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Magnetic properties of $NdMn_{1-x}Fe_xO_{3+\delta}$ system

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Abstract. Magnetization, AC susceptibility and specific heat measurements were performed on polycrystalline $NdMn_{1-x}Fe_xO_{3+\delta}$ compounds (x = 0.0, 0.1 and 0.2). Substitution of Fe for Mn reduces the Néel temperature T_N, which is associated with magnetic ordering of Mn sublattice, from 85.5 K to 57.0 K. The temperature dependence of magnetization for x = 0.2 exhibits the compensation temperature and the pole inversion below T_{comp} = 26.7(5) K. Initial magnetization curves present a remnant magnetization in the ordered region with the sign of remnant magnetization depending on temperature. The substitution of Fe for Mn changes hysteresis loop of $NdMnO_{3+\delta}$ from the ferromagnetic-like one ($\mu_0 H_c$ = 0.09 T) by expanding the width of the loop ($\mu_0 H_c$ = 0.55 T) for x = 0.1 and then shrinking the central part of the loop to "butterfly" type ($\mu_0 H_c$ = 0.35 T) for x = 0.2.

RETO_3 compounds (*RE* = rare earth, *T* = 3*d*-metal) attract large attention for their very interesting physical properties e. g. multiferroism [1], ferroelectricity [2, 3], strange "butterfly-type" hysteresis loops [4], compensation temperatures [5, 6] and other effects. Substitution on the rare earth site or 3*d* metal site is the basic approach of tuning physical properties of these compounds. Up to now, the substitutions were done mainly on the *RE*-site by Na, K, Ca, Sr and Ba [7]. On the other hand, there is only scarce information about the doping on the 3*d*-metal site. In our work we study effect of Fe for Mn substitution on $NdMn_{1-x}Fe_xO_{3+\delta}$ polycrystalline compounds.

Both parent compounds $NdMnO_3$ and $NdFeO_3$ adopt the orthorhombic crystal structure (space group *Pnma*). Nd atoms occupy the 4*c* position, Mn/Fe atoms occupy 4*b* and oxygen atoms occupy 4*c* and 8*d* crystallographic positions in the unit cell. In both compounds the Nd and Mn/Fe sublattices order magnetically [8, 9]. In the case of $NdMnO_3$, the Mn sublattice orders at T_N = 82 K with magnetic moments parallel to *b*-axis and Nd sublattice orders ferromagnetically (moments parallel to *c*-axis) at $T_1 \approx 20$ K [8, 10]. On the other hand Fe sublattice of $NdFeO_3$ orders above room temperature and undergoes spin reorientation transition in temperature range 70 – 160 K [9], but Nd sublattice orders only at very low temperatures ($T_1 \approx 1.5$ K) [11]. Considering known magnetic properties of parent compounds one could suggest that Fe substitution for Mn in $NdMnO_3$ will raise the T_N to higher temperatures, but T_1 will decrease. Up to now, the only studied Fe-Mn substitution compound was $NdMn_{0.9}Fe_{0.1}O_3$ [6]. For this compound $T_1 \approx 14$ K, which is lower than T_1 for the $NdMnO_3$ compound (agreement with expectations), but T_N also decreases [6], which is in contradiction with expectations. These evidences imply that the concentration dependence of T_N is not as straightforward as one can expect, and the more detailed study of Mn-Fe substitution has to be undertaken. Since this study has not been done before, we have prepared several compounds of the general formula $NdMn_{1-x}Fe_xO_{3+\delta}$ and studied their magnetic and thermal properties.

Our textured polycrystalline samples were prepared by floating zone method in a mirror furnace. As a starting materials we used high purity oxides of MnO_2 (purity 3N, supplier: Alpha Aesar), Nd_2O_3 (purity 3N, supplier: Sigma Aldrich) and Fe_2O_3 (purity 2N, supplier: Sigma Aldrich). The starting materials were mixed, cold pressed into the rods and sintered at 1200 °C for 24 hours in air. The float zone experiment was performed using the

Table 1. Lattice parameters of studied $NdMn_{1-x}Fe_xO_{3+\delta}$ compounds.

x	a (nm)	b (nm)	c (nm)	V (nm^3)
0	0.5843(2)	0.7546(3)	0.5415(2)	0.2387(7)
0.1	0.5807(2)	0.7572(3)	0.5415(2)	0.2381(7)
0.2	0.5774(2)	0.7602(3)	0.5421(2)	0.2380(7)

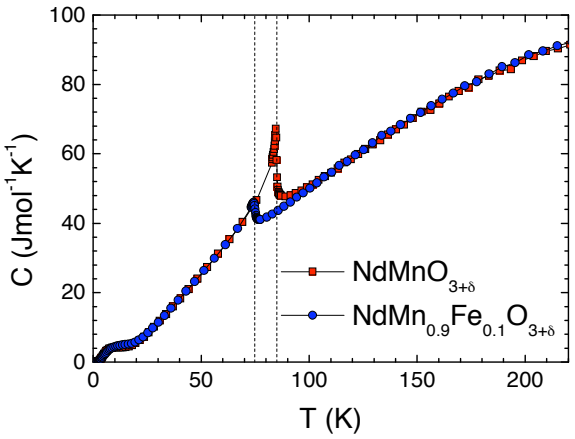

Fig. 1. Temperature dependence of specific heat presented in $C(T)$ representation. The dashed lines represent the positions of T_N.

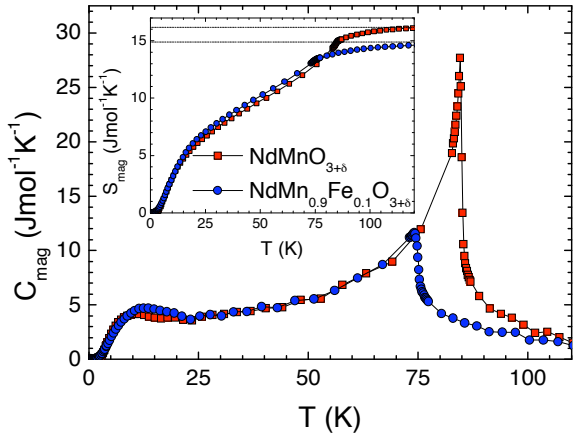

Fig. 2. Magnetic part of the specific heat as obtained using $NdGaO_3$ as a nonmagnetic analogue. The insert visualize the calculated magnetic entropy. The dashed lines represent position of $R\ln 6$, and $R\ln 7$, respectively.

flowing air (1 l/min) atmosphere. All samples which were used for the experiments were checked by X-ray powder diffraction and were proved to be single-phased. The obtained lattice parameters are summarized in Table 1. The oxygen content of all samples was checked by iodometric titration and was found small excess of oxygen, δ = 0.035, 0.095, 0.065 for x = 0, 0.1, 0.2, respectively. We have also tried to prepare samples in Ar atmosphere (ambient pressure and pressure of 8 bar), but we have observed the reduction of Mn^{4+} ion into the Mn^{2+} ion and thence the MnO impurities in the grown ingots.

Magnetization (M) and susceptibility (χ) data were measured using the SQUID magnetometer from Quantum Design with RSO option. The samples were prepared by powdering the grown ingot. The sample's typical mass was around 6 mg. The heat capacity (HC) data were measured on bulk, highly textured samples directly cut from the grown ingot. The sample's mass was between 8 and 14 mg. For HC measurements we have used Physical Property Measurement System (Quantum Design).

Temperature dependence of HC (Fig. 1) clearly exhibits lambda-like anomaly at 85.1(2) K for $NdMnO_{3+\delta}$ and at 74.8(2) K for $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$. Taking into account data from neutron diffraction [8, 10] these anomalies indicate the ordering of Mn sublattice into

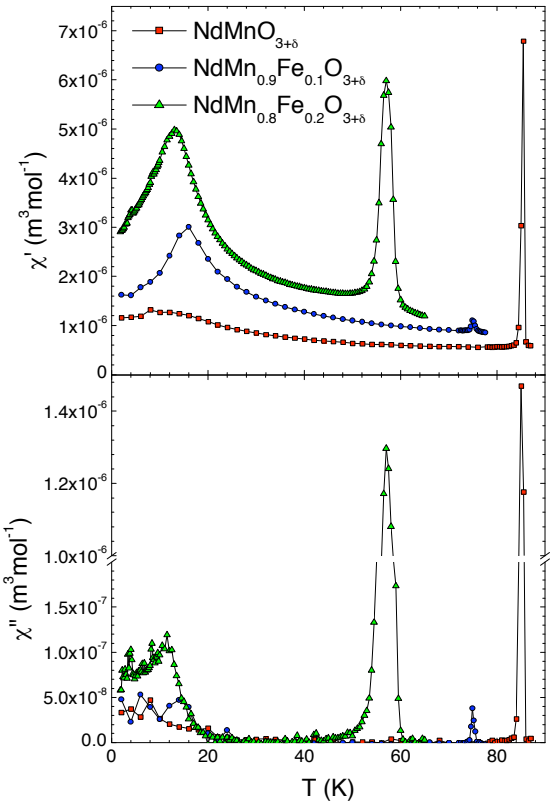

Fig. 3. The AC susceptibility measured with driving field of 2.5×10^{-4} T and in frequency 11.1 Hz.

type-A antiferromagnetic structure. HC shows additional large anomaly below 25 K which was attributed by other authors to Schottky-type contributions [12, 15]. Contrary to this, magnetization measurement revealed a larger ferromagnetic component at low temperature which cannot be explained reasonably by the canting of the A-AF structure of Mn spins [13], and neutron diffraction experiments [8, 10] suggest ferromagnetic ordering of Nd sublattice at this temperature. Substitution of Fe for Mn leads to shift of the anomaly at T_1 to higher temperature.

In order to estimate magnetic part of the specific heat (C_{mag}) we have subtracted phonon contribution using heat capacity data of $NdGaO_3$ nonmagnetic analogue. The specific heat data for this compound were presented by Schnelle et al. [14]. The resulting C_{mag} vs. T curve (Fig. 2) clearly shows that the low temperature bump has the maximum at 10.5(5) K for $NdMnO_{3+\delta}$ and at 12.5(5) K for $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$ (Fig. 2). This bump is consistent with the specific heat data published previously [12, 15]. The calculated magnetic entropy saturates for both compounds reaching the value $R\ln 7$ and $R\ln 6$ (R = gas constant) for $NdMnO_{3+\delta}$ and $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$, respectively (insert of Fig. 2).

AC susceptibility measurements for both in phase part (χ') and out phase part (χ'') of susceptibility are displayed in Fig. 3. These measurements revealed that antiferromagnetic transition decreases with Fe doping, shifting T_N from 85.5(2) K to 74.9(2) K and to 57.0(3) K for x = 0.0, 0.1 and 0.2, respectively. The anomaly of $\chi'(T)$ at T_1, which is associated with Nd sublattice, becomes more pronounced and for smaller doping (x = 0.1) shifts to higher temperature from 10 K to 16 K and then decreases to 13 K for x = 0.2. These results are again

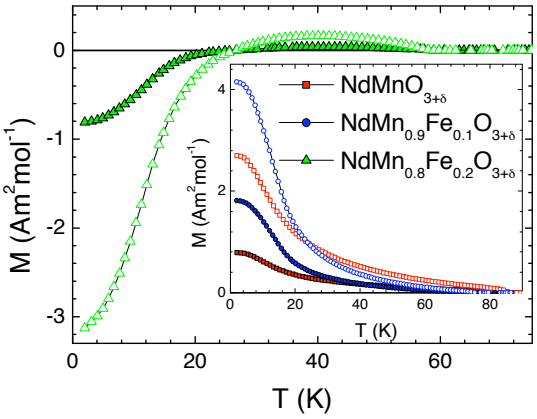

Fig. 4. ZFC (full symbols) and FC (opened symbols) curves measured in magnetic field of 1 mT.

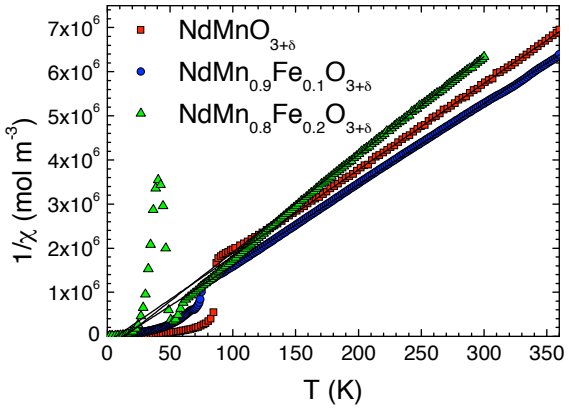

Fig. 5. Inverse DC susceptibility measured in field of 0.1 T. The lines represent the best fit due to Curie – Weiss law in temperature range 175 – 360 K for $NdMnO_{3+\delta}$; 100 – 360 K for $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$ and 170 – 300 K for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$.

not consistent with the expectation, which we made taking into account magnetic properties of parent compounds $NdMnO_3$ and $NdFeO_3$. Results of AC susceptibility correspond to anomalies observed in HC.

Temperature dependence of magnetization measured in zero-field-cooled (ZFC) and field-cooled (FC) regimes (Fig. 4) shows a hysteretic behaviour for all samples. Bifurcation temperature T_b, i. e. the temperature where the ZFC and FC curves bifurcate, is very close to T_N. (T_b = 85.2(5) K; 75.2(5) K and 58.0 (4) K for for x = 0.0, 0.1 and 0.2, respectively). In this type of compounds the strongest interaction is the superexchange between Mn^{3+} ions [16]. This is responsible for the magnetic ordering at T_N. However, at these temperatures Nd sublattice remains disordered. At lower temperatures, Mn^{3+} ions polarize Nd^{3+} ions and Nd sublattice orders due to Nd – Mn interaction [16]. For x = 0.0 and x = 0.1 the anomaly at T_N is presented only by small upturn of magnetization which smoothly increases down to 25 K (temperature at where polarization of Nd-sublattice becomes important) and then a steeper increase at lower temperatures is observed. This is commonly accepted magnetic scenario for the case that both magnetic sublattices are acting in cooperation [17]. Another scenario will take place if both sublattices are acting in competition (x = 0.2). In this case both ZFC and FC curves pass through broad maximum around 40 K, then decrease to zero (compensation temperature) at T_{comp} = 26.7(5) K and show the magnetization reversal effect. Thence at the low temperatures the compound is ferrimagnetic and due to different temperature evolutions of the magnetizations in different sublattices, we have observed the magnetization reversal effect. The magnetization inversion and T_{comp} depends on the applied external magnetic field. Previously, T_{comp} was observed for $NdMnO_{3+\delta}$, in applied external field of 0.1 T [16] and for $NdMn_{0.9}Fe_{0.1}O_3$ in magnetic field of 5 mT [6].

The susceptibility of all three compounds obeys Curie – Weiss law (CW) $\chi = C/(T-\theta_p)$ at sufficiently high temperatures above T_N (see Fig. 5). Since parameter C scales with effective magnetic moment (μ_{eff}), we present the results of fitting directly in μ_{eff} and θ_p (paramagnetic Curie temperature). The fitted parameters are θ_p = 7.3(5) K, μ_{eff} = 5.70(1) μ_B for $NdMnO_{3+\delta}$; θ_p = 12.5(3) K, μ_{eff} = 5.88(1) μ_B for $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$; and θ_p = 14.2(5) K, μ_{eff} = 5.35(1) μ_B for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$, respectively. Despite the fact that $NdMnO_3$ orders into A-type antiferromagnetic structure [8] and we extrapolate that doped compounds also order antiferromagnetically, we have found θ_p positive for all three compounds. Also the absolute value of θ_p does not scale with T_N at all. Our CW fit for $NdMnO_{3+\delta}$ resulted to completely different parameters, than previously-published parameters of Muñoz et al. [10] (θ_p = -37 K; μ_{eff} = 6.48 μ_B). Note that we have prepared our samples by melting the starting oxides, while Muñoz et al. [10] took the citric acid route which might lead to very fine powders, probably with size on the order of 10 nm.

From the magnetic point of view, most interesting part of these compounds is that all of them have two different, interpenetrating magnetic sublattices. First sublattice consists purely of Nd^{3+} ions and the other one consists of Mn^{3+}, Mn^{4+} and Fe atoms. Following Muñoz et al. [10] we use:

$$\mu_{eff} = \sqrt{\mu_{at1}^2 + \mu_{at2}^2} \qquad (1)$$

where μ_{eff} is the measured effective moment; μ_{at1} is the magnetic moment of the atoms in first sublattice and μ_{at2} is the effective moment of the atoms in second sublattice. Using 3.62 μ_B as the effective moment for Nd atoms (ground state term $^4I_{9/2}$), we calculate 4.4 μ_B; 4.6 μ_B; and 3.9 μ_B for the Mn/Fe sublattice for $NdMnO_{3+\delta}$, $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$ and $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$, respectively. Except for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$, this is in good agreement with the combination of magnetic moments of Mn^{3+} (4.90 μ_B), Mn^{4+} (3.87 μ_B) and Fe^{3+} (5.92 μ_B) placed in strong crystal field (freezing of orbital moment). For $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$, the calculated moment is unexpectedly small.

The hysteresis loop measured at temperature 2 K (Fig. 6) for $NdMnO_{3+\delta}$ is a ferromagnetic-like with remanence ($\mu_0 H_R$) of 1.25 μ_B/f. u. and coercive field ($\mu_0 H_c$) of 0.09 T. With iron doping, $\mu_0 H_R$ decreases to 1.2 μ_B/f. u. for 10 % Fe and to 0.89 μ_B/f. u. for 20 % Fe. However, the hysteresis loop changes from the ferromagnetic-like one; at first expanding in the middle for 10 % of Fe ($\mu_0 H_c$ = 0.55 T) and then shrinking in the middle to "butterfly" type ($\mu_0 H_c$ = 0.35 T) hysteresis

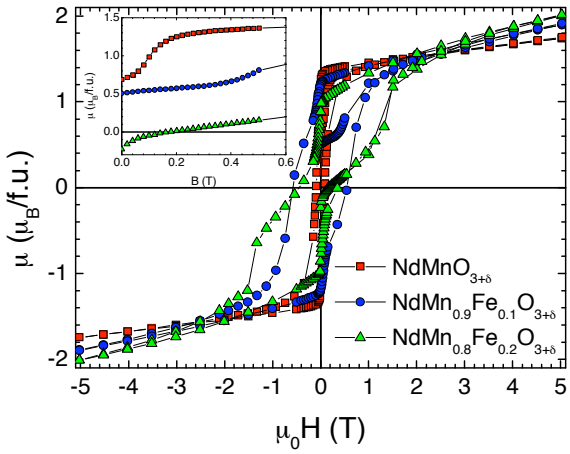

Fig. 6. The magnetization curves measured at temperature T = 2 K. The insert visualizes the virgin curves.

loop. The "butterfly" type of hysteresis loops can be directly connected with the ferrimagnetic origin of the compounds. The remnant magnetization was observed after ZFC procedure below magnetic phase transition on any sample and varies from negative to positive values as it is visible from the insert of Fig. 6. The negative value of remnant magnetization observed on $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$ is consistent with the pole inversion observed in the ZFC – FC data. Our hysteresis loops for $NdMnO_{3+\delta}$ are similar to the results published in [10]. The shape of the hysteresis loop for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$ is similar to the shape of the hysteresis loop for $LaMnO_3$ [4]. Magnetization vs. magnetic field curves measured at T = 150 K (not shown) are linear for all three compounds. This implies that all compounds are paramagnetic at this temperature, and more importantly, our samples are pure from the magnetic impurities with ordering temperatures higher than 150 K.

To check the consistence of our data with the literature, we take the $NdMn_{0.9}Fe_{0.1}O_{3+\delta}$ as an example. This is the only iron-substituted compound, for which the data from another experimental group exist. I. O. Troyanchuk [6] has observed the compensation temperature on the FC magnetization measured at 5 mT. We have not seen this effect in our data measured in several different magnetic fields (1, 5, 10, 100 and 240 mT). Also, I. O. Troyanchuk [6] has observed the peak on magnetization at T_1. We did not observe it on our DC susceptibility. The reason for this might be that the other authors have used vibrating sample magnetometer (VSM), but we have used the SQUID magnetometer. Note, that we have seen peak connected with T_1 on AC susceptibility already at very low driving frequencies (11.1 Hz), which is comparable frequency to the one, in which the standard VSM operates (for example 40 Hz for VSM from Quantum Design). This point out that ordering of Nd atoms might have some non-trivial dynamics. The study of this dynamics is still in progress. The property, in which we are not consistent with I. O. Troyanchuk [6] is the value of T_N. He presents the peak at approximately 56 K, but we present 74.8(1) K. Note, that we have found T_N = 57.0(3) K for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$ compound.

In conclusion, we have prepared $NdMn_{1-x}Fe_xO_{3+\delta}$ ($x \leq 0.2$) compounds and measured their magnetic properties. We have found that T_N shifts to lower temperatures roughly by rate 15 K per 10% of iron doping. Considering T_1, in all three measured compounds, we have found no anomalies on the data measured by "static" methods (DC magnetization, specific heat), but we have found anomalies on the AC susceptibility. All compounds obey Curie-Weiss law at sufficiently high temperatures, but absolute value of θ_p does not scale with T_N. We have found T_{comp} = 26.8 K and magnetization reversal effect only for $NdMn_{0.8}Fe_{0.2}O_{3+\delta}$ compounds and step-like hysteresis loops for all iron-substitutional compounds. These results strongly suggest that the low temperature ground state of all compounds is ferrimagnetic.

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