Role of magnetic interparticle coupling on the field dependence of the superparamagnetic relaxation time

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Magnetic properties of Co-SiO_2 granular films are displayed and explained by means of a phenomenological model that takes into account the effects of magnetic interparticle coupling on the superparamagnetic relaxation behavior. The model is based on the analysis of coupled nanoparticles through a modified random anisotropy model that takes into account the concentration and size of the nanoscopic particles, as well as the field dependence of the correlation length. The proposed model leads to an accurate description of the field dependence of the blocking temperature, substantially better than the power law usually employed to describe noninteracting particles.

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Interest on magnetic nanoparticles has increased in recent years due to their intriguing scientific properties and potential applications in many important fields.[1] The relaxation time, a fundamental quantity of these systems that describes how rapidly the magnetization reversal of the particles occurs by thermal activation, can be expressed as,[2]

$$\tau = \tau_0 \exp(KV/k_BT), \tag{1}$$

where the characteristic time constant τ_0 is usually taken in the range $10^{-11}-10^{-9}$ s, k_B is the Boltzmann constant, K is the uniaxial anisotropy constant, V is the particle volume, and T is the temperature. The product KV represents the energy barrier between two easy directions. There is a critical temperature, at a given observation time (τ_{obs}), called blocking temperature T_B, given by[3]

$$T_B = \frac{KV}{\ln(\tau_{obs}/\tau_0)k_B}, \tag{2}$$

below which the magnetization of an assembly of identical single-domain particles is blocked (it presents hysteresis);[4] on the contrary, above T_B the assembly exhibits a superparamagnetic behavior.[5]

The effect of external magnetic field on the blocking temperature for uniaxial magnetic systems has been analyzed by several authors.[5,6] A simple analytical expression is usually employed,

$$T_B(H) = \frac{KV}{k_B \ln(\tau_{obs}/\tau_0)}\left[1 - \frac{H}{H_K}\right]^{\alpha}, \tag{3}$$

where H_K is the anisotropy field ($H_K = 2K/M_S$, M_S being the saturation magnetization) and the exponent α is close to 1.5.[7,8]

Equations (1)–(3) form the base of the study of single-domain particles-based materials, but they are strictly valid for noninteracting systems. A detailed understanding of the effects of interparticle interactions and of the subsequent modification of those equations represents one of the most difficult, but important, tasks of the renewed interest in magnetic nanoparticle systems.

We have developed a simple modification of the random anisotropy model (RAM) that takes into account the concentration and size of the nanoparticles as well as the field dependence of the correlation length. By doing so we provide a quantitative analytical expression relating individual and collective properties of nanoparticle systems for a wide range of concentrations.

We have systematically measured the magnetic properties of a batch of $Co_x(SiO_2)_{1-x}$ samples with Co volume concentrations $x=0.28$, 0.45, and 0.52, respectively. The samples with thicknesses of $\approx$600 nm were produced by cosputtering deposition onto Kapton substrates, preparation details can be found elsewhere.[9] Magnetization measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer in the temperature range 5–300 K. Small angle x-ray scattering (SAXS) experiments were performed at room temperature in the transmission mode at the SAXS Beamline of the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil; a wavelength of 1.756 nm was used, and a 60 cm long camera allowed us to measure SAXS intensity in a scattering vector range of $0.01291 \leqslant q \leqslant 0.49263$ Å^{-1}. Transmission electron microscopy (TEM) images were taken with a JEOL-1030 microscope operating at 300 kV (1.7 Å resolution) at the LNLS. The TEM characterization revealed that the films are granular, with Co nanoparticles having a mean diameter of 3.2 nm for the $x=0.28$ and of 3.9 nm for $x=0.45$, with a hexagonal close packed (hcp) crystalline structure. We use SAXS in order to obtain a more accurate nanostructural analysis, since the area illuminated by the beam contains 10^{19} particles cm^{-3}.[10] Figure 1 shows the spectra corresponding to the samples with $x=0.28$ and $x=0.52$, respectively, measured at room temperature. A hard-sphere model was employed to fit the peaks at $q \approx 0.24$ Å^{-1} for $x=0.28$ and $q \approx 0.15$ Å^{-1} for $x=0.52$, produced by spatial coherence among nanoparticles.[11] The fitted parameters are shown in Fig. 1 and the consequent estimated mean diameters of the systems are displayed in Table I. It is worth noting, however, that SAXS and TEM results display a remarkable good agreement in describing the behavior of mean particle size vs. concentration (see Table I).

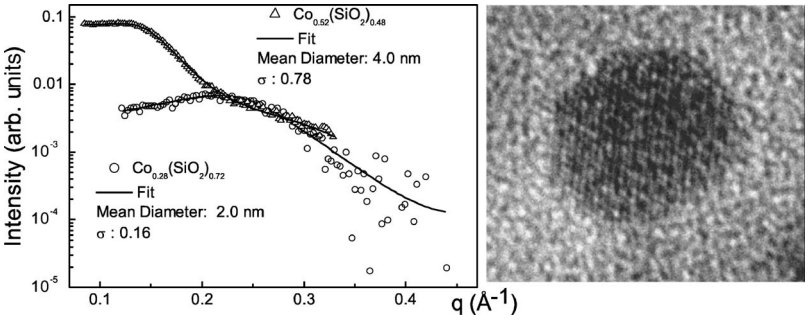

FIG. 1. Left: Section of the SAXS spectrum corresponding to $Co_x(SiO_2)_{1-x}$ (x=0.28 and 0.52) samples. σ is the Gaussian distribution width, fitted by means of the procedure described in Ref. 9. Right: High-resolution transmission electron miscroscopy (TEM) image of a sample with x =0.28. Planes {0110} and {0111} are seen.

Figure 2(a) shows a representative example of the temperature dependence of zero-field cooled (M_{ZFC}) and field cooled (M_{FC}) magnetization measured for all samples (applied field H_{DC}=20 Oe). From the shape of the M_{ZFC} and M_{FC} curves it can be inferred that in such systems the dipolar interactions are the dominant ones.[12] In a superparamagnetic system of noninteracting identical particles, the peak of the M_{ZFC} curve is strongly related to T_B. In real systems, the distribution of T_B ($f(T_B)$) can be calculated as the temperature derivative of the difference between the M_{FC} and M_{ZFC} magnetizations ($d[M_{FC}-M_{ZFC}]/dT$), easily estimating the mean blocking temperature $\langle T_B \rangle$.[13,14] As a first approach, we tried to relate $\langle T_B \rangle$ to the volume calculated from SAXS data in the framework of noninteracting superparamagnetic approach by using Eq. (2) and $\ln(\tau_{obs}/\tau_0)=25$. This analysis can give a misleading value of the anisotropy (about 5 times that of bulk Co) since it does not consider the interaction effects in the volume effective value.[14,15] An estimation of both K and V can be obtained by studying the field dependence of the blocking temperature.

Figure 2(b) shows the M_{ZFC} and M_{FC} curves for the x =0.45 sample for different applied fields. Similar curves were obtained for the other samples. The T_B distributions obtained at different applied fields are shown in Fig. 3. Figure 3(b) shows that the normalized width of $f(T_B)$ appears to be universal, at least for $H_{DC}<500$ Oe, thus reinforcing the existence of only one structural phase in the sample.[16] Although some authors have used Eq. (3) with modified exponents to describe the field dependence of $\langle T_B \rangle$,[6,7] in our case this procedure results in a rather poor fit. As an example, the dashed-dotted lines in Fig. 4 are the results of the best fits by using α=1.5, K and the particle diameter D as free parameters, and the M_S of bulk Co (1420 emu/cm^3). As it can be observed in Table I (uncoupled particles model), the D values obtained from the fits are much larger than the D values obtained by the SAXS analysis; on the other hand, the K values estimated through the fit turn out to be well below those of bulk Co.

A different approach to take into account the interaction effects on the field dependence of $\langle T_B \rangle$ can be carried out in the framework of the RAM. According to this model, the anisotropy is averaged to an effective value K_{eff} within the correlation length due to the magnetic interactions, whose value decreases with increasing correlation length due to a statistical random walk effect.[17] However, some difficulties arise when the RAM is applied to systems of nanoparticles. (i) The model was developed to be used for amorphous and nanocrystalline materials or nanoparticles embedded in a ferromagnetic matrix,[17,18] and, consequently, modifications are required if it is to be applied to nanoparticles in a nonmagnetic matrix, basically taking into account the microstructure in terms of the nanoparticles volume fraction x and the fact that dipolar interactions dominate the process.[19] (ii) The field dependence of the correlation length and of the effective particle volume and anisotropy should also be considered.[20]

The relevant parameters for the magnetization processes of a system of ferromagnetically correlated particles, with correlation length L, are the effective anisotropy and the effective volume of the particles (Λ) in the correlation volume (L^3). Two simple modifications of the RAM expressions for K_{eff} and Λ that account for point (i) are

$$K_{eff}=\frac{K}{\sqrt{N}}, \quad \Lambda=\frac{\pi}{6}[D^3+x(L^3-D^3)], \tag{4}$$

Where N is the number of correlated particles, i.e,

TABLE I. Experimentally measured particles size (SAXS and TEM) and fitting parameters obtained by means of the uncoupled particles model (Eq. (3)) and the modified RAM (Eq. (8)).

	Results obtained by different studies					
			Uncoupled particles model		Coupled particles model	
Sample	SAXS D (nm)	TEM D (nm)	D (nm)	K (erg/cm^3)	L_0 (nm)	K (erg/cm^3)
$Co_{0.28}(SiO_2)_{0.72}$	2.0	3.2	1.0	1.7×10^6	6	5.8×10^6
$Co_{0.45}(SiO_2)_{0.55}$	3.1[a]	3.9	9.4	0.6×10^6	13.7	3.2×10^6
$Co_{52}(SiO_2)_{0.48}$	4.0	4.6[a]	12.0	0.5×10^6	18.3	2.4×10^6

[a]Values estimated from size-concentration curves.

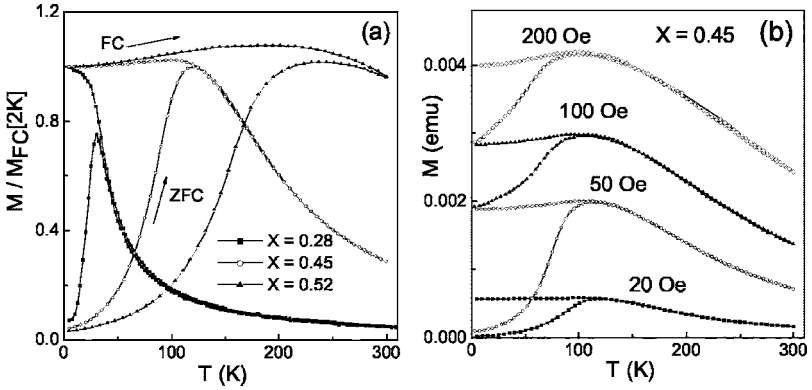

FIG. 2. Magnetization as a function of temperature after zero field cool (ZFC) and field cool (FC) for all samples and an applied field $H_{DC}=20$ Oe, (a) for $x=0.45$ and different applied fields (b).

$$N=\left[1+x\frac{(L^3-D^3)}{D^3}\right]. \tag{5}$$

Both expressions tend, respectively, to the anisotropy and volume of an individual particle when interactions are very weak and $L\rightarrow D$; on the other hand, when $L\gg D$, they tend to the usual relations used in the study of correlated particles systems (see Refs. 15 and 18).

Regarding point (ii), a recent work by Michels *et al.*[20] evidenced, by means of small-angle neutron scattering, that the correlation length of Ni and Co electrodeposited nanocrystals decreases with increasing applied field. This result is reasonable, since L is a measure of the average distance over which magnetization fluctuations are correlated.[21] The experimentally observed correlation length can be expressed as a function of the applied field as

$$L_H=D+\sqrt{\frac{2A_{\mathrm{eff}}}{M_S H_{DC}}}, \tag{6}$$

where A_{eff} represents the interaction intensity which, for nanocrystalline alloys, is the intergranular exchange constant A.[22] This expression adequately explains the near saturation asymptotic behavior ($H^{-1/2}$) predicted by the micromagnetic theory,[23] which was derived under small magnetization misalignment conditions, thus being valid for the M_{ZFC} measurements near T_B in our experiments. However, Eq. (6), in principle, presents a divergence at zero field, which we have overcome by adding a parameter C to the denominator, yielding a similar field dependence expected for high field range[23]

$$L_H=D+\sqrt{\frac{2A_{eff}}{M_S H_{DC}+C}}, \tag{7}$$

This new expression still presents the previously mentioned asymptotic behavior for high fields, while it tends to the initial correlation length or cluster size at zero applied field ($L_0=L(H=0)=D+\sqrt{2A_{eff}/C}$). Observe that using A_{eff} value of particles clustered together, the parameter C should give the variation of the interaction intensity with particle concentration.

By substituting the anisotropy and volume of individual particles in Eq. (3) by the effective anisotropy and particle volume, K_{eff} and Λ, respectively, one can calculate the field dependence of the blocking temperature for coupled particles in terms of the structural parameters of nanoparticulate systems:

$$T_B=\frac{K\pi[D^3+x(L_H^3-D^3)]}{6k_B\ln(\tau_{obs}/\tau_0)[1+x(L_H^3-D^3)/D^3]^{1/2}}\times\left[1-\left(\frac{H_{DC}M_S[1+x(L_H^3-D^3)/D^3]^{1/2}}{2K}\right)\right]^{1.5} \tag{8}$$

We have used this expression to fit the experimental data of Fig. 4. The fits, represented by the solid lines, were carried out by using the experimental D values (previously estimated by SAXS), $M_S=1420$ erg/cm^3 (the bulk Co value) and $A=3.1\times10^{-7}$ erg/cm^{-1},[24] and K and C as free parameters. Expression (8) provides a very good description of the field dependence of T_B of all our samples by employing K_{eff} values of the order of magnitude of the bulk anisotropy of Co and in agreement with its expected particle size dependence,[25] as shown in Table I. Furthermore, the C val-

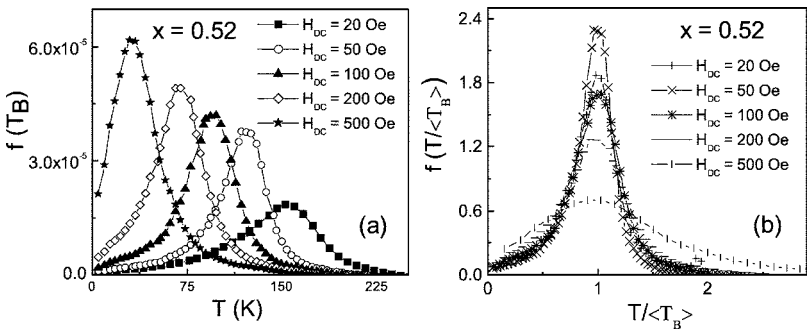

FIG. 3. Blocking temperature distribution obtained from ZFC and FC curves obtained at various magnetic fields: (a) as obtained and (b) presented in a normalized scale.

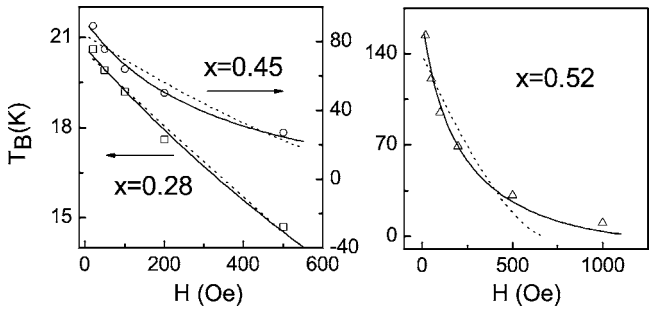

FIG. 4. Field dependence of the blocking temperature for all samples. Fits by using Eq. (3) (dashed-dotted line) and the modified RAM expression, given by Eq. (8) (solid line).

ues employed in the fit lead to L_0 values that are consistent with its expected concentration dependence, i.e. they increase with increasing Co concentration.

It is worth noting that interactions compete with the magnetic anisotropy and the external field in determining the orientation of the particle moments. Different models can be used to analyze their effects: the RAM supplies a reasonable description of the behavior of these systems when intergranular exchange dominates;[17,23] on the other hand, the analytical models that account for the effects of dipolar interactions are usually valid only in the small concentration limit.[26] While dipolar interactions are always present in granular systems, intergranular exchange can occur when grains are dispersed in a metallic matrix via polarization of the conduction electrons. There is considerable evidence that both kinds of interactions can make a collection of individual superparamagnetic moments behave as a collective magnetic system.[8,27,28] The specific collective state induced by the interactions in a given system depends on its structural features—mainly particle concentration and size distribution—and on the nature of the matrix (metallic or insulating). In the case of granular systems with just dipole-dipole interactions, there is evidence that small closed flux structures can appear.[8,29] There are also strong indications of the presence of correlations among the particles with a characteristic length longer than the particle size.[13,28,30] In the specific case of granular Co-SiO_2 films, ferromagnetic-like correlations have been experimentally found both by direct (small-angle neutron scattering) and indirect (magnetoresistance and magnetization) measurements.[13,14,30] Independent of the mechanism responsible for the interparticle coupling in nonpercolated systems, the existence of a ferromagnetic correlation suggests the existence of an effective (averaged) anisotropy,[17] and consequently, our model can be applied.

In conclusion, we have developed an extension of the RAM that can be used to describe the magnetic behavior of granular systems in terms of their structural features, allowing a quantitative analysis of the field dependence of the blocking temperature. We have used this novel approach to study a set of $Co_x(SiO_2)_{1-x}$ samples with concentrations in the range $0.28 < x < 0.52$. An excellent agreement was obtained by using fitting parameters with meaningful physical values, which are not easily estimated through conventional procedures. We believe that the proposed phenomenological model can be extended to other nanocrystalline systems, because it does not depend on the specific coupling mechanism.

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