Exchange Bias Effect in NdFeO₃ System of Nanoparticles

M. Vavraᵃᵇ*, M. Zentkováᵃ, M. Mihalikᵃ, M. Mihalik Jr.ᵃ, J. Lazúrováᵃ, V. Girmanᵇ, M. Perovicᶜ, V. Kusigerskiᶜ, P. Roupcovaᵈ and Z. Jaglicicᵉ

ᵃInstitute of Experimental Physics, SAS, Watsonova 47, 040 01 Košice, Slovakia
ᵇP.J. Šafářik University, Faculty of Science, Košice, Slovak Republic
ᶜThe Vinca Institute, University of Belgrade, 11001 Belgrade, Serbia
ᵈInstitute of Physics of Materials, ASCR, Zizkova 22, Brno, Czech Republic
ᵉMPM & FGG, Jadranka 19, 1000 Ljubljana, Slovenia

We study the effect of nanometric size on the crystal structure, magnetic environment of iron and magnetization in NdFeO₃ system of nanoparticles. The average particle size of NdFeO₃ 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_N 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.

DOI: 10.12693/APhysPolA.131.869

PACS/topics: 75.47.Lx, 75.50.Tt, 75.70.Rf, 75.60.Jk

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 Hₑ ≠ 0 and vertical shift which can be characterised by remnant asymmetry μₑ. 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_ef. 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 Pr₁₋ₓCaₓ/₂MnO₃ [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 La₁₋ₓCaₓMnO₃ [5, 6], Nd₀.₅Ca₀.₅MnO₃ [7] and Pr₀.₅Ca₀.₅MnO₃ [8] nanoparticles.

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

The physical and structural properties of NdFeO₃ were widely studied and they attracted large attention due to interesting magnetic properties such as spin-reorientation phase transition [9]. Magnetic properties of NdFeO₃ are mostly determined by Fe–Fe, Fe–Nd, and Nd–Nd exchange interactions. Magnetic ordering of Fe³⁺ ions creates a canted antiferromagnetic ordering of G-type below the Néel temperature at about T_N = 690 K and the magnetic moments of Fe³⁺ exhibit spin reorientation from G₂ type to combination of G₁ and G₂ 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 NdFeO₃ nanosize particles system.

2. Experimental details

NdFeO₃ 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 Kα₁,α₂ doublet radiation. The Mössbauer spectra
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.](image)

The presence of superparamagnetic particles was indicated by the Mössbauer measurements in this system 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. Broading 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...
Exchange Bias Effect in NdFeO$_3$ System of Nanoparticles

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

This work was supported by the projects VEGA02/0132/16, ERDF EU No. ITMS26220120047 and SKSRB-2013-0050.

References