Exchange Bias Effect in NdFeO$_3$ System of Nanoparticles

M. Vavra[a,b,*], M. Zentková[a], M. Mihalik[a], M. Mihalik Jr.[a], J. Lazúrová[a], V. Girman[b],
M. Perovic[c], V. Kusigerski[c], P. Roupcova[d] and Z. Jaglicic[e]

[a]Institute of Experimental Physics, SAS, Watsonova 47, 040 01 Košice, Slovakia
[b]P.J. Šafárik University, Faculty of Science, Košice, Slovak Republic
[c]The Vinca Institute, University of Belgrade, 11001 Belgrade, Serbia
[d]Institute of Physics of Materials, ASCR, Zizkova 22, Brno, Czech Republic
[e]MPM & FGG, Jadranska 19, 1000 Ljubljana, Slovenia

We study the effect of nanometric size on the crystal structure, magnetic environment of iron and magnetization in NdFeO$_3$ system of nanoparticles. The average particle size of NdFeO$_3$ nanoparticles increases with annealing at $600\,°C$ from about 15 nm to 40 nm. The smallest particles on annealed sample have size approximately 30 nm and typically have character of single crystalline samples. All samples adopt orthorhombic crystal structure, space group *Pnma* with lattice parameters $a = 5.5817$ Å, $b = 7.7663$ Å and $c = 5.456$ Å for as prepared sample. The presence of superparamagnetic particles was indicated by the Mössbauer measurements. The reduction of dimensionality induces a decrease of T_{N1} from 691 K to 544 K. The shift of magnetic hysteresis loop in vertical and horizontal direction was observed at low temperatures after cooling in magnetic field. We attribute such behaviour to exchange bias effect and discuss in the frame of core–shell model.

1. Introduction

The exchange bias (EB) was discovered more than 55 years ago, by Meiklejohn and Bean on Co/CoO core–shell nanoparticles [1], and its characteristic signature is the horizontal shift of the centre of magnetic hysteresis loop from its normal position at $H = 0$ to another one at $H_e \neq 0$ and vertical shift which can be characterised by remnant asymmetry μ_e. EB usually occurs in systems which are composed by an antiferromagnet (AFM) that is in atomic contact with a ferromagnet (FM) after the system is cooled, below the respective Néel and Curie temperatures T_N and T_C, in an external cooling field H_{cf}. EB phenomena were observed in various materials like the Laves phases, intermetallic compounds and alloys, binary alloys, the Heusler alloys [2] or on layered bulk fluorometallocomplex [3], where different aspects of magnetism were focused from the EB effect. The first evidence of the EB effect in mixed-valent manganites having perovskite structure was reported in a spontaneously phase separated system $Pr_{1/3}Ca_{2/3}MnO_3$ [4] which stimulated new interest for study of the EB effect in structurally single-phase compounds. In the case of a nanoparticle (NAP) system the surface to volume ratio becomes significantly large compared to the bulk counterpart. In such a case the surface effect dominates over and core–shell model can provide good interpretation of observed phenomena. Both concepts were frequently used for interpretation of EB effects in the $La_{1-x}Ca_xMnO_3$ [5, 6], $Nd_{0.5}Ca_{0.5}MnO_3$ [7] and $Pr_{0.5}Ca_{0.5}MnO_3$ [8] nanoparticles.

The physical and structural properties of NdFeO$_3$ were widely studied and they attracted large attention due to interesting magnetic properties such as spin-reorientation phase transition [9]. 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 at about $T_{N1} = 690$ K and the magnetic moments of Fe^{3+} exhibit spin reorientation from G_x type to combination of G_x and G_z- type in the region from 100 K to 200 K. The moments of Nd were found to undergo a collective *C*-type antiferromagnetic ordering at $T_{N2} = 1.5$ K [10]. In our paper we study crystal structure and magnetic properties of NdFeO$_3$ nano-size particles system.

2. Experimental details

NdFeO$_3$ nanoparticles (NAP) were prepared by the self-propagating of high-temperature synthesis (SHS) which is based on a brief, exothermic burning reaction between oxidizing agent (potassium nitrate), organic fuel (glucose) and relevant metal nitrates [11]. The as prepared samples were annealed at $600\,°C$ for 2 h in air using a muffle furnace. All samples have been characterized by scanning electron microscope (SEM) methods including the energy dispersive X-ray (EDX) microanalysis on Mira III FE SEM produced by Tescan. An additional characterisation of prepared sample was performed by transmission electron microscopy (TEM) using a scanning transmission electron microscope JEOL JEM 2100F UHR. Crystal structure of all samples was investigated by X-ray powder diffraction (XRD) technique in the Bragg–Brentano geometry by a D8 (Bruker) diffractometer using Cu $K_{\alpha1,\alpha2}$ doublet radiation. The Mössbauer spectra

———————

*corresponding author; e-mail: vavra@saske.sk

of powder samples were collected in a standard transmission geometry using a radioactive source of ^{57}Co in Rh matrix (50 mCi) at room temperature. A calibration was done using a 25 μm thick natural foil; isomer shifts values are referred to α-iron. Magnetic measurements were carried out by MPMS SQUID magnetometer in applied magnetic field below 5 T.

3. Results and discussion

The analysis of SEM images of NdFeO$_3$ NAPs [12] revealed that aggregations of very well crystallized cuboid microsized particles with large distribution of size are randomly spread on the surface of agglomerates which are built from NAP with relatively uniform size. The average particle size increases with annealing at 600 °C from about 15 nm to 40 nm. The smallest particles on annealed sample have size approximately 30 nm and typically have character of single crystalline samples as it was revealed by TEM study (Fig. 1). In agreement with [13] both samples adopt orthorhombic crystal structure, space group *Pnma* with lattice parameters $a = 5.5817$ Å, $b = 7.7663$ Å and $c = 5.456$ Å for as prepared sample.
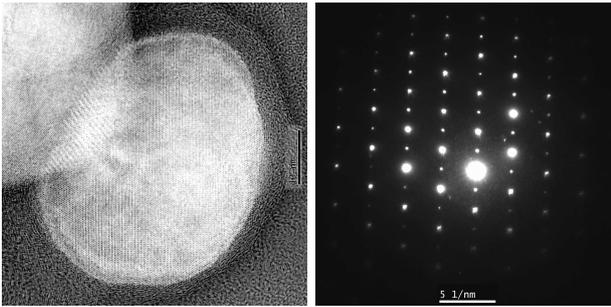

Fig. 1.   TEM image of the individual particle taken from the annealed sample, white line represents the distance of 10 nm, and the diffraction pattern.

The presence of superparamagnetic particles was indicated by the Mössbauer measurements in this system of NAP. The room temperature Mössbauer spectra for both as prepared and annealed NdFeO$_3$ nanoparticles are composed of a sextet and quadrupole doublet components [12]. Hyperfine parameters for sextet components agree with the values published for NdFeO$_3$ [14]. Since Fe^{3+} is in high spin state and in octahedral coordination, the spectrum should consist only from one sextet component at the room temperature. The doublet component can correspond to the super-paramagnetic spin relaxation of the investigated NAP samples. The component is reduced with the thermal treatment at 600 °C, i.e. with the increase of the particle size confirming our suggestion [12].

The magnetic transition at T_N and the spin-reorientation temperature T_{SR} were determined from magnetization measurements $\mu(T)$ (Fig. 2). In the case
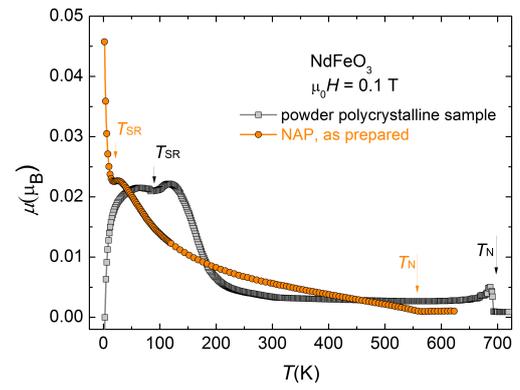

Fig. 2.   Effect of sample preparation on spin reorientation T_{SR} and the magnetic phase transition T_N.

of NdFeO$_3$ a spin reorientation transition is observed between 100 and 200 K with gradual changes of the directions of the Fe^{3+} ordered magnetic moments [9]. In our paper we defined T_{SR} as the temperature at which the process of reorientation is finished and we assign it to the local minimum on $\mu(T)$ curve (Fig. 2). The reduction of dimensionality to nanoscale decreases T_{SR} from 85 K to 20 K. Synthesis of NAP introduces distortion of lattice which can be considered as an effective barrier for spin reorientation and as result the reorientation process is finished at lower temperature. The transition from paramagnetic to canted antiferromagnetic state is accompanied by sharp peak on $\mu(T)$ curves for polycrystalline sample (Fig. 2), which can be attributed to the Hopkinson effect. System of NAP contains superparamagnetic particles and the magnetic interaction can be reduced due to surface effect that is why the magnetic transition occurs at lower temperature $T_{N1} = 544$ K. Broadening of the transition can be attributed to enhanced probability of different surroundings of Fe.

Cooling down in the static magnetic field H_{cf} with induction of 1 T from paramagnetic state gives rise to displacement of the magnetic hysteresis loop, which was measured at 1.9 K, in vertical and horizontal direction, which is the typical manifestation of the EB effect (Fig. 3). The shift of magnetization at 5 T or –5 T is
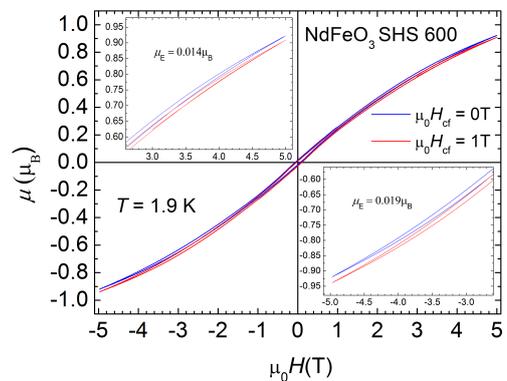

Fig. 3.   Hysteresis loops taken after cooling in zero magnetic field and in field with induction $\mu_0 H = 1.0$ T.
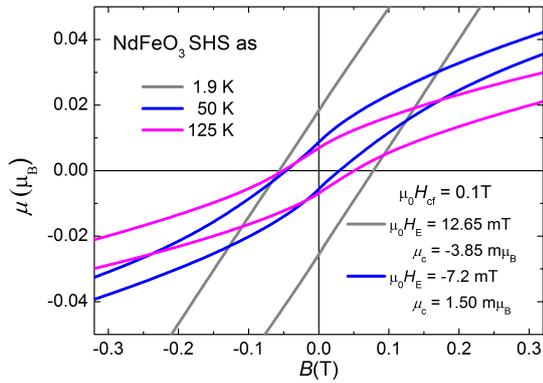
Fig. 4. Detail of hysteresis loops taken at different temperatures after cooling in magnetic field $\mu_0 H = 0.1$ T.
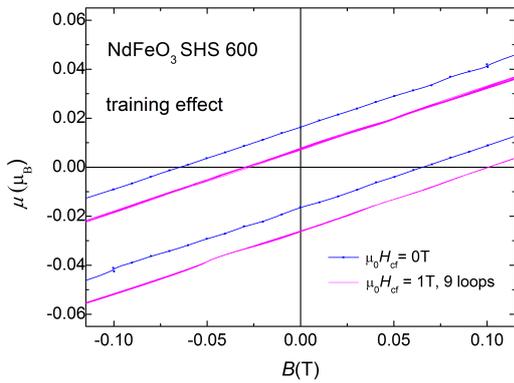

Fig. 5. Training effect, measurements of 9 magnetization reversal loops after cooling in field $\mu_0 H = 1.0$ T.

$\mu_e = 0.014$ μ_B and $\mu_e = 0.019$ μ_B, respectively. The asymmetry of hysteresis loop is temperature dependent and disappears at higher temperatures as it is demonstrated in Fig. 4. The coercive magnetization, which is defined as $\mu_c = (\mu_{r+} + \mu_{r-})/2$ changes from –3.85 mμ_B to –1.50 mμ_B for measurements in $\mu_0 H = 0.10$ T at 1.9 K and 50 K. We did not observe any asymmetry of the hysteresis loop at 125 K. The temperature dependence of the hysteresis loop asymmetry is again typical for EB effect. The difference between subsequent magnetization reversal loops which were measured after cooling in $\mu_0 H_{cf} = 1$ T, the training effect, is shown in Fig. 5. Measurement of magnetization reversal loop was repeated 8 times at 1.9 K. Both parameters $H_e = (H_{c+} - H_{c-})/2$ and μ_c, describing the horizontal and vertical shift of loop do not change significantly with consecutive number of cycles. Such behaviour indicating very weak training effect is unusual for system with EB effect. In summary our measurements of magnetization reversal loops on NdFeO₃ system of nanoparticles revealed manifestation of exchange bias effect in this system.

4. Conclusions

Our investigation revealed presence of superparamagnetic particles in samples, the reduction of dimensionality induces a decrease of T_{N1}. We attribute the shift of magnetic hysteresis loop to exchange bias effect and explain in the frame of core–shell model.

Acknowledgments

References

[1] W.P. Meiklejohn, C.P. Bean, *Phys. Rev.* **102**, 1413 (1956).

[2] S. Giri, M. Patra, S. Majumdar, *J. Phys. Condens. Matter* **23**, 073201 (2011).

[3] Z. Jagličić, M. Zentková, M. Mihalik, Z. Arnold, M. Drofenik, M. Kristl, B. Dojer, M. Kasunič, A. Golobič, M Jagodič, *J. Phys. Condens. Matter* **24**, 056002 (2012).

[4] D. Niebieskikwiat, M.B. Salamon, *Phys. Rev. B* **72**, 174422 (2005).

[5] X.H. Huang, J.F. Ding, G.Q. Zhang, Y. Hou, Y.P. Yao, X.G. Li, *Phys. Rev. B* **78**, 224408 (2008).

[6] V. Markovich, I. Fita, A. Wisniewski, D. Mogilyansky, R. Puzniak, L. Titelman, C. Martin, G. Gorodetsky, *Phys. Rev. B* **81**, 094428 (2010).

[7] L. Liu, S.L. Yuan, Z.M. Tian, X. Liu, J.H. He, P. Li, C.H. Wang, X.F. Zheng, S.Y. Yin, *J. Phys. D Appl. Phys.* **42**, 045003 (2009).

[8] T. Zhang, M. Dressel, *Phys. Rev. B* **80**, 014435 (2009).

[9] W. Sławiński, R. Przeniosło, I. Sosnowska, E. Suard, *J. Phys. Condens. Matter* **17**, 4605 (2005).

[10] J. Bartolomé, E. Palacios, M.D. Kuźmin, F. Bartolomé, *Phys. Rev. B* **55**, 11432 (1997).

[11] A. Mrakovic, J. Blanusa, D. Primc, M. Perovic, Z. Jaglicic, V. Kusigerski, V. Spasojevic, *Ceram. Int.* **39**, 3771 (2013).

[12] J. Lazurova, M. Mihalik, M. Mihalik Jr., M. Vavra, M. Zentkova, J. Briancin, M. Perovic, V. Kusigerski, O. Schneeweiss, P. Roupcova, K.V. Kamenev, M. Misek, Z. Jaglicic, *J. Phys. Conf. Series* **592**, 012117 (2015).

[13] Y. Wang, X. Yan, J. Chen, J. Deng, R. Yua, X. Xing, *Cryst. Eng. Commun.* **16**, 858 (2014).

[14] M. Eibschütz, S. Shtrikman, D. Treves, *Phys. Rev.* **156**, 562 (1967).