



Critical dimension for magnetic exchange-spring coupled core/shell CoFe₂O₄/CoFe₂ nanoparticles

J.M. Soares^{a,*}, V.B. Galdino^a, O.L.A. Conceição^a, M.A. Morales^b, J.H. de Araújo^c, F.L.A. Machado^d

^a Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59610-010 Mossoró, RN, Brazil

^b Departamento de Ciências Exatas e Naturais, Universidade Federal Rural do Semi-Árido, 59625-900 Mossoró, RN, Brazil

^c Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, 59072-970 Natal, RN, Brazil

^d Departamento de Física, Universidade Federal de Pernambuco, 50670-901, Recife-PE, Brazil

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ABSTRACT

Core/shell nanoparticles of CoFe₂O₄/CoFe₂ were prepared by reducing nanoparticles of CoFe₂O₄ under hydrogen atmospheres. The structure, morphology and room temperature magnetization of the core/shell nanoparticles were analyzed by X-ray diffraction, transmission electron microscopy and magnetometry, respectively. The sample preparation procedure allowed the diameter of the CoFe₂O₄ core to be varied from 67.7 to 2.8 nm. From the magnetic data it was found that the core couples to the shell through the exchange-spring mechanism while the critical thickness of the soft phase (shell) was estimated using a current theoretical model to be 8.0 nm. This value is very close to the one (7.8 nm) obtained for nanoparticles with same composition but obtained using different synthesis route and having an average particle size (32 nm) less than half of the value estimated (73 nm) for the samples investigated in the present work.

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1. Introduction

The development of exchange-coupled magnetic materials represents cutting-edge research in modern magnetism. Exchange coupling, a general expression for a range of unique magnetic interactions involving two or more magnetic phases, constitutes a very special case at the nanoscale due to the dominant role of interfaces. Moreover, exchange coupling can be used to overcome some fundamental limitations of nanomaterials such as the superparamagnetic limit of nanoparticles smaller than a critical size [1]. In recent years, a series of multi-component magnetic nanoparticles via solution-phase chemical synthesis, thermal decomposition and ball milling method, have been successfully demonstrated [2–8]. Recently, we have prepared nanopowders of CoFe₂O₄ by using an ionic coordination reaction technique. Those powders, in turn, were reduced in an hydrogen flow for different period of time to produce core/shell nanoparticles of CoFe₂O₄/CoFe₂ [9]. The nanoparticles yielded an average diameter of about 32 nm. Their intra- and interparticle interactions were studied using δm plots [10]. These core/shell system was found to couple through the exchange-spring mechanism while the thickness that optimizes the coupling was estimated using a current theoretical model to be 7.8 nm [11].

The control in the exchange-spring coupling, the size and size distribution of these core–shell nanoparticles can enhance its performance for use as permanent magnets and data storage devices.

In the present work, cobalt ferrite powders were produced by an oxidation method which yielded an average particle size nearly twice the one obtained by the ionic coordination reaction technique. This allowed us to verify that the thickness of the shell is the parameter which indeed plays the role in the exchange-spring mechanism. The cobalt ferrite powders were heat treated at a temperature of 280 °C in a reducing hydrogen atmosphere producing core/shell (CoFe₂O₄/CoFe₂) nanoparticles with shell thicknesses ranging from 2.6 to 35.0 nm. The dependence of the coercive field with the thickness of the soft-magnetic phase yielded two well define regimes. From them we were able to determine the critical thickness, e.g., the thickness that optimizes the exchange-spring effect in these nanocomposite materials.

2. Experimental details

Nanoparticles of pure CoFe₂O₄ were produced using an oxidation process [12]. In this process, 2.5% of an aqueous solution of NaOH is mixed to 30 mL of nitrate of Fe (5.9 g) and of nitrate of Co (3.1 g), yielding 200 mL of a blended solution. The solution was heated from room temperature up to 85 °C. Next, it was added 20 mL of an aqueous solution of 0.5% KNO₃ while this new

* Corresponding author.

E-mail address: joaomsoares@gmail.com (J.M. Soares).

solution was kept under magnetic stirring for 2 h. After this step, a precipitate is formed which is washed several times and left to dry at room temperature. CoFe₂ shells with different thicknesses were readily obtained by reducing CoFe₂O₄ powder samples under a controlled hydrogen flux for various period of time (30, 60, 180, 200, and 240 min) at 280 °C. The ferromagnetic iron–cobalt shell is actually formed when the oxygen atoms are removed from the iron–cobalt ferrite core. Both phases present crystallographic cubic symmetry allowing the formation of core–shell structure. The reduction reaction occurring in the cobalt ferrite is: CoFe₂O₄ + 4H₂ → CoFe₂ + 4H₂O.

The average particle size and the structural characterization of the synthesized nanoparticles were determined by X-ray diffraction (XRD) using the CuK α radiation. Moreover, the core–shell structure and the particle size distribution were determined by transmission electron microscopy (TEM).

3. Results and discussion

Typical x-ray diffractograms are shown in Fig. 1 for CoFe₂O₄ and for samples S30, S180 and S240. In the present notation for representing the samples the numbers correspond to the length of time the samples were kept under the hydrogen flux. It is important to mention that we were able to index all the peaks to the CoFe₂O₄ and CoFe₂ phases. This indicates that metallic diffusion may not be an important process while the reduction reaction is taking place. This may be due to the low temperature (280 °C) used in the sample preparation process. The MAUD program and the Rietveld refinement were used to obtain the mean particle diameter. Assuming that the particles are nearly spherical one can estimate the thickness of both core and shell using the XRD data: $\delta_{CF} = (d_0 - d_{CFO})/2$, where d_0 is the average particle size of the starting ferrite and d_{CFO} is the average particle size of the ferrite phase after being reduced (core). Table 1 shows the values of d_{CFO} obtained for the series of samples used in the present work.

Fig. 2(a) shows a TEM image for a broad particle size distribution while the corresponding histogram obtained by using the ImageJ program is shown in Fig. 2(b). The histogram yielded an average particle size of 51.8 nm. Fig 2(c) shows details of the core–shell structure which allows one to estimate the core (dark part of the particle) to be 27.2 nm. The TEM image was also used to estimate the thickness δ_{CF} (= 25.2 nm) of the shell (CoFe₂). The overall results shown in Fig. 2 are for sample S200 and they are in good agreement with those obtained by XRD (see Table 1).

Samples of the pure and of the reduced nanopowders were packed in cylindrical glass sample holders and placed in a vibrant

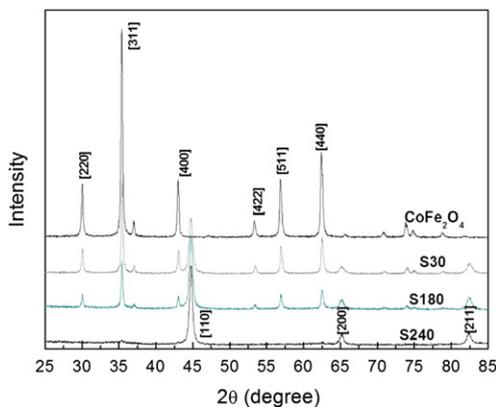


Fig. 1. X-ray diffractograms for the unreduced CoFe₂O₄ powder and for some of the reduced samples.

Table 1

Average core (CoFe₂O₄) diameter d_{CFO} , thickness of the shell (CoFe₂) δ_{CF} , coercive field H_c , and saturation M_s and remanence M_r magnetizations prepared by oxidation process.

Sample	d_{CFO} (nm)	δ_{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

sample magnetometer (VSM) for room temperature magnetization measurements. The randomly packed polycrystalline grains forms a random anisotropy nanoparticulated system. Fig. 3 shows room temperature hysteresis loops measured for samples CoFe₂O₄ and S240. For CoFe₂O₄ it was found a coercivity of 1.16 kOe, and a saturation (M_s) and a remanent (M_r) magnetization of 75.4 and 37.2 emu/g, respectively. 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 single-domain nanoparticles. As one can see in Fig. 3, the value of M_s increases from 75.4 emu/g for the precursor sample to nearly the double of this value (141.3 emu/g) for sample S240. This results is related to the width of the CoFe₂ shell (δ_{CF}) which is getting thicker and to its magnetic moment that is larger than the one for the (diminishing) CoFe₂O₄ core.

It was observed that M_r varies with the thickness according to two regimes (see inset (a) in Fig. 3): (1) the values of M_r increases for thicknesses less than 8 nm, and (2) M_r remain nearly constant above 8 nm. The crossing point between the regimes correspond to the thickness of sample S180. For this sample structure the magnetic core–shell coupling between two crystallographically compatible materials become more important and they beginning to act as a single phase material. A change in the slope of the variation of H_c with the thickness of the shell was also observed to occur near to 8 nm. This result is shown in the inset (b) of Fig. 3.

Kneller and Hawing [11] described a mechanism named exchange-spring based on the coupling of a soft magnetic phase with a hard one, which is applicable to core–shell magnetic materials. The magnetically hard phase (phase k) has a high anisotropy constant, providing a high coercivity, while the magnetically soft phase (phase m) has a high saturation magnetization giving the material a high remanence. The magnetic field required for nucleating irreversible magnetization reversal (H_n) is a signature for exchange-spring magnets. This magnetic field can be estimated from the anisotropy constant K_k of the hard magnetic phase and from the saturation magnetization of the soft one: $H_n = K_k/M_{Sm}$. For an optimum microstructured material, the critical dimension for the magnetically soft phase is given by $b_{cm} = \pi(A_m/2K_k)^{1/2}$, where A_m is the corresponding exchange constant of the soft phase. For this value of thickness, it is also expected a critical value for nucleating irreversible magnetization reversals ($H_c = H_n$). Indeed, Kneller and Hawing shown that exchange-spring magnets may have their magnetic properties optimized when H_c is related to a critical shell thickness b_m

$$H_c = \frac{\pi^2}{2} \frac{A_m}{M_{Sm} b_m^2} \quad (1)$$

In Fig. 4 one can observe two well defined regimes for the coercive fields for core–shell nanoparticles with two different average particle sizes, namely $d_{CFO} = 73$ nm (present work) and 32 nm (from Ref. [10]). For large values of δ_{CF} the CoFe₂ shell is decoupled from the CoFe₂O₄ phase (core) and the magnetizing process is reversible. In the second regime, both phases couple

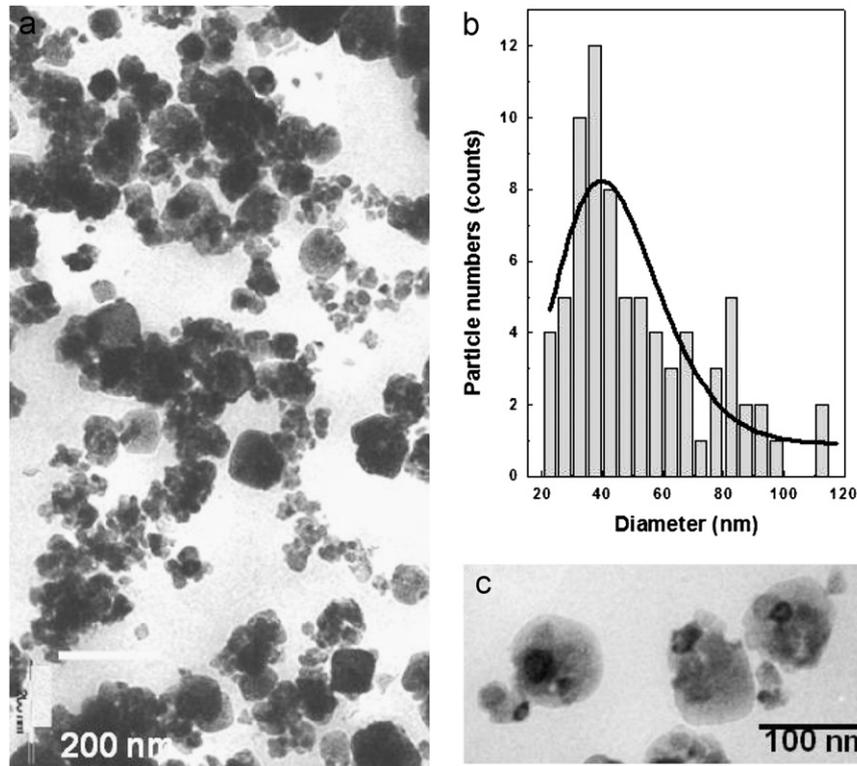


Fig. 2. Distribution (a), particle size histogram (b) and core–shell structure (c) obtained by TEM for sample S200.

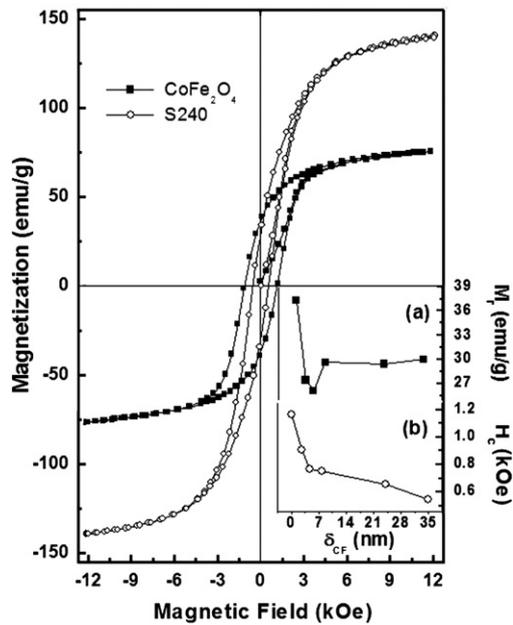


Fig. 3. Room temperature hysteresis loop for the samples: CoFe_2O_4 and S240. The inserts are the remanent magnetization M_r (a) and coercive field H_c (b) versus the thickness of the iron–cobalt alloy, δ_{CF} .

together through the exchange-spring mechanism and the coercive field increases with decreasing values of δ_{CF} . The full lines (gray and black) in Fig. 4 are a best fit for the data using Eq. (1) while the dashed line was drawn to guide the eyes. b_{cm} may be determined by taking the value of δ_{CF} at the crossing over point between the two regimes established by the dependence of H_c with δ_{CF} . For the two sets of samples it was found to be 8.0 nm for b_{cm} . Furthermore, the fitting of Eq. (1) to the part of the data corresponding to the first regime yielded 5.1×10^{-10} Oe/cm² for

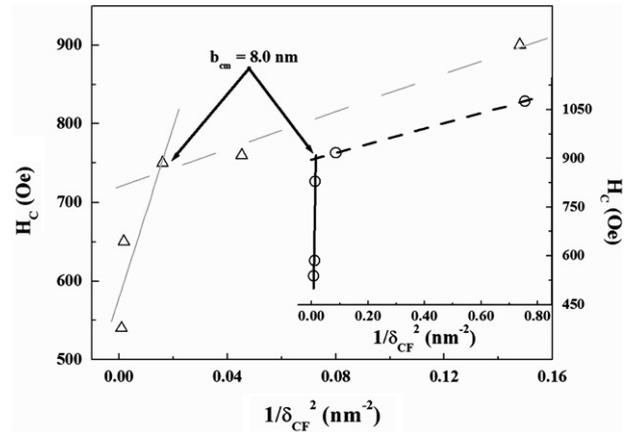


Fig. 4. Coercive field versus the inverse of the square of the shell thickness: open triangles (Δ) are experimental points this work and open circles (\circ) are experimental points of Ref. [10]. The black and gray solid lines are fits using Eq. (1) and the black and gray dashed lines are guide to the eyes.

the coefficient $\pi^2 A_m / 2M_{Sm}$. Now, using $M_{Sm} = 1850$ emu/cm³ for the saturation magnetization of CoFe_2 and the fitting parameter one get the exchange constant $A_m = 1.9 \times 10^{-7}$ erg/cm for the soft phase. In addition, A_m and b_{cm} can now be used to calculate the anisotropy constant $K_k = 1.5 \times 10^6$ erg/cm³ for the magnetically hard phase from $K_k = \pi^2 A_m / 2b_{cm}^2$. The value obtained for K_k is within the range accepted for cobalt ferrite [13].

4. Conclusions

CoFe_2O_4 nanoparticles with an average diameter of 73 nm were prepared by an oxidation process. From these nanoparticles, a series of core–shell nanoparticles of CoFe_2O_4 – CoFe_2 with shell

thickness ranging from 2.6 to 35 nm were prepared by reducing CoFe_2O_4 in hydrogen atmospheres. The core-shell of samples were found to couple through the exchange-spring mechanism and the optimum thickness parameter was estimated to be 8.0 nm using a current theoretical model for exchange-spring magnets. The critical thickness value was found to be close to the one obtained for particles with an average diameter of 32 nm. Despite the difference on their size both particles are single-domain and blocked nanoparticles. The overall results showed that the critical thickness of the soft phase is indeed the most relevant parameter for determine the exchange-spring regime. It was also shown that the results are in good agreement with a current theoretical model.

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