Journal of Magnetism and Magnetic Materials 350 (2014) 69–72

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Exchange-bias and exchange-spring coupling in magnetic core–shell nanoparticles

J.M. Soares [a,*], V.B. Galdino [a], F.L.A. Machado [b]

[a] Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59610-010 Mossoró, RN, Brazil
[b] Departamento de Física, Universidade Federal de Pernambuco, 50670-901, Recife-PE, Brazil

ARTICLE INFO

Article history:
Received 19 August 2013
Received in revised form
5 September 2013
Available online 25 September 2013

Keywords:
Cobalt ferrite
Core–shell
Nanoparticle
Exchange-spring
Exchange-bias

ABSTRACT

Nanopowders of $CoFe_2O_4$ with an average particle size of 72.7 nm were produced by an oxidation process and they were used to obtain core–shell nanoparticles of $CoFe_2O_4/CoFe_2$ by reducing them under hydrogen atmospheres. Hysteresis loops were measured from 10 to 300 K by field-cooling the sample under an applied magnetic field of 12 kOe. The exchange coupling among the core–shell structure was found to vary with the thickness of the shell. A phenomenological model which takes into account the thickness of a disordered layer at the core–shell surface was used for determining the exchange-bias anisotropy constant K_{EB} (=0.22 erg/cm^2).

1. Introduction

Magnetic nanoparticles have great potential for application in technologies such as data storage [1], in biomedicine [2], contrast enhancement in magnetic resonance imaging [3] and manufacture of permanent magnets [4]. It should be emphasized that materials with high coercivity (H_c) and high saturation magnetization (M_S) are essential for these applications. However, the majority of available magnetic materials has large values of M_S and small values of H_c or vice versa. Usually hard magnetic materials have large H_c and moderate M_S, while soft magnetic materials have high M_S but almost no coercivity. The search for increasing the coercivity and magnetization resulted in the development of composite materials which consist of hard and soft magnets, commonly referred as exchange-spring magnets [5,6]. It has also been demonstrated that magnetic core–shell nanoparticles behave as exchange-spring magnet [7]. However, to grow these nanoparticles it is necessary to have seeds with crystalline phases with the same crystalline symmetry. Two magnetic materials that fulfill this requirement are the cobalt ferrite and iron–cobalt alloy. Ferrimagnetic nanoparticles (FiM) of $CoFe_2O_4$ have moderate saturation magnetization (M_S=80 emu/g) and the coercivity H_c can reach values between 5 and 10 kOe [8–10]. It is known that ferromagnetic (FM) nanoparticles of FeCo are magnetically soft with a high saturation magnetization (M_S=230 emu/g) [11,12]. Thus, a combination of the high coercivity of the $CoFe_2O_4$ ferrite with high saturation magnetization of the CoFe alloy in $CoFe_2O_4$/FeCo core–shell nanostructures may result a composite material with higher magnetization and higher coercivity. In addition to the exchange-coupling spring, it has been reported that core–shell nanoparticle with ferrimagnetic core and ferromagnetic shell (or conversely) presents the so-called exchange-bias phenomenon, i.e., exhibits displacement of the hysteresis loops in the magnetic field axis [13–16].

In this work, we present a study of the exchange-spring and exchange-bias magnetic couplings in core–shell nanoparticles of $CoFe_2O_4/CoFe_2$ with diameter around 73 nm, synthesized by a chemical reduction process [17]. Hysteresis loops were obtained for different temperatures (T) and under zero-field- and field-cooling conditions. The thickness of the shell was varied while the average particle size remained constant. The paper is organized as follows: in Section 2 we describe details of the experimental procedures used to have the results depicted and discussed in Section 3, and in Section 4 we present the conclusions.

2. Experimental details

Five samples of $CoFe_2O_4/CoFe_2$ core–shell nanoparticles were prepared by reducing nanoparticles of $CoFe_2O_4$ under a controlled hydrogen atmosphere. The pure $CoFe_2O_4$ nanoparticles were synthesized by using an oxidation process reported in detail in a previous work [17]. This procedure allows one to obtain powder samples with thickness of the $CoFe_2$ (t_{CF}) shell ranging from 2.6 to

* Corresponding author. Tel.: +55 218 433 152196.
E-mail address: joaomsoares@gmail.com (J.M. Soares).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.09.040

Table 1
Average core ($CoFe_2O_4$) diameter d_{CFO}, thickness of the shell ($CoFe_2$) t_{CF}, coercive field H_c, and saturation M_S and remanent M_R magnetizations for core–shell nanoparticles.

Sample	d_{CFO} (nm)	t_{CF} (nm)	H_c (kOe)	M_S (emu/g)	M_R (emu/g)
S30	67.6	2.6	0.90	82.4	27.4
S60	63.3	4.7	0.76	80.0	26.1
S180	57.0	7.9	0.75	94.6	29.6
S200	24.5	24.1	0.65	111.4	29.0
S240	2.8	35.0	0.54	141.3	30.0

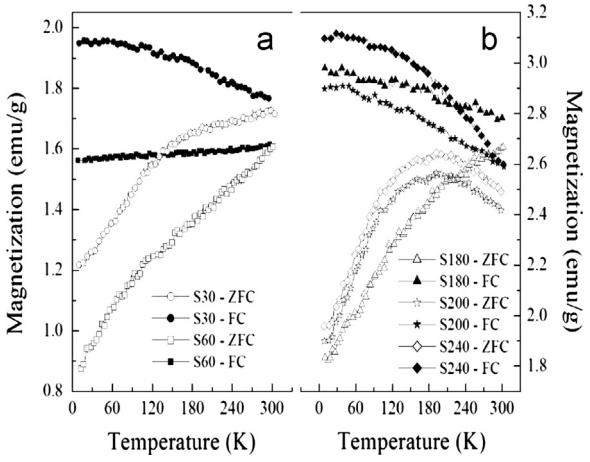

Fig. 1. ZFC and FC measurements vs. *T*data for $H=100$ Oe.

35.0 nm. The samples were labeled S30, S60, S180, S200, and S240 and their specifications are depicted in Table 1. The numbers in the label of the samples correspond to the length of time that a sample remained exposed to a hydrogen flux and higher the length of time, higher the thickness of the shell. A vibrating sample magnetometer was used for measuring the *T*-dependence of the ZFC and FC magnetizations in the range 10–300 K for an applied field of 100 Oe. The exchange-bias field was determined for each sample from hysteresis loops measured for $T=10$, 30, 50, 100, 200 and 300 K after field-cooling the sample from room temperature at an applied field of 12 kOe.

3. Results and discussion

Fig. 1 shows the temperature dependence for the ZFC and FC magnetizations measured with the samples being warmed up with $H=100$ Oe. The transition from a blocked regime to the superparamagnetic state is characterized by a blocking temperature T_B. T_B is usually associated to the temperature below which the ZFC magnetization decreases faster with *T* due to the freezing of the magnetic moments of the nanoparticles. For powder samples with narrow particle size distributions it is found that the blocking temperature is close to the temperature where the irreversibility among the ZFC and FC magnetizations disappears. However, if the particle size distributions are wide the irreversible behavior remains well above T_B as observed in the samples investigated in the present work (see Fig. 1). In this case, it seems more appropriate to discuss the data in terms of a blocking regime established by the irreversible behavior. Even so, one may keep the parameter T_B as the blocking temperature for the particles with size close and below to the average particle size. By taking this into consideration, the value for T_B for samples S200 and S240 is close to 195 K. This is a somewhat surprising result because the size of the core is close to 10 nm and it is coupled to the shell through the exchange-spring mechanism. Thus, one would expect a value for T_B closer or above room temperature. The size of the core for samples S200 and S240 was estimated by using transmission electron microscopy (TEM) images (see Fig. 2) to be in the range 8–10 nm. For sample S180, on the other hand, the ZFC magnetization was found to vary monotonically with *T* suggesting that the core and the shell are coupled by the exchange-spring mechanism [7]. Finally, the ZFC magnetization data for the S30 sample shows a broad hump around 140 K. This behavior has been associated to a strong interaction among particles of $CoFe_2O_4$ which, in turn, leads to a magnetic ordered state with higher anisotropy [18].

Fig. 3 shows room temperature hysteresis loop measured for sample $CoFe_2O_4$. It was found that a magnetization saturation M_S of 75.4 emu/g is close to the expected value for bulk $CoFe_2O_4$ (90 emu/g). The M_r/M_S ratio was found to be close to 0.49 which is the appropriated value for coherent magnetization rotation occurring in uniaxial single-domain nanoparticles. Fig. 3 also shows magnetic hysteresis loops measured at $T=10$ K after cooling the samples under an applied magnetic field of 12 kOe. A hysteresis loop for a pure $CoFe_2O_4$ sample was included in Fig. 3(a) for comparison. As one can see, the values for the magnetization measured at the highest applied field are about the same for all samples despite the broadness of the hysteresis loops. Besides, the core–shell sample presenting the highest exchange-bias field is the one (S240) with broadness that resembles the one for the pure $CoFe_2O_4$ sample which presented no shifting in the hysteresis loop. Thus, we believe that the horizontal shifts in the hysteresis loops are indeed due to the exchange-bias effect and not the minor loop effect [19,20]. Fig. 3(a) shows the hysteresis loops for samples S30 ($M_S=80.5$ emu/g) and S60 ($M_S=73.5$ emu/g). For these samples, the size of the core is in the range 63.3–67.7 nm and the corresponding $CoFe_2$ thickness is smaller than the critical value for $CoFe_2O_4/CoFe_2$ [17]. Thus, for these particles systems the core–shell is not strongly coupled. Therefore, the $CoFe_2O_4$ ferrimagnetic phase dominates the magnetic behavior. The values for the M_R/M_S ratio are between 0.63 and 0.67 and are in good agreement with the values reported in the literature [19,20]. These results are also within the ones expected for a set of randomly oriented assembly of single-domain particles. For this case, the coercive field H_C is proportional to ratio of the anisotropy constant *K* and M_S. Besides, $M_R/M_S=0.5$ and $M_R/M_S=0.83$–0.87 for axial and cubic anisotropy, respectively. So, based on the M_R/M_S ratio the particles investigated in the present work are more likely to have uniaxial anisotropy rather than the cubic one own of bulk cobalt ferrite samples [21]. For the other samples, i.e., S180, S200 and S240, the thicknesses of the shells are greater than the critical value (8 nm) leading to a strong exchange-spring coupling [6,7]. For this critical thickness the coupling is maximized and the sample has the saturation magnetization and remanence enhanced. Indeed, as seen in Fig. 3(b), the sample S180 has the thickness closer to the critical value and it has the highest values for M_S ($=100$ emu/g) and for M_R ($=58$ emu/g).

The low temperature hysteresis loops were also found to be shifted towards negative values of *H* yielding exchange-bias fields (H_{EB}) in the range 140–450 Oe (see Fig. 4). The highest value for H_{EB} was obtained for the sample with smallest shell thickness (t_{CF} between 2.6 and 4.7 nm). The origin of the H_{EB} in FiM/FM core–shell systems has been associated to the randomness of the spin distribution at the core–shell interface which, in turn, leads to a spin-glass behavior at low temperatures [15]. The Meiklejohn–Bean model ($H_{EB}\propto 1/t_{CF}$) [22] has been used to calculate the interface anisotropy constant in core–shell Fe/Fe_3O_4 [14]. This model was found to be appropriated for thin films but it need to be modified for taking into consideration the core–shell structure and the disordered surface layer present nanoparticle systems [23]. Indeed, the exchange-bias field can be related to the ratio of