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Magneto-crystalline anisotropy of $NdFe_{0.9}Mn_{0.1}O_3$ single crystal

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ABSTRACT

Our present study on oriented single crystal revealed huge magneto-crystalline anisotropy with respect to principal crystallographic axes, even several magnetic transitions were observed below T_N = 748 K (*c*-axis) at 700 K (*a*-axis) as well 657 K (*b*-axis). The spin reorientation of magnetic moment takes place in very narrow temperature range between 135 K and 125 K and is attributed to vanishing of ferromagnetic component aligned along *b*-axis. Measurements of magnetic isotherms trace the development of ferromagnetic component and revealed the intermediate temperature range between 120 K and 20 K which is characterised by zero ferromagnetic components in any principal crystal direction. The ferromagnetic component develops consecutive at low temperature below 20 K along *a*-axis. Our study indicates completely different magnetic structure of $NdFe_{0.9}Mn_{0.1}O_3$ below 135 K in comparison with $NdFeO_3$.

1. Introduction

The physical and structural properties of $NdFeO_3$ are widely studied due to interesting magnetic properties such as spin-reorientation transition [1]. The compound adopts orthorhombic structure (space group *Pnma*), where Nd occupies 4c position, Fe atoms occupy 4b, O atoms 4c and 8d positions in the unit cell [1]. Magnetic properties of $NdFeO_3$ are mostly determined by Fe–Fe, Fe–Nd and Nd–Nd exchange interactions. Magnetic ordering of Fe^{3+} ions creates a canted antiferromagnetic ordering of G-type below the Néel temperature T_{N1} = 690 K and the magnetic moments of Fe^{3+} exhibit spin reorientation transition [3] from G_z type to combination of G_z and G_y type in the region from 100 K to 200 K [7] due to the competition of the Fe–Fe and Nd–Fe interactions [4]. The moments of Nd were found to undergo a collective C-type antiferromagnetic ordering at T_{N2} = 1.5 K [1,2]. Electronic magnetic moments are polarized by the Nd–Fe exchange field in the range from *T*N2 = 1.5–25 K [2]. The crossover from the above polarization of Nd under the Nd–Fe exchange to proper long-range ordering due to Nd–Nd interaction takes place near T_{N2} [2].

The substitution of the Mn^{3+} for the Fe^{3+} ion in $NdFe_{x-1}Mn_xO_3$ system introduces both the Jahn-Teller (JT) distortions of the unit cell and distortion resulting from structural mismatch. The symmetry of the orthorhombic crystal structure (space group *Pnma*) remains unchanged in the whole concentration range. The lattice parameters and the unit cell volume change monotonically with substitution showing two distinguished regions below x = 0.4 and above x = 0.7 [5]. In the high Fe - region with $x \leq 0.4$ the unit cell volume is almost intact by substitution and lattice distortion is given mainly by tilting of Mn/FeO6 octahedrons. The unit cell volume increases on further substitution and the lattice distortion can be attributed to both the JT distortion and the tilting of octahedrons [5].

Low concentration substitution of Mn for Fe (x = 0.1) can be regarded as an external parameter affecting magnetic ordering of Fe^{3+} ions. Low temperature heat capacity measurement for sample with x = 0.1 revealed that substitution of Mn for Fe will strengthen Nd–Fe magnetic interaction because a Schottky maximum in low temperature heat capacity shifts to higher temperatures [6]. Another anomaly is generated by doping at about 11 K. The anomaly is smeared out by magnetic field confirming magnetic origin of the anomaly [6]. The anomaly in AC susceptibility, related to spin reorientation, vanishes with substitution [5,6]. Recently we have shown that the Néel temperature decreases from T_N = 691 K to T_N = 621 K, and [5,6]. In our paper we study magneto-crystalline aniso-tropy of $NdFe_{0.9}Mn_{0.1}O_3$ single crystal and the obtained results we discuss and compare with $NdFeO_3$.

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2. Sample preparation and experimental details

Single crystals were prepared by floating zone method in 4-mirror optical furnace (type: FZ-T-4000 from Crystal Systems corporation). We used MnO_2 (purity 3 N, supplier: Alpha Aesar), Nd_2O_3 (purity 3 N, supplier: Sigma Aldrich) and Fe_2O_3 (purity 2 N, supplier: Sigma Aldrich) as starting materials, which were mixed in a Nd: Mn: Fe stoichiometric ratio as intended for the final compound. Subsequently the powders were cold pressed into rods and sintered at 1100 °C for 20 h in air. The crystals were grown in air flow 1 l/min with grown rate 7 mm/h and rotation 15 rpm of upper and lower shafts rotating in the opposite direction.

The grown crystal was characterised by scanning electron microscope (SEM) methods including the energy - dispersive X-ray (EDX) microanalysis on Mira III FE SEM produced by Tescan. Crystal structure was determined by the X'Pert (PanAnalytical) diffractometer using Co $K_{\alpha1,\alpha2}$ radiation with a help of qualitative analysis provided by *HighScore*® software and the JCPDS PDF-4 database [5]. For a quantitative analysis *HighScore plus*® with Rietveld structural models based on the ICSD database was applied. Powder data were treated using Rietveld method implemented in *FullProf* software [8]. The quality check and the alignment of the grown single crystals were performed by Real-time Laue Single Crystal Orientation Tool (Photonic Science).

Measurements of magnetic isotherms were performed on the SQUID magnetometer MPMS-3 (Quantum Design) in applied magnetic fields up to 7 T at different temperatures. The sample was glued by GE varnish on glass cylinder which was inserted into brass holder; typical mass of the samples was between 6 and 11 mg. VSM magnetometer in PPMS (Quantum Design) apparatus with oven option was used as well for low temperature and the high temperature magnetization measurements up to 1000 K. In this case the samples were fixed by Zirconia cement.

3. Results and discussion

3.1. Sample characterization

Both grown crystals $NdFeO_3$ and $NdFe_{0.9}Mn_{0.1}O_3$ have black (NdFe0.9Mn0.1O3) or dark brown (NdFeO3)- glistening colour, with diameter of about 6 mm and length 45 mm or 55 mm, respectively. X-ray powder diffraction from powdered crystals revealed that both samples crystallizes in orthorhombic (GdFeO3 type) structure and the structure can be described using *Pnma* space group with lattice parameters a = 0.55879 nm; b = 0.77612 nm; c = 0.54505 nm for $NdFeO_3$ and a = 0.58067 nm; b = 0.75721 nm; c = 0.54154 nm for $NdFe_{0.9}Mn_{0.1}O_3$. Laue patterns taken from $NdFe_{0.9}Mn_{0.1}O_3$ are shown in Fig. 1 for principal axes. The sharp reflection spots indicate good quality of the crystal. The closer inspection of the direction [0 0 1], which is very close to crystal growth direction, suggests existence of another sub-grain with small miss orientation within several degrees. The SEM analysis from the disks which were cut from the start and the end of crystals perpendicularly to the crystal growth direction did not find any evidence of a secondary phase and confirmed nominal composition of the sample. The SEM analysis included imaging in back-scattered electrons as well EDX analysis.

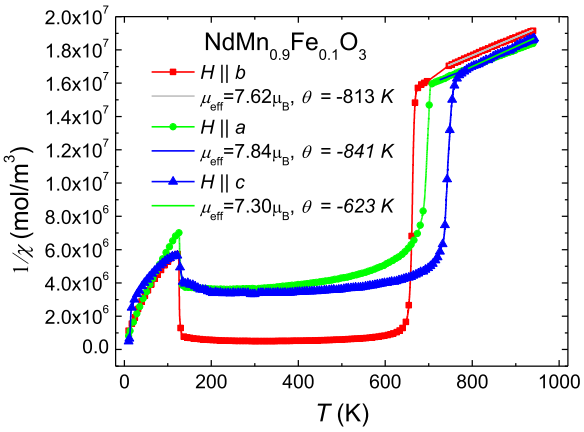

Fig. 2. Representative data of inverse susceptibility for $NdMn_{0.90}Fe_{0.10}O_3$ crystal which were measured in applied field μ_0H = 0.1 T. Lines represent the best fit due to Curie-Weiss law.

3.2. Magnetic measurements

Prior to any high temperature magnetization or susceptibility measurements the sample was heat up above the magnetic phase transition and subsequently cooled down to the lowest possible temperature. The Néel temperature T_N is in this paper defined as the temperature of minimum on $d\mu/dT$ curve in vicinity of magnetic phase transition.

Inverse susceptibility was measured along all three main crystal directions for $NdFe_{0.9}Mn_{0.1}O_3$ sample (Fig. 2). These data show linear dependence at high temperatures obeying the Curie – Weiss law above 700 K. Value of θ scales over the broad range of negative values indicating antiferromagnetic correlations, which can be ascribed to the strong magneto crystalline anisotropy in the system. The effective magnetic moment is within the range 7.3–7.84 μ_B. In $NdFe_{0.9}Mn_{0.1}O_3$ compound, one expects that there are three magnetic ions. One can estimate the theoretical effective moment of such a system as:

$$\mu_{eff} = \sqrt{\mu^2_{eff;Nd} + 0.9\mu^2_{eff;Fe} + 0.1\mu^2_{eff;Mn}}$$

where the terms on the right side of the equation represent the effective moments of individual magnetic ions. Using $\mu_{eff;Nd}$ = 3.62 μ_B (theoretical value for 3+ valence); $\mu_{eff;Fe}$ = 5.92 μ_B (Fe^{3+} ion in high spin state) and $\mu_{eff;Mn}$ = 4.9 μ_B (Mn^{3+} ion in high spin state), one can calculate μ_{eff} to be around 6.86 μ_B, depending on x. The average estimated effective magnetic moment of about 7.59 μ_B is a little bit higher than calculated one. The enhanced moment probably indicates that magnetic susceptibility data contain an additional paramagnetic contribution represent-

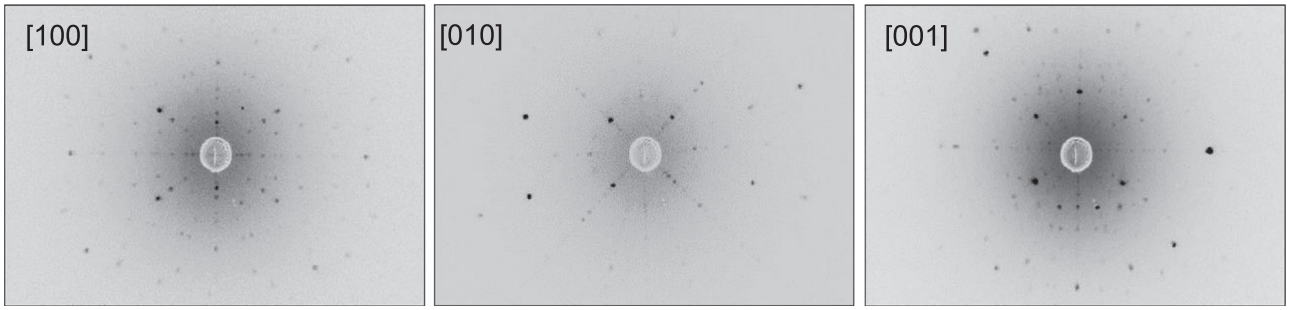

Fig. 1. Laue patterns for principal crystal axes of $NdFe_{0.9}Mn_{0.1}O_3$.