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The phenomenon of magnetic exchange bias in ferromagnetic nanocomposites grown by electron beam evaporation

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Abstract. For the first time, in ferromagnetic nanocomposites $Co/CoO/Al_2O_3$ formed by two-crucible electron beam evaporation with deposition on a policor substrate, the magnetic exchange bias was observed. It is associated with the magnetic interaction of the ferromagnetic metal core of Co nanoparticles with antiferromagnetic CoO layer on their surface. The low value of magnetic exchange bias is attributed to the small thickness of the CoO shell, inasmuch as the energy of exchange magnetic anisotropy, which decreases with diminishing the antiferromagnetic CoO layer thickness, cannot provide a significant increase of the coercive force when changing the magnetic field direction. The ferromagnetic nanocomposites with the magnetic exchange bias can be used as a bias magnetic layer for magnetoresistive sensors.

Keywords: nanocomposites, ferromagnetic nanoparticles, magnetic exchange bias, electron beam deposition.

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1. Introduction

The phenomenon of magnetic exchange bias (MEB is the shift of the hysteresis loop along the axis of magnetic field) observed in ferromagnetic (FM) – antiferromagnetic (AFM) structures. It occurs in systems where the Curie temperature of ferromagnetic exceeds the Neel temperature of antiferromagnetic. The effect was firstly discovered in 1956 year by Meiklejohn and Bean in the film structure Co/CoO [1]. Opposite to metalic cobalt, which is FM with Curie temperature $T_C = 1394$°K, CoO reveals AFM properties with Neel temperature $T_N = 290$ K.

The shift is observed after cooling the system in an external magnetic field on the initial temperature $T_N < T < T_C$ to $T < T_N$. The MEB nature relates to the magnetic exchange interaction between the magnetic moments (M) of Co and CoO at their interface.

The AFM layer prevents rotation of the FM Co magnetic moment at the interface Co/CoO. Back reorientation of the Co magnetic moment in these structures needs a larger magnetic field at its opposite direction as compared with a situation when Co NP's are not covered by CoO AFM layer.

Thus, the exchange energy at the interface grows, and giant magnetic anisotropy $E_a = -k_a \cos\theta$ appears (θ is the angle between orientation of the Co magnetic moments to the interface (in the nearest AFM layer) and magnetic field H). The value of anisotropy constant k_a reaches ~10^5 J/m^3 [2]. This leads to a shift of the center of hysteresis loop toward the negative magnetic field (relatively to the direction of the first applied one). This shift is called "magnetic exchange bias" and is defined by the equation:

$$MEB = \frac{1}{2}\left(H_c^- + H_c^+\right), \quad (1)$$

where H_c^-, H_c^+ are coercivities for the negative and positive directions of magnetic field.

Table 1. The main technological growth conditions.

Samples set number	303	302
T_{cond}, °C	80…200	80…200
$I_{Al_2O_3}$, A	0.49	0.44
I_{Co}, A	0.34	0.34
δ, μm	12…19.5	4.5…8
V_{cond}, μm/min	2…3.2	0.7…1.2
C_{Co}, at.%	12.5…28.5	35.5…53

Table 2. The characteristics of the studied samples.

Sample	T_{cond}, °C	C_{Co}, at.%	δ, μm
303-9	80	12.27	16.8
303-14	80	22.42	18.4
302-22	145	42.87	7.57

MEB can find applications in magnetoresistive sensors and magnetic memory as a bias magnetic layer. We investigated MEB for ferromagnetic nanocomposites (FMNC) $Co/CoO/Al_2O_3$ formed by electron-beam evaporation with condensation on polycore substrate, which demonstrate sufficiently high values of negative tunnel magnetoresistance. Also the electric and thermoelectric properties in the wide range of temperatures (5…300 K) and magnetic fields were studied in our paper [2]. FMNC $Co/CoO/Al_2O_3$ are three-phase materials. Ferromagnetic Co nanoparticles (NP) surrounded by CoO shells are distributed in a dielectric Al_2O_3 matrix. It gives the possibility to observe MEB in this system [2, 3].

The main objectives for this work were as follows: 1) to identify MEB at different temperatures T ($T_N < T < T_C$); 2) to research the dependence of MEB on the magnetic field and Co concentration in FMNC.

2. Experimental details

Ferromagnetic nanocomposites Co/CoO in Al_2O_3 matrix were grown using the electron-beam facility. It operates on the basis of two-crucible scheme with simultaneous evaporation and condensation of Co and Al_2O_3 on a planar policore substrate. The main technological parameters for controlling the structure and properties of FMNC condensates are the rates of components evaporation, which are proportional to the currents of the electron beam evaporators ($I_{Al_2O_3}$, I_{Co}) and substrate condensing temperature (T_{cond}). The latter influences on (1) the concentration of metalic cobalt (C_{Co}), (2) the rate of condensation V_{cond} of the composite and (3) formation of Co NPs. Co content in FMNC depends on the ratio $I_{Co}/I_{Al_2O_3}$. Determination of the condensate elemental composition was carried out by X-ray microanalyzer (EDX attachment to the scanning electron microscope CamScan 4D) supplied by the program Inca-2000 for processing results. The main technological parameters and Co content (C_{Co}) in the FMNC sets 302 and 303 are shown in Table 1.

Hysteresis loops were measured using the vibrating sample magnetometer (VSM) within the temperature range 5…300 K.

3. Results and discussion

The hysteresis loops were measured after sample cooling in the magnetic field (FC) of 200 Oe from the temperature $T > T_N$ to the temperature of measurements ($T < T_N$). The MEB determination was made on the samples Nos 303-9, 303-14, 302-22. Their main characteristics are summarized in Table 2.

High resolution transmission electron microscopic investigations of the sample No 302-22 with 42.87 at.% Co were carried out (Fig. 1). The images for FMNC revealed Co NPs in the form of separate inclusions inside the dielectric Al_2O_3 matrix (Fig. 1). Dark areas of the bright field image represent Co NPs with the average size 7…10 nm. They have a crystalline γ-Co structure (Fig. 2).

The most clearly pronounced hysteresis loops are shown for the sample 302-22 with 42.87 at.% Co (see Fig. 3). These loops were measured at three temperatures 5, 150, and 300 K.

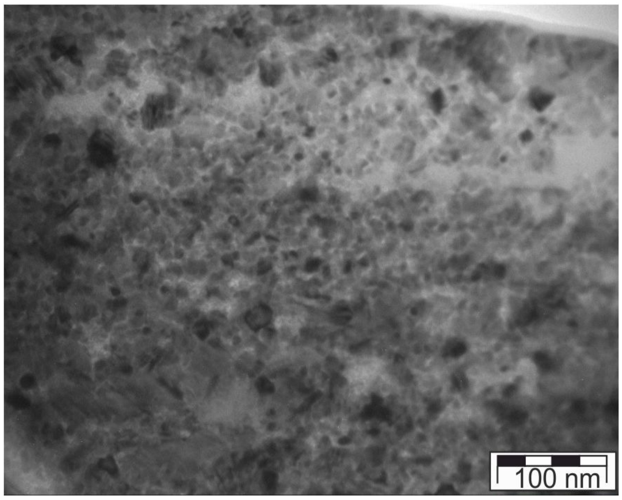

Fig. 1. Transmission electron microscopy bright-field image (scale 100 nm) of FMNC sample 302-22 with 42.87 at.% Co.

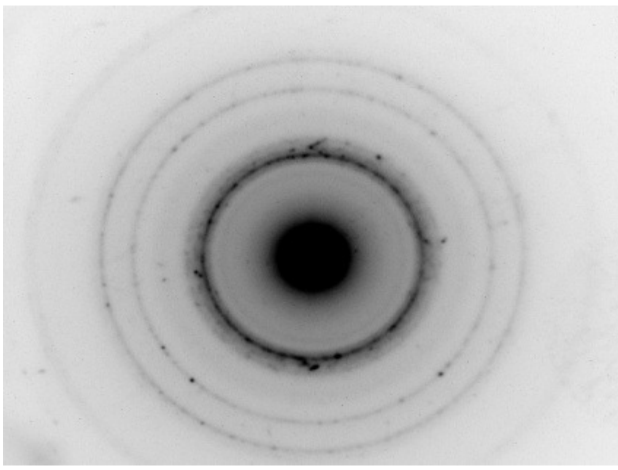

Fig. 2. Electron diffraction pattern of FMNC sample 302-22 with 42.87 at.% Co.

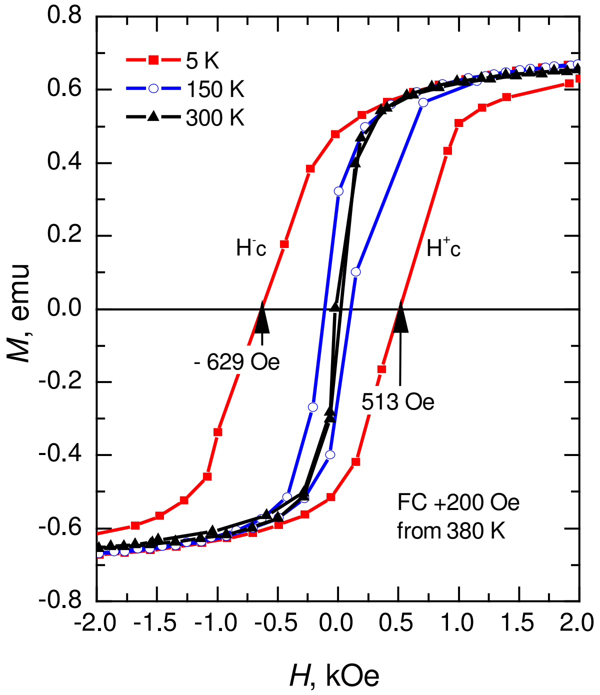

Fig. 3. Hysteresis loops of FMNC sample 302-22 with 42.87 at.% Co measured at different temperatures.

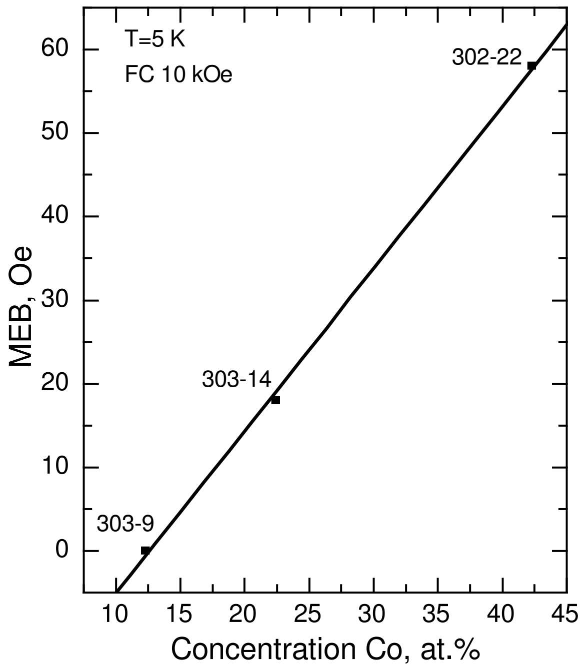

Fig. 4. The dependence of the magnetic exchange bias in FMNC on the Co concentration.

The coercive field H_c^- decreases from 629 Oe down to 121 and 20 Oe at the temperature increase from 5 up to 150 and 300 K, respectively. The largest shift of the hysteresis loop was observed for measurements at 5 K (MEB = 58 Oe). It is interesting that at $T = 300$ K, the hysteresis loop does not disappear. This behavior is associated with the transition from the state of a spin glass at temperatures below the blocking one ($T_B = 200$ K) [2] to the region of ferromagnetic ordering, obliged to the effect of the magnetostatic interaction between Co/CoO NPs. At $T = 300$ K instead of the usual superparamagnetic state there is an intermediate region of magnetic ordering for the ensemble of NPs [4].

The MEB dependence on the Co content in FMNC at $T = 5$ K for the samples cooled from 380 K in the magnetic field $H = 10$ kOe is shown in Fig. 4. MEB growth with an increase of Co content and hence the size of NPs, what agrees with [5], but in our case the magnitude of MEB is two orders lower.

The magnetic exchange bias growth can be explained by the fact that with increasing the fraction of Co in the composite, the size of Co NPs increases [6], and therefore the volume of the AFM CoO layer enlarges, too. It leads to an increase of magnetic anisotropy, and therefore to an increase of MEB. It is interesting that for a certain value of the magnetic field for FC regime (in our case 200 Oe) MEB saturates (Fig. 5). It means that the exchange energy of Co/CoO NPs in this field reaches its maximum magnitude and the further increase of the magnetic field does not lead to the increase of MEB.

Results of other experimental studies of MEB for core/shell NPs Co/CoO in dielectric matrixes carried out in [4-7] are listed in Table 3.

One can suppose that this low MEB magnitude in our case can be caused by the small thickness of CoO layer. Indeed, accordingly to [8]:

$$\text{MEB} \propto J_{FM-AFM} \propto \sqrt{t_{AFM}} \, , \qquad (2)$$

where $J_{FM\text{-}AFM}$ is the exchange energy at the interface FM/AFM, t_{AFM} – thickness of AFM layer.

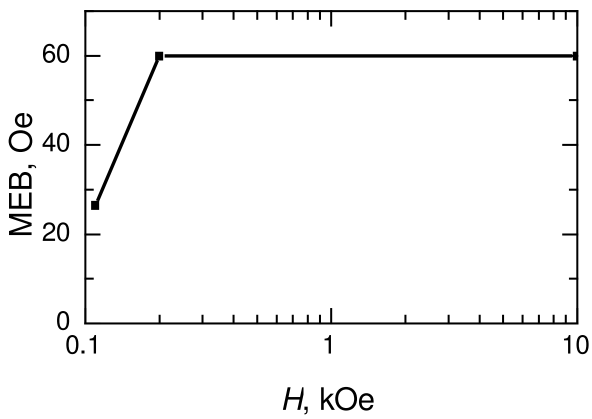

Fig. 5. The magnetic exchange bias dependence for the $Co/CoO/Al_2O_3$ sample 302-22 on the magnetic field in the FC regime at $T = 5$ K.

Table 3. Parameters of nanoparticles Co/CoO in dielectric matrixes.

The deposition method	FMNC substrate	Size of nanoparticles, nm	MEB	References
Two-crucibles EB PVD	$Co/CoO/Al_2O_3$	7	0.058 kOe at 5 K	this research
Pulsed laser deposition	$Co/CoO/Al_2O_3$ Si(111)	2	0 kOe at 5 K	[7]
Standard reactive sputtering	$Co/CoO/Al_2O_3$ Si(111) Co/CoO Si(111)	5	0.05 kOe at 5 K 7.4 kOe at 5 K	[8]
Laser-ablated	$Co/CoO/ZrO_2$	~2	0.9 kOe at 1.8 K	[9]
Magnetron sputtering	Co/CoO/MgO Si(100)	5	2.46 kOe at 2 K	[10]

Besides, a mismatch between lattice periods of NPs and dielectric matrix, as the authors [8, 10] noted, results in a significant decrease of the MEB value. Therefore, we have the lowest MEB value close to 58 Oe for Al_2O_3 dielectric matrix (the lattice mismatch for Co and Al_2O_3 is 42.6%, whereas for MgO it is equal to 1.1%).

In the case when the value of MEB increases with the thickness of the AFM CoO shell on Co NP, a lower MEB value in our case of investigated FMNC can be explained by a small thickness of CoO layer.

But there exist another reason for low MBE magnitude. This reason is a non-perfect structure of CoO shell: 1) due to its non-homogeneous character (availability of CoO nano-inclusions in Co NPs Al_2O_3 matrix surrounding) [8]; 2) due to large stresses generated by great misfit between Co/CoO and Al_2O_3 matrix [10].

Nevertheless, the same circumstances are actual to other experimental results represented in Table 3. FMNC samples were grown by authors [7-10] in more non-equillibrium conditions than in our case of electron beam evaporation. But those conditions did not lead to lower values of MBE. Therefore, we suppose that in our case conditions of FMNC layer growth during electron beam evaporation of constituents could not lead to non-homogeneous Co/CoO distribution in Al_2O_3 and to stresses in Co/CoO.

4. Conclusions

FMNCs containing Co within the concentration range 12…53 at.% were grown by two-crucible electron beam evaporation with deposition on the policor substrates. Firstly, the “magnetic exchange bias” was observed in nanocomposites $Co/CoO/Al_2O_3$ grown by the above mentioned method. This bias is associated with the magnetic exchange interaction between the ferromagnetic Co metallic cores and AFM CoO layers on the surface of Co NPs. The small magnetic shift (58 Oe) in FMNCs $Co/CoO/Al_2O_3$ is significantly lower than in the case of Co NPs treated in oxygen at the high temperature ~1000 °C, accordingly to literature data (-9.5 kOe). It can be explained by lowering the energy of the exchange magnetic anisotropy, which decreases with the thickness of antiferromagnetic layer CoO and leads to small MEBs.

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