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Exchange Bias in Iron-Oxide Particles Nanocasted in Periodic Porous Silica

A. Zeleňáková[a], J. Kováč[b] and V. Zeleňák[c]

[a]Department of Solid State Physics, University of P.J. Šafárik
Park Angelinum 9, 041 54 Košice, Slovakia

[b]Institute of Experimental Physics, Slovak Academy of Sciences
Watsonova 47, 040 01 Košice, Slovakia

[c]Department of Inorganic Chemistry, University of P.J. Šafárik
Moyzesova 51, 041 54 Košice, Slovakia

Iron-oxide nanoparticles were nanocasted in the periodic mesoporous silica matrix, consisting of two-dimensional hexagonally ordered channel system with the mean diameter of the channels about 7 nm. The magnetic measurements of dc magnetization confirm behavior typical of a superparamagnetic system, such as the irreversibility of the zero-field-cooled and field-cooled curves, presence of a maximum in zero-field-cooled curve related with blocking temperature T_B and revealing of coercivity H_C below T_B. The existence of negative exchange bias effect below T_B was confirmed in our system represented by value of exchange bias field $H_{EB} = -970$ Oe measured at the temperature 2 K.

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1. Introduction

In recent years the exchange bias (EB) phenomenon has a great deal of attention because of its potential use in controlling magnetization in devices, such as in giant-magnetoresistance-based spin valves in magnetic reading heads and magnetic random access memories or other spintronics applications [1, 2].

The mechanism of EB is explained on layered or core/shell systems with ferromagnetic/antiferromagnetic (FM/AFM) interfaces due to the existence of a unidirectional anisotropy induced at exchange coupling of FM/AFM system. The main characteristic of this induced anisotropy is a shift of hysteresis loop along the field axis. The exchange bias is initialized by field cooling the heterosystem to below the blocking temperature T_B, where antiferromagnetic order establishes at least on mesoscopic scales [3]. A variety of models have been developed to explain an exchange bias and many experiments have been performed, but a detailed microscopic understanding of this phenomenon is still missing [4]. Recently, exchange bias effect has been also observed in antiferromagnetic nanoparticles system in which the hysteresis originates from the exchange coupling of uncompensated surface spins [5]. A good candidate of the biasing material due to their high Néel temperature and the antiferromagnetic behavior was supposed to be α-Fe_2O_3.

In the present work we have studied the exchange bias phenomenon in the nanocomposite system, Fe_2O_3/SiO_2, composed from α-Fe_2O_3 nanoparticles (hematite) incorporated in the pores of periodic ordered silica matrix.

2. Experimental

The nanocomposite Fe_2O_3/SiO_2 material was prepared by wet-impregnation of the porous matrix using precursor containing Fe^{2+} ions followed by calcination of the sample at 500°C. The structure of nanocomposite system was studied by a powder X-ray diffraction (XRD), by small angle X-ray scattering (SAXS) measurements and by a transmission electron microscopy (HRTEM). Magnetic measurements were performed on a commercial SQUID-based magnetometer (Quantum Design) over a wide range of temperatures (2–300 K) and applied dc fields (up to 50 kOe). The exchange bias field was estimated from field-cooled (FC) hysteresis loop by standard procedure [5, 6] as $H_{EB} = \left(H_{C+}^{FC} + H_{C-}^{FC}\right)/2$.

3. Results and discussion

Iron-oxide nanoparticles were embedded into the pores of periodic silica matrix (SBA-15 type), which exhibits a two-dimensional hexagonally arranged channel system, with mean diameter of the channels about 7 nm.

The characterization of the sample by SAXS and HRTEM measurements showed that the regular hexagonal pore architecture was preserved after nanocasting of iron particles in the silica matrix. In Fig. 1 there is shown the HRTEM micrograph of the sample taken along the hexagonal axis of the material. The uniform structure of the Fe_2O_3/SiO_2 material is obvious from the figure. The analysis of the phase composition sample using wide angle X-ray powder diffraction showed that iron-oxide particles are formed by hematite phase.

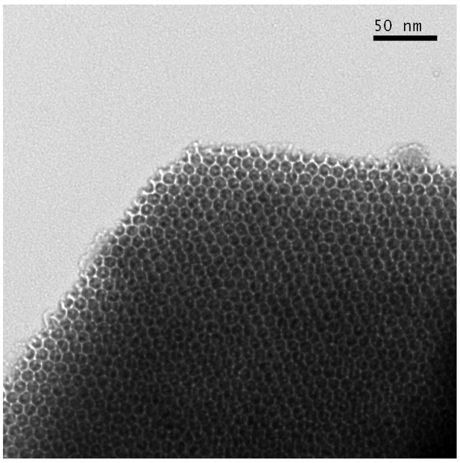

Fig. 1. HRTEM micrograph of the Fe_2O_3/SiO_2 nanocomposite.

The temperature dependence of magnetization measured in regimes zero-field-cooled (ZFC) and FC in applied dc field of 500 Oe is shown in Fig. 2. FC magnetization curve rapidly increases with decreasing temperature and ZFC magnetization exhibits a maximum at the peak value of $T_B \approx 32$ K, related with the blocking temperature T_B. The irreversibility of ZFC and FC curves and presence of ZFC maximum indicates that above blocking temperature T_B ($T > T_B$) the particles are characterized by superparamagnetic behavior, whereas below T_B ($T < T_B$) the magnetic moment of each particle is frozen in the local field direction. Néel noted that antiferromagnetic nanoparticles could exhibit superparamagnetic relaxation of their spin lattices as well as permanent moments arising from uncompensated surface spins.

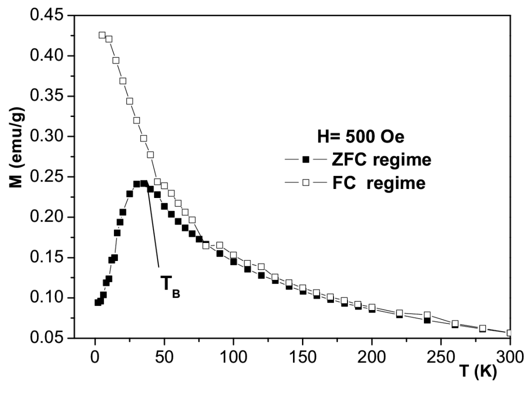

Fig. 2. Zero-field-cooled (full squares) and field-cooled (open squares) magnetization curves measured in dc field 500 Oe in Fe_2O_3/SiO_2 nanocomposite system.

To confirm the freezing process in antiferromagnetic α-Fe_2O_3 particles nanocasted and distributed in the amorphous periodic silica matrix we have measured also the field dependence of magnetization at various temperatures in the temperature range below and above blocking temperature T_B.

The field dependence of magnetization measured at 300 K confirm the superparamagnetic relaxation of spins above blocking temperature characterized by vanishing of coercivity and decrease in saturation magnetization. Magnetization curves recorded at temperatures below blocking temperature ($T < 30$ K) exhibit a value of coercivity of several kOe.

To observe the exchange bias effect, the M–H loops were measured before and after field cooling in a dc field of 10 kOe at temperatures below T_B. The FC magnetization curve exhibits the typical features of an exchange bias system, namely a shift of the hysteresis loop toward negative magnetic fields and enhancement coercivity, see Fig. 3. The value of the displacement defines directly the exchange bias field $H_{EB} = (H_{C+}^{FC} + H_{C-}^{FC})/2$. During the experiment, the following values of H_{EB} were observed: $H_{EB} = -974$ Oe at $T = 2$ K, $H_{EB} = -770$ Oe at $T = 5$ K, $H_{EB} = -468$ Oe at $T = 10$ K. Moreover, it was observed that the H_{EB} also strongly depends on the cooling field. This may suggest that the polarization of uncompensated spins increases with increasing cooling field. The detailed study of this behavior will be the subject of our further work.

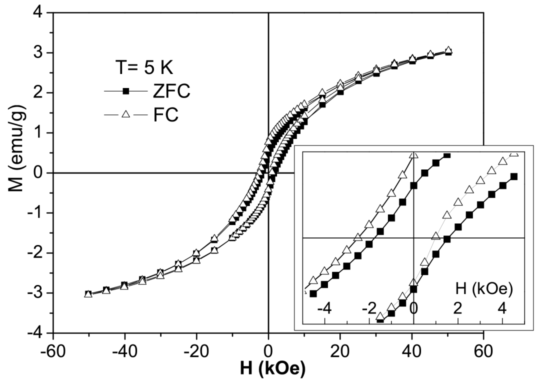

Fig. 3. Hysteresis loop of Fe_2O_3/SiO_2 nanocomposite at temperature 5 K after ZFC (full squares) and after FC (open circles) under an applied dc field of 10 kOe. The inset shows the detail of FC loop shift.

The temperature variation of coercivity H_C^{FC} and the absolute value of exchange bias field H_{EB} measured in a cooling field of 10 kOe and coercivity H_C^{ZFC} measured in zero-field cooling regime are shown in Fig. 4. The large values of H_C^{FC} and H_C^{ZFC} as well as H_{EB} decrease with increasing temperature and drop to zero near the blocking temperature of the sample (H_{EB} diminishes at 30 K). With increase in temperature the enhancement of coercivity ($\Delta H_C = H_C^{FC} - H_C^{ZFC}$) also decreases. The observed experimental dependences confirm the existence

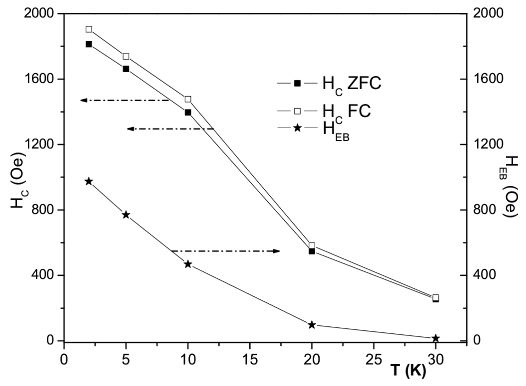

Fig. 4. Variation of coercivity H_C (ZFC), H_C (FC) and the absolute value of exchange bias field H_{EB} at different temperature below blocking temperature of Fe_2O_3/SiO_2.

of uniaxial induced anisotropy resulted to exchange bias. This anisotropy is produced due to the exchange coupling between uncompensated surface spins of antiferromagnetic particles.

4. Conclusion

In summary, iron-oxide nanoparticles (hematite) have been prepared via nanocasting the route in hexagonally ordered porous array of amorphous silica. The magnetic properties of prepared nanocomposite Fe_2O_3/SiO_2 is determined by surface effects. The surface spins behavior results from superparamagnetic relaxation above blocking temperature T_B and freezing of magnetic moments arising from uncompensated surface spins below T_B. Furthermore, the exchange coupling between uncompensated surface gives the large exchange bias field $H_{EB} = -974$ Oe at $T = 2$ K.

Acknowledgments

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