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ABSTRACT

Magnetic effects caused by dipolar interactions in single-domain magnetic ensembles at finite temperatures are described. A modified superparamagnetic approach based on the mean field theory and random anisotropy model has been developed to describe the magnetization curves of nanoparticle assemblies. The model was used to fit experimental zero-field-cooled and field-cooled magnetization curves in Fe3O4 nanoparticles embedded in paraffin. The fitting parameters were based on structural properties of the materials and the strength of the interactions between nanoparticles. The model provides a quantitative description of the effects of the nanoparticle interaction with good agreement with the experiment. In addition, the model was adapted to describe magnetic properties of a NiFe thin film patterned into a nanodot array, showing potential to be used as a framework to predict magnetic interaction effects in high-density 2D arrays such as bit patterned media.

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I. INTRODUCTION

Magnetic nanoparticles have shown great potential for applications in many fields of science and technology.1–3 Experimental studies of these systems have revealed that magnetic interactions between nanoparticles often play an important role in their collective behavior. However, the theoretical description of magnetic behavior for single-domain systems is often based on a superparamagnetic framework that neglects interaction effects. Such interactions can be manifested through exchange, indirect exchange, Ruderman-Kittel-Kasuya-Yosida (RKKY), or dipole-dipole interactions.4 In fact, deviations between the magnetization expected from a superparamagnetic model and experimental data have been reported even for very dilute nanoparticle systems.4–6

Experimental and modeling studies indicate that the magnetic response of single-domain assemblies is characteristic of coupled reversal of clusters of nanoparticles with an effective volume that exceeds the physical volume of the particles.7,8 For example, in particulate or thin film magnetic recording media, there are features in the noise spectra that are consistent with the formation of chains or clusters of particles with a common magnetization direction.6–11 Interactions are also expected to play a role in the behavior of high-density bit patterned media in which one bit of information is stored in an individual nanostructure in close proximity to its neighbors.

Interactions influence not only the measured switching field distribution but also the temperature-dependent magnetic stability.12–14 Interaction effects may be identified by analysis of the blocking temperature obtained from AC or DC magnetization curves.6,15 Nevertheless, there is still a lack of modeling approaches that are able to predict and describe the macroscopic magnetic behavior such as the zero-field-cooled (ZFC) and field-cooled (FC) curves that are widely used to characterize single-domain magnetic systems.

In this paper, we present magnetic measurements of two different nanomagnet systems: iron oxide nanoparticles embedded in paraffin and a patterned film consisting of FeNi nanodots. We observe that the FC curve is considerably affected by interactions between nanoparticles even for highly dilute samples (lower than 0.05 vol. % of iron oxide). Increasing the concentration of nanoparticles leads to an increase of the temperature at which the ZFC curve exhibits a maximum. The FeNi nanodots exhibit magnetic behavior similar to that observed for samples with high concentrations of nanoparticles.
We propose a phenomenological model to describe the observed interaction effects on the magnetization curves that accounts for the behavior of all the samples in this study. To achieve this end, we compared experimental data with predictions of the superparamagnetic model and adapted the model to describe the effects of the magneto-static interactions. Even for the more dilute nanoparticle system of this study, deviations between the experimental data and the superparamagnetic model are observed. In this case, a simple inclusion of an effective interaction field within the mean field approximation was found to be quite appropriate. However, this model is unable to express the increase in the magnetic stability temperature with increasing interaction strength. Thus, a further modification is performed to include the possibility that neighboring nanoparticles reverse together, i.e., the nanoparticles are magnetically correlated within a volume that depends on the interaction strength. Each group of coupled nanoparticles is considered to behave as an effective nanoparticle with volume and anisotropy that can be obtained by a simple adaptation of the random anisotropy model (RAM). Our model provides a quantitative analytical expression relating the individual and collective properties to the magnetization curves of nanoparticle systems for a wide range of concentrations.

II. EXPERIMENTAL

Magnetic iron oxide nanoparticles capped by an oleylsarcosine surfactant were prepared by colloidal synthesis. The oleylsarcosine covers the FeO4, which limits agglomeration and permits a good dispersion of the particle in nonpolar solvents like toluene, hexane, and paraffin. Details of the sample preparation and structural characterization have been reported elsewhere. The as-synthesized nanoparticles are mainly composed of Fe, but the slow oxidation process leads to a disordered nanocrystalline Fe oxide. Mössbauer spectroscopy showed that the majority of magnetic phase resembles magnetite, Fe3O4. Images obtained by transmission electron microscopy (TEM) revealed spherical nanoparticles with a mean diameter $D_{TEM} = 7.1$ nm and a very narrow size distribution $\sigma_{TEM} = 0.08$. The small angle x-ray scattering (SAXS) analysis gave $D_{SAXS} = 7.3$ nm, similar to TEM, but a larger size distribution $\sigma_{SAXS} = 0.17$. In the quantitative analyses performed here, we have used the size distribution obtained by SAXS since its data are obtained from a larger volume of material. The TEM size distribution is likely an underestimate because particles of similar size tend to aggregate during dispersion on the TEM grid.

To evaluate the dipolar magnetic interactions, we studied samples with different concentrations of Fe3O4 nanoparticles dispersed in paraffin. The dilution was performed just above the paraffin melting point and followed by sonication. The solution has uniform color and a good stability even when the paraffin was liquid, indicating uniform dispersion. The mass concentrations of the colloidal samples were 0.05%, 0.5%, 5%, and 45%. Considering the paraffin and Fe3O4 densities of 0.9 g/cm$^3$ and 5.17 g/cm$^3$, respectively, the volume fraction ($x$) was 0.0087%, 0.087%, 0.91%, and 12.5%, respectively. For comparison, a powder sample was made without paraffin. Its volume fraction $x$ was estimated considering the average spacing between nanoparticles ($\sim 4.4$ nm) leading to $x \sim 31.5$.

A sample of magnetic dots made from a thin film of Ni$_{50}$Fe$_{50}$ was made using block copolymer lithography. A sputtered NiFe film was coated with a polystyrene-b-polydimethylsiloxane block copolymer, which was annealed and subsequently etched to produce oxidized polydimethylsiloxane dots on the surface that serve as an etch mask. Ion beam etching in Ar was used to transfer the pattern into NiFe. The resulting sample consisted of locally close-packed dots of NiFe with an average diameter of 3.14 nm, thickness of 18.6 nm, and center-to-center spacing of 38.6 nm.

ZFC and FC (at 20 Oe) magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL7). Fits were performed with a weighted least-squares fit method and assuming that each data point provides equally precise information about the deterministic part of the total process variation, i.e., the standard deviation of the error term is constant over all values of the variables.

III. RESULTS AND DISCUSSION

A. Signature of magnetic interactions in colloidal nanoparticles

Figure 1 shows the ZFC and FC magnetization curves obtained for samples of Fe3O4 nanoparticles with mass concentrations of 0.05%, 0.5%, 5%, 45%, and the Fe3O4 powder sample. For the most dilute sample (0.05%), the distance between particles is very large ($\approx 150$ nm), and, therefore, it is expected that magnetic interactions have negligible effects on the magnetic behavior of this sample. Therefore, we fit the ZFC and FC curves using the superparamagnetic model that is described in the Appendix [Eqs. (A5) and (A6)], considering the average diameter and the distribution of size obtained by SAXS, the temperature dependence of saturation magnetization is given by $M_s(T) = M_s(T = 0) \left(1 - T/T_{C}^{FeO_4}\right)^{1/2}$, where $M_s = 490$ emu/cm$^3$ and $T_0 = T_{C}^{FeO_4} = 800$ K as the saturation magnetization and Curie temperature of bulk Fe3O4, respectively. Magnetic anisotropy was treated as a fitting parameter, yielding a value of $K = (3.75 \pm 0.03) \times 10^3$ erg/cm$^3$. The fitting results are shown in Fig. 1 (dashed-dotted black lines). The superparamagnetic model offers a good description of the ZFC curve for the most dilute sample, but there is a deviation between the fitting curve and the FC data, mainly at lower temperatures ($<50$ K) where the magnetization of the sample is high and the superparamagnetic model (SPM) overestimates the magnetization. Many authors have attributed such deviations to magnetic interactions between the nanoparticles since the superparamagnetic model does not consider magnetic interactions. For example, Bender et al. found that 10 nm diameter superparamagnetic iron oxide formed clusters with sizes on the order of 70 nm.

Figure 1 shows that as the concentration of nanoparticles increases, so does the temperature where the ZFC magnetization is maximum and the low-temperature range where the FC curves flatten out. We conclude that although the superparamagnetic model describes the ZFC magnetization curve of the highly dilute sample quite well, it does not fit well to either of the ZFC or FC magnetization curve for samples with higher nanoparticle concentrations.

B. Interaction model

To better describe the experimental results, we propose a modification of the superparamagnetic model based in the mean field theory. We consider the existence of a mean interaction field.
$H_{\text{int}}$ affecting all particles whose magnitude is proportional to the magnetization of the sample

$$H_{\text{int}} = H_{\text{int}}^0 \frac{M(H, T)}{M_{\text{max}}},$$

where $H_{\text{int}}^0$ is the maximum mean field interaction value and $M_{\text{max}} = 25M_s^2H_{\text{DC}}/3KT$ is a normalization factor that we assume is equal to the maximum value of the FC magnetization curve for a superparamagnetic system. Therefore, if an external magnetic field $H_{\text{DC}}$ is applied, the nanoparticles will be subject to an effective field $H_{\text{eff}}$ given by the sum of the external applied field and the mean interaction field $H_{\text{int}}$, i.e.,

$$H_{\text{eff}} = H_{\text{DC}} + H_{\text{int}}.$$  

Replacing $H_{\text{DC}}$ by $H_{\text{eff}}$ in Eqs. (A5) and (A6) (see the Appendix) shows that the magnetization does not have a trivial analytical solution. To solve this equation, we use an iterative method where at least three iterations were needed to obtain a good convergence for all curves studied in this work.

Inserting the mean field interaction $H_{\text{int}}$ into the superparamagnetic model, it was possible to fit the ZFC and FC curves of the most dilute sample, shown by the dashed blue line in the upper panel of Fig. 1. The adjustable parameters were $K = (3.74 \pm 0.04) \times 10^5$ erg/cm$^3$ and $H_{\text{eff}}^0 = -(6.3 \pm 0.2)$ Oe. Therefore, by including the mean field interaction, it is possible to describe the reduction of the magnetization observed at low temperatures for the FC curves compared to the superparamagnetic prediction. The part of the data most affected by the inclusion of an interaction field is exactly the range with the highest magnetization value, which validates the use of relation (1).

Although this modification to the superparamagnetic model is able to describe the ZFC and FC data of the highly diluted sample, it does not work very well to fit the magnetization curves of samples with higher concentrations of nanoparticles, shown by the dashed blue lines in Fig. 1. The mean field interaction fails to describe the increase of the energy barrier (the temperature where the ZFC curves exhibit a maximum) as the nanoparticle concentration increases, as reported by several authors.23–25

It is well established that the large effective dipole moments of nanoparticles can result in cooperative magnetic behavior when the nanoparticles are densely packed, even leading to a ferromagnetic domain structures observed in cases such as monolayers of ordered nanoparticles or nanoparticles within a SiO$_2$ matrix.25 Nunes et al.25 developed a phenomenological model that assumes a ferromagnetic coupling between nanoparticles to describe the dependence of the average blocking temperature on the interaction. This model was based on the random anisotropy model, originally developed to explain the ferromagnetic properties of amorphous ferromagnets.27–29

The authors considered the existence of ferromagnetic coupling of nanoparticles within a distance $L$ (called the correlation length) that depends on the magnetic field and according to a relation obtained from small angle neutron scattering data30

$$L = D + \sqrt{\frac{2A_{\text{eff}}}{M_s(H_{\text{DC}} + C)}},$$

where $D$ is the average diameter of the particles and $A_{\text{eff}}$ is an interaction intensity parameter describing how strongly the particles can be coupled, which for amorphous ferromagnets is the exchange stiffness. Parameter $C$ is a constant field introduced to eliminate the divergence of $L$ when the magnetic field goes to zero.30 When $H_{\text{DC}} = 0$, we have an initial correlation length

![FIG. 1. Experimental and fitted ZFC and FC magnetization curves for Fe$_3$O$_4$ nanoparticles diluted in paraffin with concentrations of 0.05%, 0.5%, 5%, 45%, and the powder sample (from top to bottom). The dashed-dotted black line is the fitting of the experimental results using the superparamagnetic model (SPM). The dashed blue lines are the fitting curves considering the existence of a mean interaction field between the nanoparticles. The solid red lines are the fitting curves considering the mean interaction field as well as magnetic correlations between nanoparticles. Data used with permission from Phys. Rev. B 72, 184428 (2005). Copyright 2005 American Physical Society.](Image)
\[ L_0 = L_{BD(C=0)} = D + \sqrt{2A_{eff}/M_C} \]  

depends on the interaction strength and magnetic history.

Here, we will use Eq. (3), replacing \( H_{BD} \) by \( H_{eff} \). In this case, the temperature dependence of the effective field \( H_{eff} \) from Eq. (2) will generate a temperature dependence for \( L \) so that the highest value of \( L \) will occur at the temperature at which the ZFC curve exhibits a maximum. Such behavior was observed in a neutron scattering experiment on Co nanoparticles in a SiO\(_2\) matrix\(^\text{21}\) but was not taken into account in the original model.

When the magnetization of the nanoparticles is correlated by the effects of \( H_{int} \), the system still preserves its superparamagnetic properties but with particle volume and anisotropy now corresponding to the group of interacting particles. This represents a renormalization based on the parameters of the cluster: the effective magnetic anisotropy \( K_{eff} \) and effective nanoparticle volume \( V_{eff} \). These are related to the individual nanoparticle parameters \( (V \text{ and } K) \) by the relations

\[ K_{eff} = \frac{K}{\sqrt{N}}, \quad V_{eff} = \frac{\pi}{6} D^3 N, \quad N = 1 + x \left( \frac{L^3 - D^3}{D^3} \right), \quad (4) \]

where \( N \) is the number of correlated particles in each group and \( x \) is the volume fraction of magnetic nanoparticle in the matrix.

Based on the above, the correlated energy barrier for coupled nanoparticles \( (K_{eff} V_{eff}) \) and the effective blocking temperature \( (T_{int}) \) can be calculated by replacing the energy barrier of an individual particle in Eq. (A3) by the parameters of the cluster

\[ T_{int} = \frac{\pi K D^4}{150 k_B} \sqrt{N} \left[ 1 - \frac{H_{eff} M_S \sqrt{N}}{2K} \right]^2, \quad (5) \]

Experimental curves obtained from interacting single-domain magnetic systems can be fitted using this value of \( T_{int} \), and taking \( H_{eff} = H_{BD} + H_{int} \).

### C. Magnetization curve fitting

The interacting nanoparticle model described above was fitted to experimental ZFC and FC curves of Fe\(_3\)O\(_4\) samples at different concentrations. We considered the renormalized parameters for blocking temperature [Eq. (5)] and the effective field [Eq. (2)] in the superparamagnetic approach [Eqs. (A5) and (A6)]. We assumed the saturation magnetization value of \( M_s = 490 \text{ emu/cm}^3 \) and \( T_{BD} = T_{FSB} = 800 \text{ K} \) for bulk Fe\(_3\)O\(_4\); we fixed the average diameter as the value obtained by SAXS \( (D = 7.3 \text{ nm}) \) and the external applied field \( H_{BD} = 20 \text{ Oe} \). The anisotropy \( K \) and exchange stiffness \( A_{eff} \) were regarded as free parameters only in the fitting for the powder sample, which yields values of \( K = 3.2(0.5) \times 10^6 \text{ erg/cm}^3 \) and \( A_{eff} = 7.7(5.6) \times 10^{-7} \text{ erg/cm} \), respectively. These values were assumed fixed in the fitting process of samples with lower concentrations. Therefore, we fitted the other samples \((x = 0.05 \text{ to } x = 45\%)\) using only three parameters: \( C, \ H_{int} \), and \( \sigma_{eff} \). Table I shows the best fit parameters obtained from fitting the interacting model to the ZFC and FC curves of Fe\(_3\)O\(_4\) nanoparticles. The red lines in Fig. 1 are the best fit curves. The model fits the experimental ZFC and FC curves very well for all the values of nanoparticle concentration in this study. The previously published model that addresses the interactions between nanoparticles considering the random anisotropy model is able to describe the variation of the average blocking temperature as a function of the external applied magnetic field.\(^\text{1} \) However, considering the mean interaction field together with the random anisotropy model in the present work, it was possible to describe all properties of the ZFC and FC curves from the structural data of the nanoparticles.

The best fit values for both \( C \) and \( H_{int} \) increase with the particle concentration. \( C \) is positive and \( H_{int} \) is negative, which means that field \( C \) has the same direction as the external applied field \( H_{BD} \) and \( H_{int} \) has the opposite direction. Sankar et al.\(^\text{1} \) have shown by neutron scattering that the groups of ferromagnetically correlated nanoparticles are arranged in a closed flux configuration in order to minimize the stray field. Therefore, \( C \) may be associated with dipolar interactions between neighboring nanoparticles, while \( H_{int} \) is associated with a demagnetizing field acting between groups of nanoparticles. These two parameters, therefore, relate to dipolar interactions, which are the only type of magnetic interaction between the nanoparticles.

In order to provide insight into the proposed interacting model, we show in Fig. 2(a) the number of correlated particles \( N \) at 0 K as a function of particle concentration \((x_{v})\) acquired by fitting the interacting model [Eqs. (2), (5), (A5), and (A6)] to the ZFC and FC magnetization curves. \( N \) is almost independent of the magnetization measurement mode (ZFC or FC) and increases with the particle concentration. Also, we show in Fig. 2(c) the distribution of effective blocking temperature \((f(T_{int}))\) determined from the model. The width of the effective energy barrier distribution \((\sigma_{eff})\) as a function of \( N \) has a minimum, shown in Fig. 2(b). We can see that groups of correlated nanoparticles with the same number of nanoparticles in each, \( N \), it is expected that the width of the distribution of the effective energy barrier will decrease according to \( \sigma_{eff} \sim \sqrt{N} \). However, in a real system, the number of correlated particles is not the same for all groups, i.e., there is a distribution \((f(N))\) that affects \( \sigma_{eff} \). This behavior is more evident when the number of correlated nanoparticles increases. This effect may explain the increases observed for \( \sigma_{eff} \) for larger \( N \) in Fig. 2(b).

We also study the effect of interactions on the temperature dependence of the coercive field \( H_C \) of the Fe\(_3\)O\(_4\) nanoparticles. Figure 3 shows \( H_C \) curves as function of the temperature for different Fe\(_3\)O\(_4\) nanoparticle concentrations (5%, 45%, and the powder sample).

The coercive field vs temperature curve, \( H_C(T) \) of an assembly of single-domain particles can be calculated from their distribution.

| Sample | \( C \) (Oe) | \( H_{int} \) (Oe) | \( \sigma_{eff} \) | \( N \) |
|--------|-------------|-----------------|-----------------|-----|
| 0.05%  | 0 ± 4       | -10.4 ± 0.1     | 0.29 ± 0.01     | 1.6 |
| 0.5%   | 20 ± 1      | -10.6 ± 0.2     | 0.31 ± 0.04     | 3.1 |
| 5%     | 95 ± 1      | -12.5 ± 0.1     | 0.25 ± 0.01     | 6.1 |
| 45%    | 692 ± 8     | -13.4 ± 0.1     | 0.27 ± 0.01     | 8.2 |
| Powder | 759 ± 19    | -16.0 ± 0.2     | 0.41 ± 0.03     | 17.4 |
of blocking temperatures according to the model described in Ref. 21. Here, we use this model to fit experimental $H_c(T)$ curves of the Fe$_3$O$_4$ nanoparticles using two different effective distributions of blocking temperature $f(T_{B_{eff}})$. First, we calculated $f(T_{B_{eff}})$ resulting from the ZFC analysis using the interacting model described in Sec. III B. $H_c$ calculated from $f(T_{B_{eff}})$ in the interacting model fails to match the experimental data of all the samples, shown in the red dashed lines in Fig. 3. $H_c$ obtained from the fitting process overestimates the experimental values, indicating that $f(T_{B_{eff}})$ obtained from the ZFC and FC curves has a higher average blocking temperature than the $H_c$ experimental data, as also observed by Nunes et al. 21 We also fitted $H_c$ vs $T$ curves considering $H_{int}$ as the only free parameter for each sample. The values for these samples are shown in Table II. The adjusted $H_{int}$ values exceed those obtained from ZFC/FC curves, indicating that the $H_c$ vs $T$ curve has a distribution of energy barriers different from that associated with the ZFC/FC curves.

For an assembly of single-domain magnetic particles, the interaction effects depend on the history of the magnetization state of the system.21 In the ZFC (FC) measurement, the sample is cooled at zero (small) external applied field, and the measurement starts when the magnetization is not well oriented. In contrast, the $H_c$ data are obtained starting from the saturated state. Therefore, the prior state of magnetization of the ZFC/FC measurements differs from that of the $H_c$ measurements, and according to Eq. (2), the internal interaction field of the two curves is expected to be different. This assumption is confirmed by comparing the $H_{int}$ values with the $H_{int}$ values shown in Tables I and II.

D. 2-Dimensional nanodot array

We have applied our phenomenological model to study the interaction effects on a NiFe (Ni$_{50}$Fe$_{50}$) nanodot array. The morphology of the nanodots can be seen from the top-view and cross-section SEM images shown in the left column of Fig. 4. The particles are circular in shape with a domelike height profile and are arranged in a two-dimensional close-packed pattern with structural correlation length of order 10 periods. The distributions of particle diameters and heights are shown in the right column of Fig. 4. The top-view SEM image shows a narrow distribution of diameters ($\sigma = 0.11$) following a Gaussian distribution with an average value of $D = 31.4 \text{ nm}$. An estimate of the average center-to-center distance is $d = 38.6 \text{ nm}$, and the fractional surface coverage of metal is $x = 0.60$. The analysis from the cross-section SEM image resulted in an average height of $h = 18.6 \text{ nm}$ and a distribution width of $\sigma = 0.19$.

Figure 5(a) shows the ZFC and FC magnetization curves of the nanodots measured under an external magnetic field of 50 Oe applied parallel to the substrate. The ZFC exhibits a maximum around 230 K. The FC magnetization curve deviates from superparamagnetic behavior, exhibiting a decrease of magnetization as the temperature decreases below the maximum of the ZFC curve. In order to describe this behavior observed for ZFC and FC magnetization curves, we adapt the interacting model to consider interactions in two dimensions. In this case, $N$ should be written as

$$N = 1 + x \left( \frac{L^2 - D^2}{D^2} \right).$$

\( \text{FIG. 2.} \) (a) Number of correlated nanoparticles, $N$, obtained from the ZFC and FC fitting as a function of concentration of Fe$_3$O$_4$ nanoparticles. (b) Width of the distribution of the effective energy barrier $\sigma_{eff}$ as a function of $N$. (c) Distribution of effective blocking temperature $f(T_{B_{eff}})$. The solid red line in (b) shows $\sigma_{eff}/\sqrt{N}$. J. Appl. Phys. 126, 173905 (2019); doi: 10.1063/1.5125595

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Since the particles have a semiellipsoidal shape with height $h$ and diameter $D$, the effective magnetic volume of correlated particles will be given by

$$V_{\text{eff}} = N \frac{2\pi}{3} h D^2,$$

(7)

and based on Eqs. (6) and (7), the blocking temperature for this system will be

$$T_{\text{Beff}} = K \frac{2\pi}{75k_B} \sqrt{NhD^2} \left[ 1 - \frac{H_{\text{Beff}}M_S}{2K} \right]^{1/2}.$$

(8)

Considering the blocking temperature described by Eq. (8) and the internal field $H_{\text{int}}$ due to interactions [Eq. (2)] in the Eqs. (A5) and (A6), we obtain a modified expression based on the superparamagnetic model to describe the ZFC and FC magnetization curves. We fitted this interacting model to the ZFC and FC magnetization curves, using the structural parameters obtained by SEM images, the saturation magnetization measured from the magnetization curve at 10 K ($M_S = 300$ emu/cm$^3$), and the magnetization vs temperature dependence used in Sec. III B with $T_0 = 800$ K (Curie temperature of bulk Ni$_{50}$Fe$_{50}$). The measured $M_S$ is assumed to be

| Sample  | $H_{\text{Beff}}$ (Oe) |
|---------|-------------------------|
| 5%      | 91 ± 6                  |
| 45%     | 407 ± 15                |
| Powder  | 186 ± 76                |

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reduced from its bulk value due to surface oxidation of the nanodots; by using the bulk $M_S$, a lower particle volume is inferred. Finally, we assumed $H_{int}$, $C$, $A_{eff}$, $K$, and $\sigma_{eff}$ were free parameters of the fitting. The interacting model gave a good match to the experimental data for both ZFC and FC magnetization curves over the temperature range, as shown in Fig. 5. The best fit values were $K = 2.0(1) \times 10^4$ erg/cm$^3$, $\sigma_{eff} = 0.33(1)$, $C = 2300(300)$ Oe, and $A_{eff} = 8(2) \times 10^{-7}$ erg/cm.

In order to check the consistency of the proposed model, some of the parameters obtained from the ZFC and FC curve fitting were used in the analyses of the $H_k$ vs temperature behavior of the nanodots. The experimental data and the fitted curve using the model described in Ref. 21 are shown in Fig. 5(b). The fit was performed considering $H_{int}$ and the anisotropy field $H_k$ as free parameters, which yields $H_{int} = 450(20)$ Oe and $H_k = 1430(120)$ Oe. Considering this value of $H_k$ and assuming that the easy axes of magnetization of the nanodots are randomly oriented, we can estimate the anisotropy energy for this system using the Stoner-Wohlfarth model. This gives $K = 3.8 \times 10^5$ erg/cm$^3$, which is one order of magnitude higher than the $K$ value obtained from the ZFC and FC analysis. This result may be due to the fact that the reversal of particles does not take place as a fully coherent rotation of the magnetization, as found, for example, in 30 nm diameter Ni particles.33

IV. CONCLUSIONS

We have developed a phenomenological model that describes the ZFC and FC magnetization of an ensemble of single-domain magnetic particles from the superparamagnetic to superferromagnetic state. The magnetization curves are described in terms of the structural parameters of individual single domain particles, allowing a quantitative analysis of the interaction over a wide range of particle concentration. We show that the interaction can be described by an internal magnetic field that is proportional to the magnetization and that correlated reversal of particles is also important in these systems. We observed that the interaction depends on the temperature and the magnetic history, making the effective blocking temperature distribution different for the ZFC and FC curves and with different characteristics of the size distribution. We show that magnetic correlations between the single-domain particles affect the magnetization properties of Ni$_{50}$Fe$_{50}$ nanodots in a two-dimensional array. We also insert a dependence of the correlation length on temperature and give physical insight into the fitting parameters.

APPENDIX: NONINTERACTING NANOPARTICLE SYSTEMS

Single-domain magnetic systems have been treated as undergoing uniform rotation according to the classical Stoner-Wohlfarth (SW) model.34 The particle has two low-energy states in which the magnetization is oriented along the direction of the easy axis. These states are separated by an energy barrier $\Delta E$, which can be approximated by $KV$, where $K$ is the anisotropy constant and $V$ is the particle volume. The relaxation time $\tau$ is strongly dependent on $\Delta E$ and temperature $T$ and can be described as35

$$\tau = \tau_0 \exp KV/k_BT,$$

(A1)

where the characteristic time constant $\tau_0$ is usually taken in the range of $10^{-11}$ to $10^{-9}$ s and $k_B$ is the Boltzmann constant. When $k_BT \ll KV$, the particle is blocked, and when $k_BT \gg KV$, $\tau$ is small and the particle is superparamagnetic. The temperature which separates the two regimes, called the blocking temperature $T_B$, is dependent on the observation time $\tau_{obs}$ as follows:

$$T_B = \frac{KV}{k_BT_0 \ln \left(\tau_{obs}/\tau_0\right)},$$

(A2)

where $\tau_{obs} = 100$ s is a typical measurement time used in magnetization measurements.

An external applied field $H_{DC}$ also affects the blocking temperature of a single-domain nanoparticle by changing the energy.
A simple expression is usually considered

$$T_B(H_{DC}) = \frac{KV}{k_B \ln (\tau_{fB}/\tau_0)} \left[ 1 - \frac{H_{DC}}{H_k} \right]^\alpha,$$  \hspace{1cm} (A3)

where $H_k$ is the anisotropy field ($H_k = 2K/M_b$, $M_b$ being the saturation magnetization) and the exponent $\alpha$ is close to 1.5.\(^{30,38}\)

However, in any real fine particle system, there is a distribution of particle sizes and, therefore, a distribution of blocking temperatures $f(T_B)$ with width $\sigma$. The distribution is generally assumed to be Gaussian and can be written as

$$f(T_B) = \frac{1}{\sqrt{2\pi}\sigma T_B} \exp \left[ - \frac{(T_B - T)^2}{2\sigma^2} \right].$$  \hspace{1cm} (A4)

Therefore, we can describe a typical temperature dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetization measurements, neglecting interaction effects among the particles as\(^{49}\)

$$M_{ZFC}(H_{DC}, T) = \frac{25M_b^2H_{DC}}{3K} \int_0^T T_B^2 f(T_B) dT_B,$$

$$+ \frac{25M_b^2H_{DC}}{3K} \int_T^\infty T_B^2 f(T_B) dT_B,$$  \hspace{1cm} (A5)

$$M_{FC}(H_{DC}, T) = \frac{25M_b^2H_{DC}}{3K} \int_0^T T_B^2 f(T_B) dT_B,$$

$$+ \frac{25M_b^2H_{DC}}{3K} \int_T^\infty T_B^2 f(T_B) dT_B.$$  \hspace{1cm} (A6)

where $\Omega = \int_0^\infty T_B^2 f(T_B) dT_B$ and $T$ is the absolute temperature.

Equations (A1)–(A6) form the base of the study of single-domain particle assemblies, but they are valid only for noninteracting nanoparticles. Interparticle interactions require nontrivial modifications of the model.

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REFERENCES

1. Q. Pankhurst, D. Ucko, L. Barqui, and R. Calderón, "Non-dipolar magnetic coupling in a strongly interacting superparamagnet: Nanogranular $Fe_{30}Co_{20}Al_{15}Ag_{40}$," J. Magn. Magn. Mater. 266, 131–141 (2003).
2. A.-H. Lu, E. L. Salabas, and F. Schüth, "Magnetic nanoparticles: Synthesis, protection, functionalization, and application," Angew. Chem. Int. Ed. 46(8), 1222–1224 (2007).
3. M. Knobel, W. Nunes, A. Brandl, J. Vargas, L. Socolovsky, and D. Zanchet, "Interaction effects in magnetic granular systems," Physica B 354, 80–87 (2004).
4. S. Mørup, M. F. Hansen, and C. Frandsen, "Magnetic interactions between nanoparticles," Beilstein J. Nanotechnol. 1, 182 (2010).
5. M. Hansen and S. Mørup, "Models for the dynamics of interacting magnetic nanoparticles," J. Magn. Magn. Mater. 184(1), L262–L274 (1998).
6. J. Vargas, W. C. Nunes, L. M. Socolovsky, M. Knobel, and D. Zanchet, "Effects of dipolar interaction observed in iron-based nanoparticles," Phys. Rev. B 72, 184428 (2005).
7. A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutter, and G. Thomas, "Giant magnetoresistance in heterogeneous Cu-Co alloys," Phys. Rev. Lett. 68, 3745–3748 (1992).
8. W. C. Nunes, L. M. Socolovsky, J. C. Denardin, F. Cebollada, A. L. Brandl, and M. Knobel, "Role of magnetic interparticle coupling on the field dependence of the superparamagnetic relaxation time," Phys. Rev. B 72, 212413 (2005).
9. H. N. Bertram, Theory of Magnetic Recording (Cambridge University Press, 1994), Vol. 25, no. 6.
10. L. Thurlings, "Statistical analysis of signal and noise in magnetic recording," IEEE Trans. Magn. 16, 507–511 (1980).
11. L. L. Nunnelly, D. E. Heim, and T. C. Arnoldussen, "Flux noise in particulate media: Measurement and interpretation," IEEE Trans. Magn. 32(2), 1767–1775 (1996).
12. O. Jihua, W. C. Nunes, N. M. Áimon, and C. A. Ross, "Magnetostatic interactions in self-assembled $Co_{x}Ni_{1-x}Fe_{3}O_{4}/BiFeO_{3}$ multiferroic nanocomposites," ACS Nano 10(4), 7657–7664 (2016).
13. T. Aign, P. Meyer, S. Lemerle, J. P. Jamet, J. Ferré, V. Mathet, C. Chappert, J. Gierak, C. Vieu, F. Rousseaux, H. Launois, and H. Bernas, "Magnetization reversal in arrays of perpendicularly magnetized ultrathin dots coupled by dipolar interaction," Phys. Rev. Lett. 81, 5656–5659 (1998).
14. M. Pardavi-Horvath, G. Vertesy, B. Keseru, Z. Vertesy, and R. D. McMichael, "Switching mechanism of single domain particles in a two-dimensional array," IEEE Trans. Magn. 35(5), 3871–3873 (1999).
15. T. Holence, "On the frequency dependence of the transition temperature in spin glasses," Solid State Commun. 35(2), 113–117 (1980).
16. K.-H. Tu, W. Bai, G. Liontos, K. Ntetsikas, A. Averopoulos, and C. A. Ross, "Universal pattern transfer methods for metal nanostructures by block copolymer lithography," NanoTechnology 26(37), 375301 (2015).
17. F. Hochepied and M. P. Pilieni, "Magnetic properties of mixed cobalt-zinc ferrite nanoparticles," J. Appl. Phys. 87(5), 2472–2478 (2000).
18. D. Levy, R. Giustetto, and A. Hoser, "Structure of magnetite $(Fe_3O_4)$ above the Curie temperature: A cation ordering study," Phys. Chem. Miner. 39(2), 169–176 (2012).
19. J. C. Denardin, A. L. Brandl, M. Knobel, P. Panissod, A. B. Pakhomov, H. Liu, and X. X. Zhang, "Thermoremanence and zero-field-cooled/field-cooled magnetization study of $Co_8(SiO_2)_x$ granular films," Phys. Rev. B 65, 064422 (2002).
20. D. Cangussu, W. C. Nunes, H. L. D. S. Corrêa, W. A. A. D. Macedo, M. Knobel, O. L. Alves, A. G. S. Filho, and I. O. Mazali, "$Fe_3O_4$ nanoparticles dispersed in porous ycor glass: A magnetically diluted integrated system," J. Appl. Phys. 105(1), 013901 (2009).
21. W. C. Nunes, F. Cebollada, M. Knobel, and D. Zanchet, "Effects of dipolar interactions on the magnetic properties of $yFe_3O_4$ nanoparticles in the blocked state," J. Appl. Phys. 99(8), 08N705 (2006).
22. P. Bender, E. Wetterskog, D. Honecker, J. Fock, C. Frandsen, C. Moerland, L. K. Bogart, O. Posth, W. Szczerska, H. Gavilán, R. Costa, M. T. Fernández-Díaz, D. González-Alonso, L. Fernández Barquín, and C. Johansson, "Dipolar-coupled moment correlations in clusters of magnetic nanoparticles," Phys. Rev. B 98, 224420 (2018).
23. W. C. Nunes, W. S. D. Folly, J. P. Sinnecker, and M. A. Novak, "Temperature dependence of the coercive field in single-domain particle systems," Phys. Rev. B 70, 014419 (2004).
24. Z. Mao, D. Chen, and Z. He, "Equilibrium magnetic properties of dipolar interacting ferromagnetic nanoparticles," J. Magn. Magn. Mater. 320(19), 2335–2338 (2008).
25. J. L. Dormann, D. Fiorani, and E. Tronc, "Magnetic relaxation in fine-particle systems," Adv. Chem. Phys. 98, 283–494 (1997).
26. K. Yamamoto, S. A. Majetich, M. R. McCartney, M. Sachan, S. Yamamuro, and T. Hirayama, "Direct visualization of dipolar ferromagnetic domain structures in Co nanoparticle monolayers by electron holography," Appl. Phys. Lett. 93(8), 082502 (2008).
27. G. Herzer, "Soft magnetic nanocrystalline materials," Scr. Metall. Mater. 33(10), 1741–1756 (1995).
28. R. Alben, J. J. Becker, and M. C. Chi, "Random anisotropy in amorphous ferromagnets," J. Appl. Phys. 49(3), 1653–1658 (1978).
29. A. Hernando, P. Marín, M. Vázquez, J. M. Barandiarán, and G. Herzer, "Thermal dependence of coercivity in soft magnetic nanocrystals," Phys. Rev. B 58, 366–370 (1998).
30. A. Michels, R. N. Viswanath, J. G. Barker, R. Birringer, and J. Weissmüller, "Range of magnetic correlations in nanocrystalline soft magnets," Phys. Rev. Lett. 91, 267204 (2003).
31. S. Sankar, A. Berkowitz, D. Dender, J. Borchers, R. Erwin, S. Kline, and D. J. Smith, "Magnetic correlations in non-percolated Co-SiO2 granular films," J. Magn. Magn. Mater. 221(1–2), 1–9 (2000).
32. R. C. Dorf, The Electrical Engineering Handbook (CRC Press, 1993).
33. C. A. Ross, R. Chantrell, M. Hwang, M. Farhoud, T. A. Savas, Y. Hao, H. I. Smith, F. M. Ross, M. Redjdal, and F. B. Humphrey, "Incoherent magnetization reversal in 30-nm Ni particles," Phys. Rev. B 62, 14252–14258 (2000).
34. E. C. Stoner and E. P. Wohlfarth, "A mechanism of magnetic hysteresis in heterogeneous alloys," Phil. Trans. R. Soc. Lond. A 240(826), 599–642 (1948).
35. L. Néel, "Influence des fluctuations thermiques sur la aimantation de grains ferromagnétiques très fins," Comp. Ren. Heb. San. Acad. Sci. 228(8), 664–666 (1949).
36. W. Wernsdorfer, E. B. Orozco, K. Hasselbach, A. Benoit, B. Barbara, N. Demoncy, A. Loiseau, H. Pascard, and D. Mailly, "Experimental evidence of the Néel-Brown model of magnetization reversal," Phys. Rev. Lett. 78, 1791–1794 (1997).
37. Y. D. Zhang, J. I. Budnick, W. A. Hines, C. L. Chien, and J. Q. Xiao, "Effect of magnetic field on the superparamagnetic relaxation in granular Co-Ag samples," Appl. Phys. Lett. 72(16), 2053–2055 (1998).
38. H. Victoria, "Predicted time dependence of the switching field for magnetic materials," Phys. Rev. Lett. 63, 457–460 (1989).
39. M. Respaud, J. M. Broto, H. Rakoto, A. R. Fert, L. Thomas, B. Barbara, M. Verdel, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. O. Ely, C. Amiens, and B. Chaudret, "Surface effects on the magnetic properties of ultrafine cobalt particles," Phys. Rev. B 57, 2925–2935 (1998).