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Magnetism of $GdMn_{1-x}Fe_xO_3$ ($0 \leq x \leq 1$) Nanoparticles

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Magnetic properties of $GdMn_{1-x}Fe_xO_3$ ($0 \leq x \leq 1$) substitutional system are investigated on the nanocrystalline samples prepared by glycine-nitrate method. The polarization of Gd sublattice due to Gd-3d ion exchange interaction was observed for $x = 0, 0.2$ and 1 below 10.5(5) K, 9.5(5) K, and 5.6(5) K, respectively. The magnetic ordering temperatures of $GdMnO_3$ and $GdFeO_3$ parent compounds were confirmed to be 44(2) K and 658(5) K. The ordering temperatures of 350(10) K, 570(5) K, 605(5) K, and 622(5) K for $x = 0.4, 0.5, 0.6$, and 0.8, as well as spin-reorientation temperatures of 409(5) K, 430(5) K, and 336(5) K for $x = 0.5, 0.6$, and 0.8 were systematically higher than the data reported on polycrystalline material and single crystals by other experimental groups. These effects can be explained by the grain size effects and/or amount of vacancies in the crystal structure.

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1. Introduction

$REMnO_3$ compounds (RE means Rare earth) have been extensively studied due to their interesting physical properties like multiferroic behavior [1], magnetocaloric effect [2], hyperthermia at room temperatures [3], and many others. With the aim of tuning the physical properties, doping was performed on both, RE — crystallographic site (by other RE ion, alkali metal, or transition metal) or Mn crystallographic site (by transition metal) [4]. It follows from [5–8] that especially the Fe^{3+} non-Jahn-Teller ion doping on the Mn^{3+} Jahn-Teller (JT) ion site increases the magnetic ordering temperature and other effects to room temperatures or higher, which are the desired effects for the applications.

$GdMnO_3$ orders into modulated magnetic structure below Néel temperature $T_N \sim 43$ K [1]. This modulation locks to 0 below $T_{lock} \sim 23$ K, resulting in antiferromagnetic/weak ferromagnetic phase (AFM + WFM) [1]. Below T_{lock} the ferroelectric properties can be induced for example by applied magnetic field, or pressure [1, 6]. In $GdMn_{1-x}Fe_xO_3$ doped compounds, the modulated magnetic phase diminishes for $x < 0.2$, while T_N increases [7]. For $x > 0.4$, the additional magnetic phase evolves below AFM + WFM at temperature T_S [7, 8]. This phase is supposed to be pure antiferromagnetic phase. The determination of T_S and T_N is not straightforward and there are discrepancies in the results up to 25 K reported in [7, 8]. This discrepancy might be ascribed to the preparation conditions to which the material is very sensitive. The additional question is how the physical properties change if one downscale the size of the particles. In this manuscript we address this question.

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2. System description

The samples of $GdMn_{1-x}Fe_xO_3$ ($x = 0$, 0.2, 0.4, 0.5, 0.6, 0.8, 1) were prepared by typical self-combustion method using corresponding metal nitrates in required molar ratios and glycine as a fuel. The starting materials of Gd_2O_3 (purity 99.9%), powder iron (purity 99.5%), and manganese (purity 99.7%) were dissolved in diluted nitric acid. After boiling down the solutions, the short combustion processes leading to the sample formation were observed. The samples were then annealed at 1100 °C for 1 h to get rid of reaction remnants.

The quality of the samples was checked by X-ray powder diffraction (XRPD) experiments performed on Ultima IV (Rigaku) diffractometer and, for the samples for which it was possible, the energy dispersive X-ray measurements (EDX) performed on Mira III FE scanning electron microscope (Tescan). All samples were found to be single-phased and with nominal chemical composition within the resolution of the used methods. Magnetization measurements were performed on MPMS3 (Quantum Design) in low temperature configuration and MPMS XL (Quantum Design) with oven configuration. The sample holders were straw (MPMS3) and quartz capillary (MPMS XL). The masses of the samples were in range 30–40 mg (MPMS3) or ≈ 10 mg (MPMS XL).

3. Experimental results

The XRPD measurements confirmed the $GdFeO_3$-type crystal structure (space group $Pnma$) for all concentrations. For data analysis it is convenient to define pseudocubic parameters $a_{pc} = a/\sqrt{2}$, $b_{pc} = b/2$, $c_{pc} = c/\sqrt{2}$. The evolution of pseudocubic parameters (Fig. 1) revealed two different regimes. First regime for $x < 0.3$ fulfils relation $a_{pc} > c_{pc} > b_{pc}$ which is typical for perovskites in which the distortions are dominated by both tilting of the octahedrons and JT distortion. The second

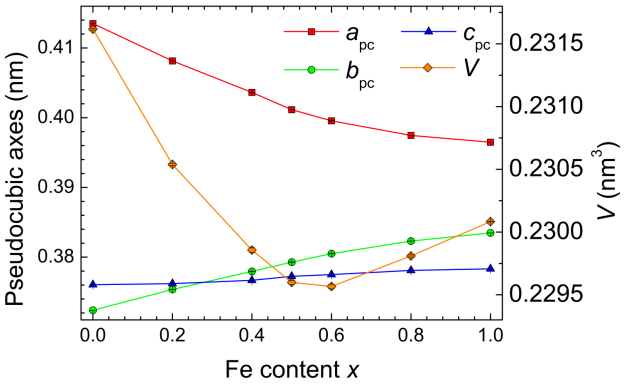

Fig. 1. The pseudocubic parametres (left y axis) together with calculated volume of the orthorhombic unit cell (right y axis) for $GdMn_{1-x}Fe_xO_3$ compounds.

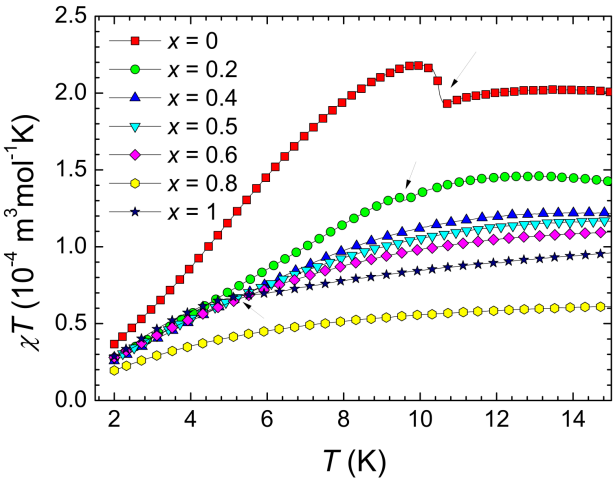

Fig. 2. Low temperature χT vs. T data measured in magnetic fields of 0.01 T. Arrows mark the position of anomalies as discussed in text.

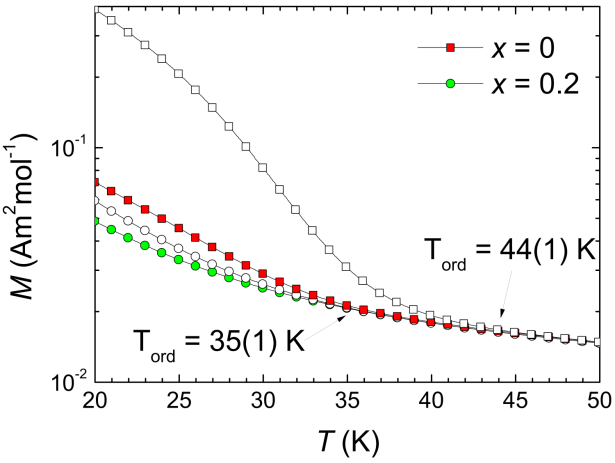

Fig. 3. The ZFC-FC curves for low x concentrations measured in magnetic fields of 0.01 T.

regime ($x > 0.3$) fulfils relation $a_{pc} > b_{pc} > c_{pc}$ which is typical if the leading distortion is the tilting of the octahedrons. So one can conclude that at room temperature, for concentrations around $x = 0.3$, lifting of JT distortion takes place. The second effect is the minimum of unit cell volume at $x \sim 0.6$. In the case of polycrystal materials, such a minimum was observed for $x \sim 0.4$ [7], showing clearly different structural properties of the polycrystalline powder and nanoparticles. The next addressed question is how small the particles are. To answer it one has to know the resolution function of the X-ray apparatus. To determine the resolution function we have measured the LaB_6 standard in the same experimental configuration as the samples. Subsequent Rietveld refinement yield particle sizes of 180 nm, 210 nm, 270 nm, and 170 nm for $x = 0$, 0.2, 0.8 and 1, respectively. For $x = 0.4, 0.5, 0.6$ the crystal size was either resolution-limited or the data did not allow to calculate the grain size due to worse match between data and model caused by the chemical disorder on the Mn/Fe 4b crystallographic site.

The temperature of a magnetic phase transition is usually defined as a minimum in partial derivation $\partial(\chi T)/\partial T$ (where χ is magnetic susceptibility), or, if the magnetic phase exhibits a magnetic history, as point of bifurcation of zero-field cooled (ZFC) and field cooled (FC) magnetization curves [8]. The low temperature χT curves (Fig. 2) show anomalies and $\partial(\chi T)/\partial T$ results to extremes at $T_{Gd} = 10.5(5)$ K, 9.5(5) K, and 5.6(5) K for $x = 0, 0.2$, and 1, respectively. The magnetization curves measured at 2 K (not shown) reach magnetic moments 6.1, 5.3, 5.9, 6.0, 6.4, and 6.9 μ_B/f.u. for $x = 0$, 0.2, 0.4, 0.5, 0.6, 0.8, and 1, respectively, at the highest applied magnetic field of 7 T. This moment is higher than the expected one for Mn^{3+} or Fe^{3+} ions. The surplus moment can be explained by the polarization of Gd ions due to Gd-3d ion exchange interaction. For that reason we ascribe T_{Gd} to the polarization of Gd sublattice. With further increase in of temperature, there is additional extreme in $\partial(\chi T)/\partial T$ which can be observed around 20 K for $x \leq 0.6$. Since in $GdMnO_3$ the modulated magnetic structure locks to AFM + WFM phase below $T_{lock} \sim 23$ K [1], we have ascribed this anomaly to magnetic structure locking in the entire concentration interval $0 \leq x \leq 0.6$. Further increase of temperature leads to the bifurcation point of ZFC and FC curves, which can be observed for $x = 0$ at $T_{ord} = 44(1)$ K and for $x = 0.2$ at $T_{ord} = 35(1)$ K (Fig. 3). This has been assigned to the ordering of Mn/Fe sublattice. For $x = 0$, T_{ord} is within the uncertainties equal to the one published in literature [7]. In case of $x = 0.2$, T_{ord} is lower than the one published before [7]. Since it is generally assumed that there might be vacancies in this perovskite structure, Pal et al. [9] have studied the impact of the cationic vacancies to the magnetic ordering of $GdMnO_3$. These vacancies lead to formation of Mn^{4+} ions which can be concluded from the detection of oxygen excess in the structure. This group of authors has

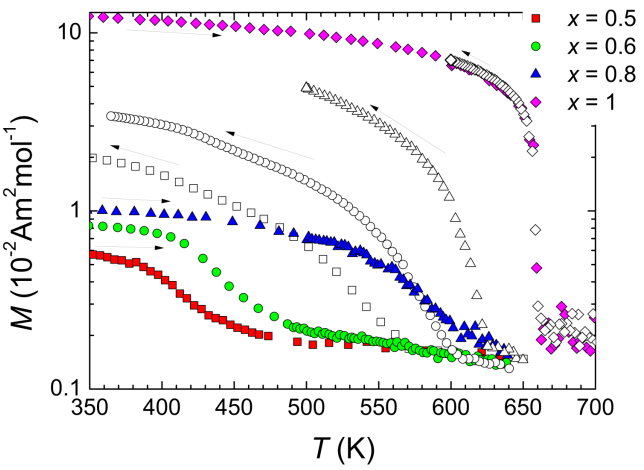

Fig. 4. High temperature magnetization measured in magnetic field of 0.01 T with increasing temperature (full symbols) and decreasing temperature (open symbols).

found 28.3 K $\leq T_{\rm ord} \leq$ 42.4 K, depending on the preparation conditions. In our materials, the EDX analysis revealed stochiometric composition for concentration $x = 0.2$. However, the sensitivity of EDX to oxygen is very low and the vacancies in $GdMn_{0.8}Fe_{0.2}O_3$ compound can not be ruled out. Extrapolating from $GdMnO_3$, it is possible that the magnetism of $GdMn_{0.8}Fe_{0.2}O_3$ is also sensitive to the amount of vacancies. This might be a reason why our $T_{\rm ord}$ is lower than the one previously published [7]. We note that the decrease of $T_{\rm ord}$ for low x concentrations was already observed in other RE $Mn_{1-x}Fe_xO_3$ compounds [5, 10, 11] and from this point of view our data are compatible with the result from other research.

The ZFC-FC hysteresis region for $x \geq 0.4$ spans well above the room temperature (Fig. 4). For these concentrations $T_{\rm ord}$ are 350(10) K, 570(5) K, 605(5) K, 622(5) K, and 658(5) K for $x = 0.4, 0.5, 0.6, 0.8$, and 1, respectively. Such a sharp jump of $T_{\rm ord}$ can be attributed to the change of the leading magnetic ion in the Mn/Fe sublattice. For low x the leading magnetic exchange interaction is Mn-O-Mn superexchange and hence, the $T_{\rm ord}$ is close to the magnetic ordering temperature of $GdMnO_3$ compound. With increasing of iron concentration, the Fe ions become dominant and Fe-O-Fe superexchange is responsible that $T_{\rm ord}$ approaches the ordering temperature of $GdFeO_3$. The second observed effect in this concentration range is the broad decrease of the magnetization with increasing temperature in ordered magnetic state for $0.5 \leq x \leq 0.8$ (see Fig. 4). These anomalies are connected with only faint jumps in temperature decreasing scans which suggest the hysteresis of this feature. Also note that similar transitions were observed for these concentrations by other authors [7, 8]. For these reasons we ascribe the anomalies to a spin reorientation phase transitions which occur at $T_{\rm S}$.

4. Conclusions

Our data allowed us to construct the magnetic phase diagram as presented in Fig. 5. We have found that ordering temperatures for $GdMnO_3$ and $GdFeO_3$ are close to these published in the literature [1, 8], while $T_{\rm ord}$ for $x = 0.2$ is systematically lower and $T_{\rm ord}$ for $0.4 \leq x < 1$ is systematically higher than results published previously [7, 8]. It is worth noting that comparing the data of Nagata et al. [8] and Pal et al. [7] leads to differences up to 25 K for $T_{\rm ord}$ or $T_{\rm S}$. For our samples $T_{\rm S}$ is higher than for samples presented in [7, 8] and $T_{\rm lock}$ extends to higher x concentrations than published before [7]. Other groups have prepared the samples by completely different preparation routes which resulted in different grain sizes as well as different amount of crystallographic vacancies in the structure. For that reasons we conclude that the magnetism of this system is very sensitive to the preparation route and in principle can be tuned by preparation conditions.

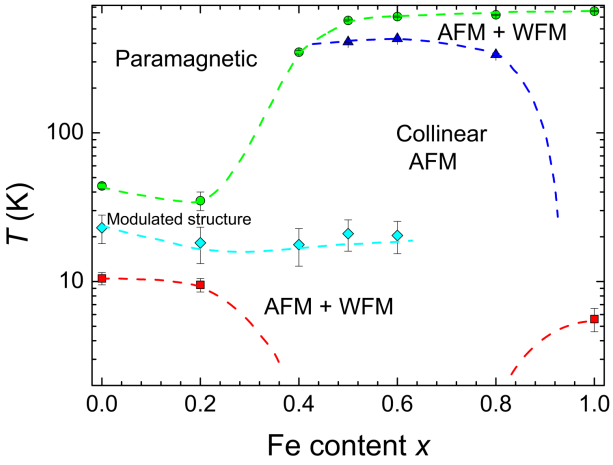

Fig. 5. Magnetic phase diagram of $GdMn_{1-x}Fe_xO_3$ system. Squares represent the ordering of Gd sublattice, circles — ordering of Mg/Fe sublattice, diamonds — locking temperature, and triangles — the spin reorientation temperature. The dashed lines are guide to the eye.

Acknowledgments

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