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Exchange-spring behavior in nanopowders of CoFe_2O_4 – CoFe_2

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The nature of the magnetic interactions among core-shell nanoparticles of CoFe_2O_4 – CoFe_2 having an average particle size of 32 nm were investigated by δm plots. It was found that the interactions are mainly demagnetizing in nature for nanoparticles with core diameters larger than 26 nm. For smaller values of core diameters, the exchange-spring phenomenon takes place due to the exchange-coupling at the core-shell interface. The critical thickness of the shell was estimated to be 7.8 nm. The overall results are in excellent agreement with current theoretical models. © 2011 American Institute of Physics. [doi:10.1063/1.3552677]

The need for improving some magnetic properties using magnetic core-shell nanoparticles has inspired an area of great scientific and technological interest.^{1–10} Exchange-coupling through the core-shell interface was found to drastically modify the magnetic properties of nanocomposite combining the high magnetization of a soft-magnetic phase with the high anisotropy of a hard one. Basically, the magnetic fields required to perform a reversible rotation of the magnetic moments in the soft phase are defined by the anisotropy field of the hard magnetic phase and this was named exchange-spring phenomenon.

In this work, the nature of the magnetic interactions in magnetic core-shell nanopowders, composed of a highly anisotropic ferrite (CoFe_2O_4) and a soft-ferromagnetic phase (CoFe_2), was investigated. The demagnetizing remanence curves allowed us to determine the distribution of critical fields. Moreover, the dependence of the critical field with the thickness of the soft-magnetic phase yielded two well defined regimes. From them, we determined the critical thickness of the shell required for optimizing the exchange-spring effect in these nanocomposite materials.

CoFe_2O_4 – CoFe_2 core-shell nanoparticles were obtained from a single-phase CoFe_2O_4 powder prepared by an ionic coordination technique.¹¹ The average particle size for the CoFe_2O_4 powder was obtained by using x-ray diffraction (XRD) microscopy and it was found to be 32 nm. CoFe_2 shells with different thicknesses were readily obtained by reducing CoFe_2O_4 powder samples under a controlled hydrogen flux for various period of time (15, 30, 60, 90, and 120 min) at 300 °C. The ferromagnetic iron-cobalt shell is actually formed when the oxygen atoms are removed from the iron-cobalt ferrite core. This procedure ensures that the exchange interaction among the spins of the soft and hard magnetic phases occur within distances of the order of the lattice parameters. The reduction reaction occurring in the cobalt ferrite is $\text{CoFe}_2\text{O}_4 + 4\text{H}_2 \rightarrow \text{CoFe}_2 + 4\text{H}_2\text{O}$. Assuming that the particles are spherical, one can calculate the thickness of both core and shell by applying the Scherrer formula to the most intense peak in the XRD data for the CoFe_2O_4 phase.

Assuming that the particles are spherical, the thickness of the CoFe_2 shell can be readily estimated, e.g., $\delta_{\text{CF}} = (d_0 - d_{\text{CFO}})/2$, 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 I shows the values of d_{CFO} obtained for the series of samples used in the present work.

Typical x-ray diffractograms are shown in Fig. 1(a) for powder samples of CoFe_2O_4 and for samples E and C. It is important to mention that we were able to index all the peaks to the CoFe_2O_4 and CoFe_2 phases. This indicates that metallic diffusion may not be an important process while the reduction reaction is taking place. The somewhat low temperature (300 °C) used to perform the reaction may be one of the reasons for this. Significant metallic diffusion, if present, would lead to the formation of a solid solution which, in turn, would be seen by XRD or it would appear in the magnetization data as a decoupled magnetic contribution. Figure 1(b) shows a transmission electron microscopy (TEM) image for the CoFe_2O_4 sample. A particle size histogram [Fig. 1(c)] based on the micrograph shows a narrow distribution with an average particle size of 31.8 nm which, in turn, is in good agreement with the one (32.0 nm) obtained by XRD. A TEM image for a nanoparticle of sample B is shown in Fig. 1(d). There, one may note a core-shell structure where the core diameter is about 24 nm. This value is also in good agreement with the one obtained by XRD ($d_{\text{CFO}} = 25.8$ nm). Samples of the pure and of the reduced nanopowders were compressed in cylindrical glass sample holders and placed in

TABLE I. Average core (CoFe_2O_4) diameter d_{CFO} , thickness of the shell (CoFe_2) δ_{CF} , coercive field H_c , and saturation M_s and remanence M_r magnetizations.

Sample	d_{CFO} (nm)	δ_{CF} (nm)	H_c (kOe)	M_s (emu/g)	M_r (emu/g)
A	30.3	1.2	1.08	73.8	29.1
B	25.8	3.4	0.92	79.5	27.8
C	15.2	8.7	0.83	103.0	29.0
D	13.6	9.5	0.59	137.8	31.0
E	10.0	11.3	0.54	184.3	49.4

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FIG. 1. (a) X-ray diffractograms for pure CoFe_2O_4 and for samples E and C. (b) TEM image for a CoFe_2O_4 powder sample. (c) Particle size histogram for sample B. (d) High resolution TEM image for a sample B nanoparticle.

a vibrant sample magnetometer for room temperature magnetization measurements. The randomly packed polycrystalline grains form a random anisotropy nanoparticulated system. Hysteresis loops obtained for the CoFe_2O_4 sample yielded a coercivity of 1.32 kOe and a saturation (M_S) and a remanent (M_r) magnetization of 68.0 and 33.7 emu/g, respectively. The M_r/M_S ratio was found to be close to 0.5, which is the appropriated value for coherent magnetization rotation to occur in single-domain nanoparticles.

The δm curves were built using the magnetizing $M_r(H)$ and demagnetizing $M_d(H)$ remanent magnetizations measured as follows. First, the isothermal remanent magnetization $M_r(H)$ is measured after a magnetic field $H(H > 0)$ is applied and removed. This procedure is repeated with the magnitude of H being gradually increased until the magnetization reaches saturation ($H = H_{\text{sat}}$). Next, the remanent demagnetizing magnetization is obtained following a somewhat similar procedure. Starting from the maximum remanence, e.g., after the sample has been saturated and H_{sat} has been removed, one applies and removes a negative field ($H < 0$) and measures the remanence. H is then gradually increased toward (negative) saturation. It is important to use the same values of H in both procedures to allow a good correlation between both remanent magnetization data. Finally, $M_r(H)$ and $M_d(H)$ are normalized by the saturation remanence $M_r(H_{\text{sat}})$: $m_r = M_r(H)/M_r(H_{\text{sat}})$ and $m_d = M_d(H)/M_d(H_{\text{sat}})$.

Figure 2 shows a graph of m_d as a function of H for each of the core-shell samples investigated in the present work.

FIG. 2. Demagnetizing remanence vs H .

The behavior of m_d for samples A and B follows the same trends. However, the curvature in $M_d(H)$ increases substantially for the core-shell samples with larger values of δ_{CF} . This is a clear indication that the mechanisms governing the magnetization process is strongly influenced by the core-shell structure. The nature of the interactions in a set of magnetic nanoparticles has been determined by using the Wohlfarth relationship established for noninteracting single-domain uniaxial nanoparticles, $m_d = 1 - 2m_r$.¹² A deviation from the Wohlfarth relationship is an indication that the nanoparticles are interacting among themselves. The deviation is better seen through a relationship known as δm and defined as $\delta m = m_d(H) - [1 - 2m_r(H)]$.¹³

The inset in Fig. 3 shows the δm plots for our samples. Note that the magnitude of δm is negative for samples A and B, while part of the curves are positive for samples C–E. A similar behavior has been observed in some metallic alloys.^{3,14} Furthermore, it was found that δm becomes less negative when the core-shell ratio is reduced. The negative peak in δm is a signature of demagnetizing (dipolar) interactions in nanopowder samples.¹⁵ The observed reduction in the size of the negative peak may be interpreted as being due to the presence of magnetizing (exchange-type) interactions. Moreover, its influence in the size of the demagnetizing peak can be made more explicit by subtracting the δm curve for

FIG. 3. δm_{exc} and δm (inset) plots.

FIG. 4. Nucleation field vs the inverse of the square of the shell thickness; open diamonds are experimental points. The solid line is a fit using a model presented in the main text and the dashed line is a guide to the eyes. The inset is the distribution of critical fields (H_n) for sample C.

CoFe₂O₄ from the δm curve for the CoFe₂O₄–CoFe₂ core-shell samples: $\delta m_{\text{exc}} = [m_{d\text{CFO}}(H) - m_d(H)] + 2[m_{r\text{CFO}}(H) - m_r(H)]$, where $m_{r\text{CFO}}$ and $m_{d\text{CFO}}$ are the magnetizing and demagnetizing remanences, respectively, for the cobalt ferrite powder sample. The δm_{exc} plots for the core-shell samples are shown in the main part of Fig. 3. There, one may note that fully positive peaks are only observed in the data for samples C–E, while nearly half of the data for samples A and B is negative.¹⁶ The intensity of peaks rapidly increases when the thickness of the CoFe₂ shell is also increased. The source of exchange-coupling is mainly twofold: from interactions occurring at the interface of the core-shell and from the contact between nanoparticles. The magnetic field required for nucleating irreversible magnetization reversal (H_n) is a signature for exchange-spring magnets. It can be estimated from the anisotropy constant K_k of the hard magnetic phase and from the saturation magnetization of the soft one:¹⁷ $H_n = K_k / M_{Sm}$. Experimentally, the nucleation field may be obtained from the magnetic field dependence of the demagnetizing remanence $M_d(H)$ by defining the quantity $D(H) = [M_r - M_d(H)] / 2M_r$. The maximum in the derivative of $D(H)$ with respect to H yields a value for H_n . The inset in Fig. 4 is a plot of $dD(H)/dH$ versus H for sample C. Thus, the maximum of $dD(H)/dH$ yields $H_n = 1040$ Oe for sample C. This analysis was also applied for the other samples and the corresponding values for H_n were plotted as a function of the inverse of the square of the shell thickness δ_{CF} in the main part of Fig. 4. Kneller and Hawig¹⁷ have shown that exchange-spring magnets may have their magnetic properties optimized when H_n is related to a critical shell thickness b_m by $H_n = \pi^2 A_m / 2M_{Sm} b_m^2$, where A_m is the exchange constant of the magnetically soft phase. In Fig. 4, one can observe two well defined regimes for the nucleation fields. For small values of δ_{CF} , the nucleation field is nearly constant ($H_n \approx 1300$ Oe). In this regime, the CoFe₂O₄ phase (core) is decoupled from the CoFe₂ shell and the magnetizing process is reversible. In the second regime, both phases couple to-

gether through exchange-coupling and the nucleation field decreases with increasing values of δ_{CF} . The full line in Fig. 4 is a best fit of H_n , while the dashed line is a guide to the eyes. b_m 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_n with δ_{CF} . For our samples, a value of 7.8 nm for b_m was found. Furthermore, the fitting yielded 8.5×10^{-10} Oe/cm² for the coefficient $\pi^2 A_m / 2M_{Sm}$. Now, using $M_{Sm} = 1850$ emu/cm³ (Ref. 18) for the saturation magnetization of CoFe₂ and the fitting parameter, one gets the exchange constant $A_m = 3.2 \times 10^{-7}$ erg/cm for the soft phase. In addition, A_m and b_m can now be used to calculate the anisotropy constant $K_k = 2.1 \times 10^6$ erg/cm³ for the magnetically hard phase from $K_k = \pi^2 A_m / 2b_m^2$. The value obtained for K_k is within the range accepted for cobalt ferrite.¹⁹

In conclusion, core-shell nanoparticles of CoFe₂O₄–CoFe₂ with shell thickness ranging from 1.2 to 11.0 nm were prepared by reducing CoFe₂O₄ in hydrogen atmospheres. Their intraparticle and interparticle interactions were studied using δm plots. The core-shell was found to couple through exchange-coupling and the optimum thickness parameter was estimated to be 7.8 nm using a current theoretical model for exchange-spring magnets. Other sample parameters were determined self-consistently using current theoretical models.

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