise to an antiferromagnetic component because the $\text{Co}^{2+}\text{-O-Co}^{2+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ exchange interactions are antiferromagnetic [28]. Second, the small observed value of the magnetic moment could be connected to the presence of trivalent cobalt ions which are in a diamagnetic low-spin state and thus do not actively participate in the exchange.

According to our magnetization measurements (see figure 2), the oxygen reduction leads to an increase in both the spontaneous magnetization and transition temperature into the paramagnetic state. Moreover, the transition becomes sharper, which is in agreement with the μSR measurements (figure 7). These changes are probably caused by both the decrease in the number of antisite defects (i.e. the homogenization of the sample) and the reduction of the Co^{3+} ions to the divalent state. That is, the high-temperature ferromagnetic phase with a large degree of ionic order and the low content of Co^{3+} ions is stabilized. However, the observed value of the magnetic moment of the stoichiometric sample ($5.5 \mu_B$) is smaller than expected, probably because the full order of the Co and Mn ions is not reached.

An external magnetic field can induce a metamagnetic transition in the $\text{Nd}_2\text{CoMnO}_{6.12}$ compound post-annealed in air. This had also been observed earlier for other oxidized $\text{RE}_2\text{CoMnO}_{6+\delta}$ ($\text{RE} = \text{Nd}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Y}$) compounds [13–17]. The large hysteresis clearly indicates a first-order transition (figure 3). We assume that the investigated samples consist of clusters with a different degree of order of the Co^{2+} and Mn^{4+} ions. The component with a small degree of ionic order is a spin-glass-like component. These clusters apparently have short-range antiferromagnetic order due to negative $\text{Co}^{2+}\text{-O-Co}^{2+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ magnetic interactions. Most likely, the presence of this component leads to metamagnetism in a class of compounds $\text{RE}_2\text{CoMnO}_{6+\delta}$, i.e. a short-range antiferromagnetic order in ionically

disordered clusters transforms into a long-range ferromagnetic one in an applied external magnetic field.

5. Conclusion

The magnetic properties of the $\text{Nd}_2\text{CoMnO}_{6+\delta}$ ($\delta = 0, 0.12$) system were investigated by Mössbauer, μSR and magnetization measurements.

Our findings are in agreement with suggestions that the samples consist of clusters with different degrees of antisite defects, i.e. with different degrees of order of the Co and Mn ions. The valence state of the ions in the partially ordered clusters is predominantly $\text{Co}^{2+}/\text{Mn}^{4+}$, and the disordered clusters are enriched with three-valent cobalt and manganese. The ionic ordering strongly affects the magnetic properties of the compounds. The highly ordered $\text{Nd}_2\text{CoMnO}_6$ compound exhibits both a pronounced ferromagnetic and a weak spin-glass-like component. On the other hand, ionic disordering in $\text{Nd}_2\text{CoMnO}_{6.12}$ leads to a partial destruction of the ferromagnetic component and to strong enhancement of the spin-glass-like one. Highly ordered ionic domains are associated with ferromagnetic order, whereas highly disordered ionic clusters are isolated and experience a short-range antiferromagnetic order due to $\text{Co}^{2+}-\text{O}-\text{Co}^{2+}$ and $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ negative magnetic interactions. Most likely, the spin-glass-like component directly transforms into the ferromagnetic one as the first-order metamagnetic phase transition in an applied external magnetic field.

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References

- [1] Troyanchuk I O, Sazonov A P, Szymczak H, Töbrens D M and Gamari-Seale H 2004 *JETP* **99** 363
- [2] Mahendiran R, Bréard Y, Hervieu M, Raveau B and Schiffer P 2003 *Phys. Rev. B* **68** 104402(R)
- [3] Dass R I and Goodenough J B 2003 *Phys. Rev. B* **67** 014401
- [4] Troyanchuk I O, Lobanovsky L S, Khalyavin D D, Pastushonok S N and Szymczak H 2000 *J. Magn. Magn. Mater.* **210** 63
- [5] Joly V L J, Joy P A, Date S K and Gopinath C S 2001 *J. Phys.: Condens. Matter* **13** 649
- [6] Joy P A, Kholam Y B and Date S K 2000 *Phys. Rev. B* **62** R8608
- [7] Nishimori N, Asai K and Mizoguchi M 1995 *J. Phys. Soc. Japan* **64** 1326
- [8] Blasse G 1965 *J. Phys. Chem. Solids* **26** 1969
- [9] Goodenough J B, Wold A, Arnett R J and Menyuk N 1961 *Phys. Rev.* **124** 373
- [10] Blasco J, Sánchez M C, Pérez-Cacho J, García J, Subías G and Campo J 2002 *J. Phys. Chem. Solids* **63** 781
- [11] Sonobe M and Asai K 1992 *J. Phys. Soc. Japan* **61** 4193
- [12] Dass R I, Yan J-Q and Goodenough J B 2003 *Phys. Rev. B* **68** 064415
- [13] Troyanchuk I O, Khalyavin D D, Lynn J W, Erwin R W, Huang Q, Szymczak H, Szymczak R and Baran M 2000 *J. Appl. Phys.* **88** 360
- [14] Troyanchuk I O, Samsonenko N V, Kasper N V, Szymczak H and Nabialek A 1997 *J. Phys.: Condens. Matter* **9** 8287
- [15] Troyanchuk I O, Samsonenko N V, Shapovalova E F, Szymczak H and Nabialek A 1997 *Mater. Res. Bull.* **32** 67
- [16] Troyanchuk I O, Samsonenko N V, Nabialek A and Szymczak H 1997 *J. Magn. Magn. Mater.* **168** 309
- [17] Troyanchuk I O, Szymczak H, Samsonenko N V, Nabialek A and Shapovalova E F 1997 *Phys. Status Solidi a* **163** 215
- [18] Sazonov A P, Troyanchuk I O, Kozlenko D P, Balagurov A M and Sikolenkob V V 2006 *J. Magn. Magn. Mater.* **302** 443

- [19] Sazonov A P *et al* 2007 in preparation
- [20] Brand R A, Lauer J and Herlach D M 1983 *J. Phys. F: Met. Phys.* **13** 675
- [21] Ganguly R, Maignan A, Martin C, Hervieu M and Raveau B 2002 *J. Phys.: Condens. Matter* **14** 8595
- [22] Krimmel A, Reehuis M, Paraskevopoulos M, Hemberger J and Loidl A 2001 *Phys. Rev. B* **64** 224404
- [23] Pissas M and Simopoulos A 2004 *J. Phys.: Condens. Matter* **16** 7419
- [24] Simopoulos A, Pissas M, Kallias G, Delvin E, Moutis N, Panagiotopoulos I, Niarchos D, Christides C and Sonntag R 1999 *Phys. Rev. B* **59** 1263
- [25] Tkachuk A, Rogacki K, Brown D E, Dabrowski B, Fedro A J, Kimball C W, Pyles B, Xiong X, Rosenmann D and Dunlap B D 1998 *Phys. Rev. B* **57** 8509
- [26] Sikora M, Kapusta Cz, Knížek K, Jiráček Z, Autret C, Borowiec M, Oates C J, Procházka V, Rybicki D and Zając D 2006 *Phys. Rev. B* **73** 094426
- [27] Sánchez D, Alonso J A, García-Hernández M, Martínez-Lope M J, Martínez J L and Møllergård A 2002 *Phys. Rev. B* **65** 104426
- [28] Cornelius A L, Light B E and Neumeier J J 2003 *Phys. Rev. B* **68** 014403