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Determination of the effective anisotropy constant of CoFe_2O_4 nanoparticles through the T -dependence of the coercive field

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We present a systematic study of the coercive field of CoFe_2O_4 - SiO_2 nanocomposites. The samples were prepared via the sol-gel method by using the Tetraethyl Orthosilicate as starting reagent. Results of X-ray diffraction, transmission electron microscopy, and X-ray fluorescence confirm the dispersion of the magnetic nanoparticles inside the silica matrix. In addition, the shift in the maximum of Zero-Field-Cooled curves observed by varying the weight ratio of CoFe_2O_4 nanoparticles to the precursor of silica is consistent with the increasing of average interparticle distances. Because our samples present a particle size distribution, we have used a generalized model which takes account such parameter to fit the experimental data of coercive field extracted from the magnetization curves as a function of applied field. Unlike most of the coercive field results reported in the literature for this material, the use of this model provided a successful description of the temperature dependence of the coercive field of CoFe_2O_4 nanoparticles in a wide temperature range. Surprisingly, we have observed the decreasing of the nanoparticles anisotropy constant in comparison to the bulk value expected for the material. We believe that this can be interpreted as due to both the migration of the Co^{2+} from octahedral to tetrahedral sites. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4942535>]

I. INTRODUCTION

Magnetic nanoparticles systems are generally composed by agglomerates of particles with nanometric dimensions and easy axes randomly orientated. It is well-known that the magnetic behavior of monodispersed and non-interacting single domain magnetic nanoparticles can be completely understood inside the framework of Néel,¹ Bean-Livingston,² and Stoner–Wohlfarth³ approaches. In this sense, the system exhibits a magnetic relaxation process that depends on the thermal effects and on the existence of energy barriers separating two or more local minima. The magnetic behavior of a nanoparticle assembly is characterized by the existence of a blocking temperature, T_B , which leads to two distinct regimes. For $T < T_B$, the energy barriers can trap the particles magnetization in two or more metastable orientations and for $T > T_B$, the thermal energy, $k_B T$, overcomes the energy barriers resulting in the well-known superparamagnetic regime (SPM). Concerning the system’s magnetization dependence on the magnetic field, high/moderate coercivity can be observed for $T < T_B$ and a nonhysteretic behavior for $T > T_B$. However, it is important to highlight that real systems often present particle size distribution, magnetic anisotropy, and non-negligible interparticle interactions which can take an important role in their magnetic relaxation process. From the sample preparation viewpoint, most of works reported on

literature reveal that the issues discussed above are strongly dependent on the used route to prepare the samples and so, it can be improved by using specific chemical methods of synthesis. For instance, it was shown by El-Hilo *et al.*^{4,5} that the particles size distribution produces a displacement in maximum of ZFC (Zero-Field-Cooled) curve described by $T_{max} = \beta T_B$, where T_B is the blocking temperature of the particles system and, in most of cases, β assumes values ranging 1.5–2.0.⁵ In the same way, to grow samples with negligible effects of interaction among particles is a very difficult task (mainly for materials with high saturation magnetization). The magnetic interaction among nanoparticles can also affect the superparamagnetic relaxation.^{6–12} In order to overcome this problem, the use of an inorganic nonmagnetic matrix as a host matrix for nanoparticles may reduce nanoparticles aggregation.

In this paper, we report on the coercivity of CoFe_2O_4 nanoparticles dispersed on a silica matrix. X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray fluorescence (XRF) confirm the dispersion of nanoparticles inside the SiO_2 matrix. The displacement of the maximum of the ZFC-FC (Zero-Field-Cooled and Field-Cooled) curves is also in agreement with such dispersion effects. At last, the coercive field extracted from MxH curves was fitted by using the generalized model.¹³

II. EXPERIMENTAL PROCEDURE

Ferrite–silica nanocomposites were produced by the sol-gel method from a mixture of tetraethylorthosilicate (TEOS)/ethyl alcohol/distilled water in a fixed molar ratio of 1/3/10. This solution was stirred at room temperature for 40 min to homogenization. After that, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ salts (Fe:Co = 2:1) were added stoichiometrically into the first solution. This mixture was stirred during 1 h to homogenization and left to stand for gelation. Gels were dried at 120°C leading to the formation of xerogels and finally annealed in air at 750 and 850°C during 3 h to form nanocomposites with 2, 10, 13, 20, 40, and 50 wt. % of cobalt ferrite nanoparticles inside the SiO_2 matrix. In the following, the obtained samples will be referred to as S2, S10, S13, S20, S40, and S50.

The powder X-ray diffraction data with CuK_α radiation were obtained from a PANalytical Empyrean diffractometer using the Bragg-Brentano geometry in continuous mode with a scan speed of $1/4^\circ/\text{min}$ in the 2θ range from 25° to 70° . The Rietveld refinements were performed using the free software DBWS9807.¹⁴ The morphology and dispersion of nanoparticles sizes were examined by transmission electron microscopy JEOL microscope model JEM-3010 operating at 300 kV. XRF data were taken from 0.45 to 8 keV in a wavelength-dispersive S4 Pioneer spectrometer (Bruker AXS) operating at 27 kV and 148 mA using Rh radiation. Magnetic measurements as a function of the magnetic field and temperature were taken using a SQUID magnetometer (Quantum Design MPMS Evercool system).

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 presents X-ray diffraction patterns measured at room temperature for selected CoFe_2O_4 - SiO_2 samples synthesized at 750 and 850°C . We also show the difference between the experimental and calculated patterns obtained via Rietveld method¹⁴ for the samples S20, S40, and S50 heated at 850°C . The analyzed XRD patterns are consistent

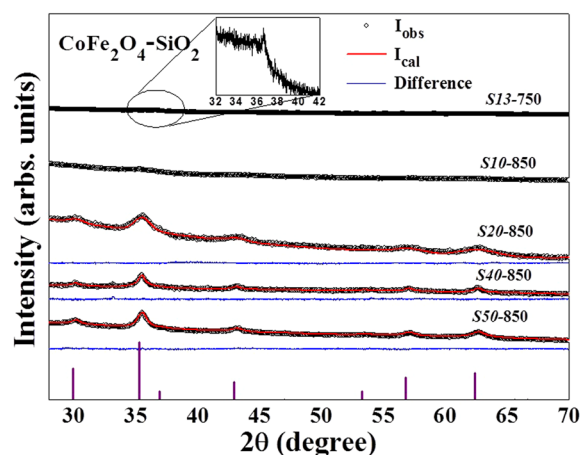


FIG. 1. XRD pattern for selected samples of CoFe_2O_4 synthesized at 750 and 850°C . The red solid lines are the fittings obtained by using the Rietveld method and the blue ones represent the difference between experimental and calculated patterns. The horizontal bars mean the standard pattern found in the Powder Diffraction File (PDF) No. 01-077-0426.

with a cubic phase of spinel crystallographic structure (space group: $Fd\bar{3}m$). The vertical bars mean the indexation to the Powder Diffraction File (PDF No. 01-077-0426). In the inset, we show a magnification of the region of the most intense diffraction peak ($2\theta = 35.4^\circ$) to the S13 sample heated at 750°C . The full width at half maximum obtained from these refinements was used to calculate the average particle size. It is worth to say that we have used heating temperatures up to 950°C and no reflections related with crystalline phase of SiO_2 have been observed.

The TEM images obtained for the samples S2 and S13 heated at 850 and 750°C , respectively, are shown in Figure 2. The upper inset displays the high-resolution TEM (HRTEM) images of an individual CoFe_2O_4 nanoparticle showing the (222) and (311) lattice fringes characterizing the crystalline particle structure of the CoFe_2O_4 . Moreover, we can observe that the nanoparticles present a spherical-like morphology. In the bottom inset, it is presented the particles size histograms which were obtained from several TEM images obtained in different regions of sample fitted by a log-normal distribution. One can notice that different dilution levels of cobalt ferrite nanoparticles inside SiO_2 matrix were obtained. However, both images show that the dilution is not homogeneous—a fact that can lead to interparticle magnetic interactions.

The XRF spectra for the sample of CoFe_2O_4 - SiO_2 heated at 750 and 850°C are shown in Figure 3. It should be noted that we show the energy region of the characteristic emission of silicon in (a) and (b) and of the cobalt and iron emissions in (c) and (d). Quantitative X-ray fluorescence analyses show that both the molar ratio magnetic phase/silica obtained experimentally and the nominal composition of the magnetic phase/silica are in good according (see Table I).

It is well established on the literature that the magnetic properties of nanoparticles systems depend strongly on their intrinsic intraparticle properties (such as finite size and surface effects), growth features (such as mean size and size distribution), and the effects caused by the interparticle interaction. In this sense, the use of an inorganic nonmagnetic matrix as a host for magnetic nanoparticles can contribute to avoid the problem of nanoparticle aggregation and, as a

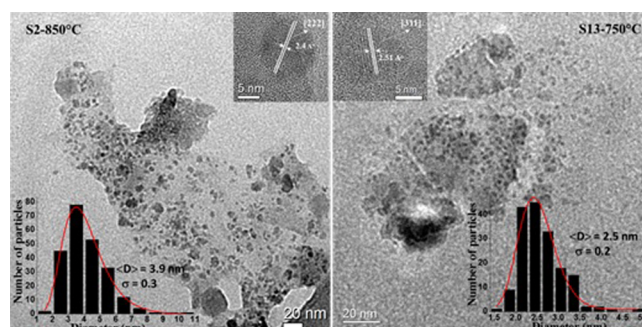


FIG. 2. Transmission electron microscopy (TEM) images for the samples S2 and S13 heated at 850 and 750°C , respectively. Upper inset: HRTEM micrographs of an individual CoFe_2O_4 nanoparticle indicating the interplanar distances characteristic of cobalt ferrite. Bottom inset: Particles size histograms obtained from different TEM images fitted by log-normal distributions.

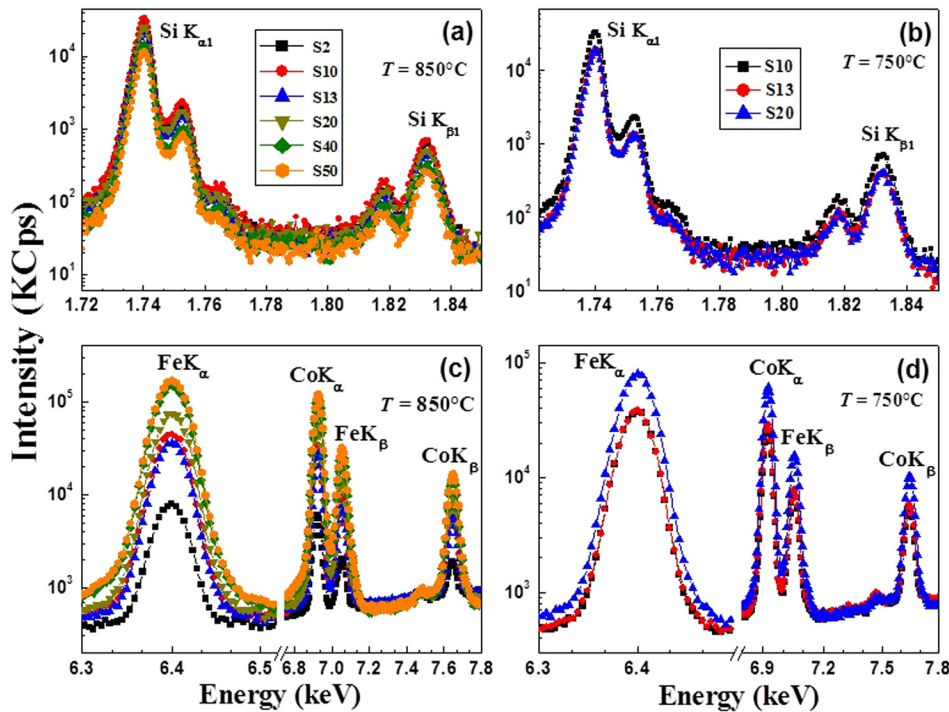


FIG. 3. X-ray fluorescence spectra for the CoFe_2O_4 nanocomposites synthesized at 850°C ((a) and (c)) and 750°C ((b) and (d)) for two distinct energy region of characteristic emission of iron, cobalt, and silicon.

consequence, to reduce the interparticle interactions. The X-ray diffraction results shown in Figure 1 confirm the success of the dilution of the cobalt ferrite nanoparticles inside the amorphous silica matrix. It must be noted that for higher concentrations of cobalt ferrite nanoparticles (S20, S40, and S50 samples heated at 850°C), it is possible to index the observed main reflections by considering the patterns found for the spinel crystallographic phase. However, we are not able to identify any Bragg reflections for the S2, S10, and S13 samples. Interestingly, as one can see in the inset of Figure 1, a tiny peak around 35° was observed. This reflection angle is consistent with the most intense peak of the CoFe_2O_4 pattern. The mean sizes calculated from Rietveld analysis of the X-ray diffraction patterns using Scherrer equation for sample S20 heated at 750°C (not shown in Fig. 1) is (3.6 ± 0.1) and for the S20, S40, and S50 samples heated at 850°C are 3.9 ± 0.9 , 5.5 ± 0.6 , and 7.6 ± 0.9 nm, respectively. In order to reinforce the X-ray diffraction data and to extract the size distribution, we carried out TEM images of the most diluted samples heated at 750 and 850°C . One can observe for both samples

the presence of nanocrystalline particles dispersed in the silica host matrix and the formation of particles clusters, mainly for S13 heated at 750°C . HRTEM analysis confirms the single crystalline features of the calcined nanoparticles (see insets of Fig. 2). The particles size distributions were fitted using a log-normal functions and the particles mean sizes are 3.9 ± 0.3 and 2.5 ± 0.2 nm to S2 and S13 samples heated at 850 and 750°C , respectively. Further verification of the nanoparticles dilution inside silica matrix was obtained through the analysis of X-ray fluorescence measurements wavelength dispersive (see Figure 2). The quantitative analyses show that Co, Fe, Si, and O were detected in all samples and the observed proportions are in agreement with a nominal composition. The increasing in the Co and Fe concomitant with the decreasing of the Si also confirms the nanoparticles dilution inside SiO_2 matrix.

Figure 4 shows the ZFC-FC magnetization data recorded at $H = 50$ Oe over a wide temperature range ($2 \leq T \leq 300$ K) for the samples S2, S10, S13, and S20 synthesized at 850°C as well as for the samples S10, S13, and S20 synthesized at 750°C . The appearing of a peak at T_{max} in ZFC curve for an assembly of identical and non-interacting magnetic nanoparticles is clearly related with blocking effects. The insets show the first derivative of the difference between the ZFC and FC curves fitted by a log-normal function for the samples S10 and S2 heated at 750 and 850°C , respectively.

The ZFC and FC temperature dependencies presented in Figure 4 reveal the main features generally observed in superparamagnetic systems, that is, a broad maximum at T_{max} , the presence of thermal hysteresis (deviation in the ZFC-FC curves) at low temperatures, and the coincidence of the ZFC and FC curves at sufficiently high temperatures. One can observe that in both samples the dilution of ferrite nanoparticles inside the silica matrix produces a decreasing of the

TABLE I. Atomic percentage of CoFe_2O_4 samples heated at 750 and 850°C .

Samples	%Co	%Fe	%Si	%O
$T_a = 850^\circ\text{C}$				
S2	0.47	0.93	45.84	52.76
S10	2.25	4.29	42.54	50.92
S13	2.72	5.17	41.67	50.44
S20	4.49	8.67	38.28	48.56
$T_a = 750^\circ\text{C}$				
S10	1.83	3.64	43.22	51.31
S13	3.13	6.00	40.87	50.00
S20	5.88	11.20	35.76	47.16

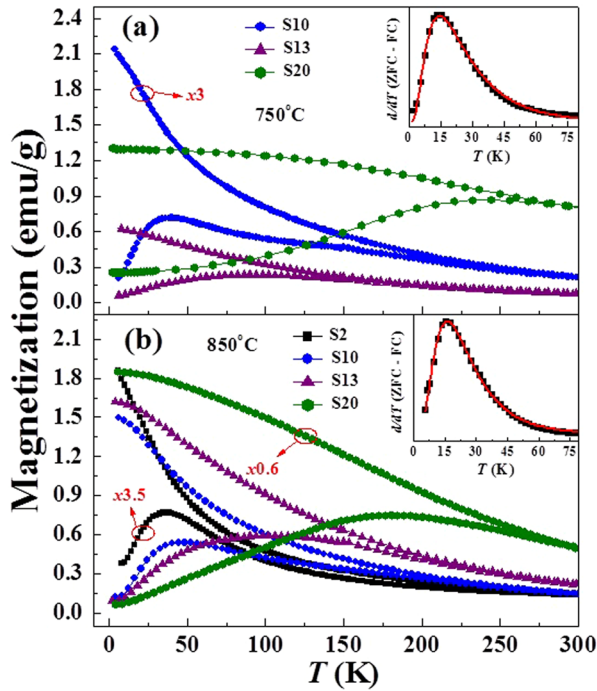


FIG. 4. ZFC-FC magnetization data measured at $H = 50$ Oe for the $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ samples heated at (a) 750 and (b) 850 °C. The insets show the first derivative of the difference between ZFC and FC curves for (a) S10 and (b) S2 heated at 750 and 850 °C, respectively, and solid red lines represent the log-normal distributions.

T_{max} . Since the derivative $d[(M_{ZFC} - M_{FC})/dT]$ ¹⁵ is proportional to the distribution of blocking temperatures $f(T_B)$, we have performed this procedure to all analyzed samples. In the inset of Figure 4, we show the results of this calculation for the S10 and S2 samples heated at 750 and 850 °C, respectively, and the respective fittings by a log-normal function. Due to the very irregular trends for samples with high particle concentrations, it is worth to comment that it was not possible to obtain of reliable fittings in such cases. In Table II, we present the estimated blocking temperature extracted from $d[(M_{ZFC} - M_{FC})/dT]$ and T_{max} . It is possible to notice that the overall effect of nanoparticle dilution is to decrease both T_B and T_{max} . The X-ray data and TEM carried out to selected samples show that there is a weak dependence of the mean

TABLE II. Values of peak of ZFC curves, T_{max} , the average blocking temperature extracted from the derivative of the difference between ZFC and FC curves, $\langle T_B \rangle$, the ratio $\beta (= T_{max}/\langle T_B \rangle)$, and the effective anisotropy constant obtained from the fits of the coercive field by using the generalized model.

Samples	T_{max} (K)	$\langle T_B \rangle$ (K)	β	$K_{eff} (\times 10^6 \text{ erg/cm}^3)$
$T = 850 \text{ }^\circ\text{C}$				
S2	36.2	22.6	1.6	1.1
S10	46.4	28.5	1.6	1.1
S13	100.6	67.4	1.5	1.0
S20	175.0	99.4	1.8	1.3
$T = 750 \text{ }^\circ\text{C}$				
S10	38.4	23.2	1.6	0.8
S13	90.7	72.1	1.2	0.8
S20	244.4	160.1	1.5	0.9

particle size with both concentration of ferrite cobalt nanoparticles inside silica matrix and synthesis temperature. The mean particle size changes from 2.5 to 3.9 nm to S13–750 °C and S20–850 °C samples, respectively. It is important to note that an estimative of the blocking temperatures using the general formula, $K_{eff}V/25k_B$ (K_{eff} = effective anisotropy constant, V = particle volume, and k_B = Boltzmann constant), is not in agreement with the experimental values. This fact can be indicating that the crescent interaction effects among the CoFe_2O_4 nanoparticles with the increasing concentration in the matrix and the broadening of particles size distribution must be taken into account.

The superparamagnetic features have also been confirmed through the measurements of MxH loops below and above T_{max} for all samples. In Figure 5, we show the MxH loops for the S20 sample heated at 850 °C in selected temperatures. In the inset, we show its coercive field as a function of temperature. It was computed by considering the average value from the negative and positive branches of the hysteresis loops.

As one can see, this sample exhibits a high value of coercive field ($H_C = 11$ kOe) at low temperatures followed by a monotonic decreasing of H_C as T increases. For samples with higher nanoparticle concentration, the M_r/M_s ratio is very close to 0.5, the value expected according to the Stoner-Wolfarth model for an assembly of noninteracting particles with uniaxial anisotropy axes randomly distributed.^{2,16} For the most diluted samples where the average distances among the nanoparticles are sufficient to prevent very strong interactions, the M_r/M_s ratio measured at $T = 5$ K is smaller than 0.5. In this sense, we argue that for samples with smaller particles concentrations, the presence of very small particles (still in the superparamagnetic state at 5 K) gives rise to lower values of the M_r/M_s ratio. The role of the size distribution and interparticle interactions on the magnetic properties of nanocrystalline CoFe_2O_4 is better evidenced through T -dependence of the coercive field. In general, for an assembly of identical and non-interacting magnetic nanoparticles, the temperature dependence of coercive field can be understood on the basis of Néel relaxation and the Bean-Livingston approaches. In this

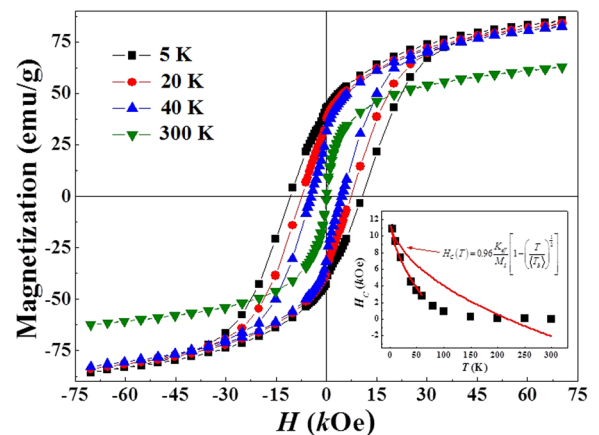


FIG. 5. MxH loops recorded at different temperatures for the sample S20 heated at 850 °C. The inset shows the temperature dependence on the coercive field. The solid lines are fittings using $H_C(T) = H_C(0)[1 - (T/T_B)]^{1/2}$ over two different temperature ranges.

scenario, the temperature dependence of the coercive field, $H_C(T)$, can be fitted by the following relation:

$$H_C(T) = 0.96 \frac{K_{eff}}{M_S} \left[1 - \left(\frac{T}{\langle T_B \rangle} \right)^{\frac{1}{2}} \right], \quad (1)$$

where, in the low temperature range, we have used an effective anisotropy constant, $K_{eff} = 10.8 \times 10^5$ ergs/cm³, a saturation magnetization, $M_S (=79.0$ emu/g) was assumed as the value of magnetization to the maximum magnetic field, and a mean blocking temperature, $\langle T_B \rangle = 99.0$ K. As one can see, such approach is in agreement with the experimental results only in the low temperatures range when most of the particles are blocked. Although this equation does not consider a size distribution, it is widely used in the study of magnetic properties of nanoparticles systems.

Because of this, we have fitted our coercive field data by using the generalized model which takes into account the temperature dependence of the average blocking temperature due to the coexistence of blocked and unblocked particles over the studied range.¹³ The coercive fields of the CoFe₂O₄-SiO₂ samples heated at 750 and 850 °C plotted as a function of temperature are shown in Figures 6 and 7, respectively. The values of $\langle T_B \rangle$ were also indicated on these figures. One must note the very good agreements between the experimental data and theoretical curves.

The existence of a broad size distribution in a real nanoparticles system causes the height of energy barriers be also broaden distributed. Since the fraction of unblocked superparamagnetic particles takes an important role on the temperature dependence of the coercive field, we applied the generalized model proposed by Nunes *et al.*¹³ to the analysis

of this magnetic property. In this model, which is a generalization of the method proposed by Kneller and Luborsky,¹⁷ the coercive field of an assembly of both (unblocked) superparamagnetic and blocked nanoparticles is given by the following expression:

$$\langle H_C \rangle_T = \frac{M_r(T)}{\chi_S + \frac{M_r(T)}{H_{CB}(T)}}, \quad (2)$$

where the remanent magnetization due to all particles in the blocked regime at the measurement temperature T is given by

$$M_r(T) = \alpha M_S \int_T^{\infty} f(T_B) dT_B. \quad (3)$$

As previously discussed, the blocking temperature distribution $f(T_B)$ can be numerically evaluated from the experimental data of FC and ZFC magnetization for each measurement temperature T by considering the following proportionality:

$$f(T_B) \propto \frac{d}{dT} [M_{ZFC} - M_{FC}]. \quad (4)$$

In Eq. (2), the coercive field considering only to the blocked particles can be written as follows:

$$H_{CB}(T) = \alpha \frac{2K_{eff}}{M_S} \left[1 - \left(\frac{T}{\langle T_B \rangle_T} \right)^{\frac{1}{2}} \right], \quad (5)$$

where the average blocking temperature $\langle T_{BT} \rangle_T$ depends on the measurement temperature T , since its calculation takes

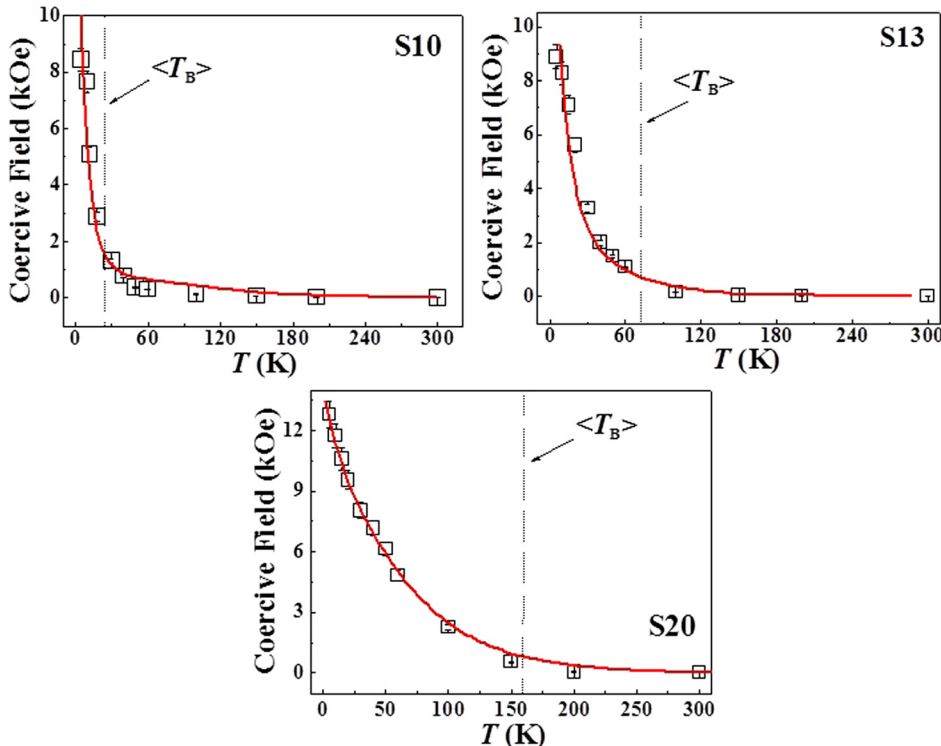


FIG. 6. Temperature dependence of the coercive field for the CoFe₂O₄-SiO₂ samples heated at 750 °C. The solid lines represent the fitting by using the generalized model.

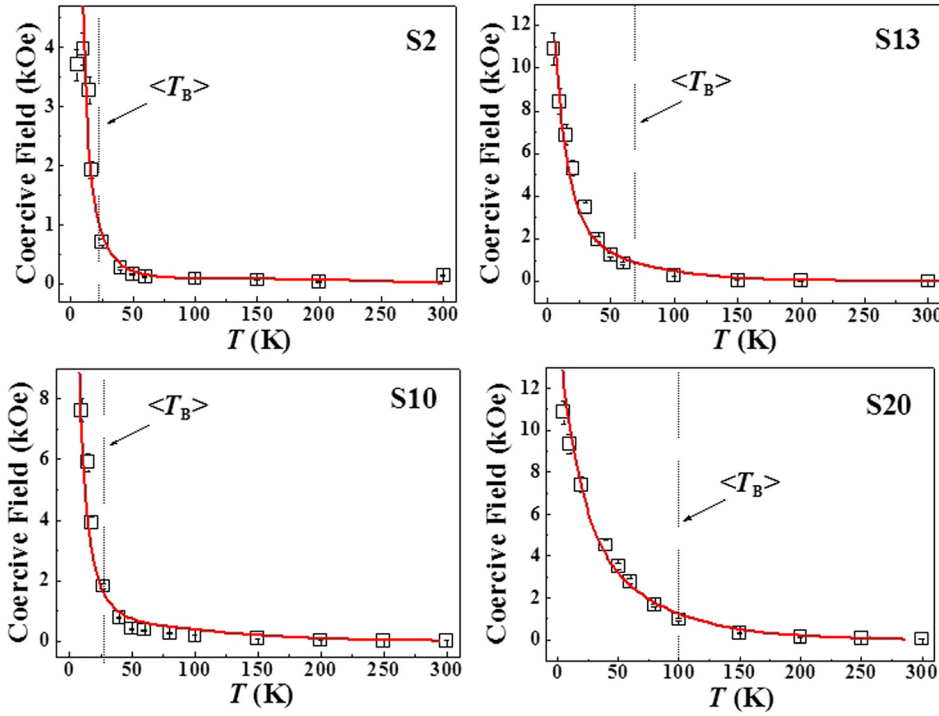


FIG. 7. Temperature dependence of the coercive field for the $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ samples heated at 850°C . The solid lines represent the fitting by using the generalized model.

into account only particles whose blocking temperatures are higher than T , i.e., particles in the blocked regime. Therefore, this quantity can be numerically evaluated for each value of T by using the following expression:

$$\langle T_B \rangle_T = \int_T^\infty T_B f(T_B) dT_B / \int_T^\infty f(T_B) dT_B. \quad (6)$$

By setting $T = 0$ in the above equation (Eq. (6)), all particles in the system are considered in the blocked regime. Thus, one should notice that, by definition, $\langle T_{BT} \rangle_T \equiv T_B$.

The parameter α in Eqs. (3) and (5) depends on the degree of orientation of particles¹³ (in the present case, one adopted $\alpha = 0.48$) and χ_S in Eq. (2) is the sum of the magnetic susceptibility attributed to the non-interacting (paramagnetic) free spins present in the matrix ($C=0$) and the superparamagnetic susceptibility attributed to the particles in the unblocked regime. Such quantity is given by

$$\chi_S = \frac{C}{T} + \frac{25M_S}{3k_B T} \int_0^T T_B f(T_B) dT_B. \quad (7)$$

As shown in Figure 4, there is a complete overlap of ZFC and FC curves at $T=300\text{K}$, showing that there is no longer any blocked particle at room temperature. The numerical procedures employed to compute Eqs. (2)–(7) for each value of T can be carried out by using the integration and differentiation tools available in a computer software like the Microcal Origin¹⁸ or similar. Alternatively, a procedure written in MATLAB was recently proposed for this purpose.¹⁹

One can notice in Figures 6 and 7 that our experimental data of coercive field are excellently fitted by using the generalized model previously explained. Such results enable us to state that the contribution of superparamagnetic (unblocked) particles and the temperature dependence of average blocking temperature are very important to correctly describe the

coercive field of the present system of CoFe_2O_4 nanoparticles in a wide temperature range. In Table II, we show the values of T_{max} , $\langle T_B \rangle$ (extracted of the first derivative of the difference between ZFC and FC curves), β (obtained from the ratio $T_{max}/\langle T_B \rangle$), and the effective anisotropy constant, K_{eff} , extracted from the best fits by using the generalized model. Keeping in mind that the effect of particles size distribution is to produce a shift of the maximum in the ZFC curve toward higher temperatures with typical values of β between 1.5 and 2.0.⁵

As one can see, the effective anisotropy constant is almost concentration independent and a value smaller than the bulk cobalt ferrite ($K_{bulk} = 1.8\text{--}3.0 \times 10^6$ ergs/cm³ (Ref. 20)) was obtained. It is important to say that, in general, the effective anisotropy constant increases with the decreasing of the nanoparticles size.²¹ However, our MxH data show that the M_r/M_s ratio measured at $T=5\text{K}$ is around 0.5 for samples with higher CoFe_2O_4 nanoparticles concentrations. This is coherent with the presence of weak magnetic interactions among nanoparticles. On the other hand, some works in literature^{15,22} show that ferrite materials at nonmetric level give rise a high degree of cationic disorder of Fe^{3+} and divalent metal between tetrahedral and octahedral sites as compared with the same materials in bulk form. In the particular case of inverse spinel structure of cobalt ferrite, the migration of cobalt ions from octahedral to tetrahedral sites seem to be the most important feature responsible by the decreasing of the anisotropy constant of CoFe_2O_4 nanoparticles.¹⁵

IV. CONCLUSIONS

In summary, we have successfully obtained $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ nanocomposites via the sol-gel method. Different concentrations of CoFe_2O_4 nanoparticles inside silica matrix were confirmed via X-ray, TEM, and X-ray fluorescence

measurements. Once the coercive does not presented a decay with the square root of temperature, the ZFC-FC data and the MxH loops allow us to analyze the coercivity by using a generalized model which takes account the contribution of both superparamagnetic and blocked particles to the coercive field. The occurrence of particle size distributions in the studied samples was considered by introducing a temperature dependent average blocking temperature. The use of such approach becomes important in order to describe the coercive field in a wide temperature range. The lower values of the anisotropy constant observed in the nanometric phase in comparison to that reported in the literature for the bulk material can be interpreted as a consequence of both the migration of the Co^{2+} from octahedral to tetrahedral sites.

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