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Evidence of random magnetic anisotropy in ferrihydrite nanoparticles based on analysis of statistical distributions

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We show that the magnetic anisotropy energy of antiferromagnetic ferrihydrite depends on the square root of the nanoparticles' volume, using a method based on the analysis of statistical distributions. The size distribution was obtained by transmission electron microscopy, and the anisotropy energy distributions were obtained from ac magnetic susceptibility and magnetic relaxation. The square root dependence corresponds to random local anisotropy, whose average is given by its variance, and can be understood in terms of the recently proposed single phase homogeneous structure of ferrihydrite.

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I. INTRODUCTION

The relation between structural and magnetic properties is important from the point of view of applied and fundamental research. This relation is not straightforward in systems with antiferromagnetic (AF) interactions and reduced dimensionality or size as in nanoparticles. In these systems, surface effects and disorder play an important role and, therefore, deviations from the superparamagnetic (SP) canonic behavior are expected. Such effects change the relation between anisotropy energy E_a, volume V, and magnetic moment μ found for typical SP systems, for which E_a and μ are proportional to V. This is also the case of ultrathin films, where anisotropy energy is proportional to surface area, leading to a perpendicular magnetization. An important contribution from surface anisotropy is also found in SP nanoparticles with ferromagnetic interactions, where surface atoms constitute a relevant fraction of the total atoms.[1] Another example of nonproportionality between E_a and V is two-dimensional Co nanostructures, where E_a was found to depend on the perimeter.[2]

The deviations from the proportionality between V and μ found in AF nanoparticles are associated with the fact that, in these systems, the net magnetic moment arises from the uncompensated and/or canted moments, μ_{un}, that may be present at the surface, throughout the volume, or both. The relation between μ_{un} and V reflects the origin of the moments. In particular, Néel showed that μ_{un} is proportional to V^q with $q=1/2$ for moments randomly distributed in the volume, 1/3 for moments randomly distributed in the surface, and 2/3 for moments distributed throughout the surface in active planes.[3] In ferritin, a protein where Fe^{3+} is stored as ferrihydrite, q was estimated to be of the order of $q=1/2$,[4,5] or to be between 1/2 and 1/3 (Ref. 6) based on magnetization measurements. These values were obtained either by using a system with a given size and estimating the power relation between the total number of ions and the equivalent uncompensated number of ions,[4,6] or by the usual comparison of systems with different average sizes.[5] The latter approach is limited by the possibility of synthesizing identical systems with different average volumes that usually covers less than 1 order of magnitude. An alternative approach that takes advantage of the size distribution is developed here. A sample with a wide distribution can be regarded as one system containing a set of different average sizes. A method reminiscent of this approach was first used by Luis *et al.*[1] for the determination of the origin of magnetic anisotropy in Gaussian size-distributed Co nanoparticles. They concluded that surface anisotropy has an important contribution, since the E_a distribution is narrower than the V distribution. The effect of size distributions on the magnetic properties was used later by Rusponi *et al.*[2] to study two-dimensional Co structures. The idea was based on the fact that the shape of the in-phase component of the ac susceptibility χ' was critically dependent on the chosen distribution, namely, surface, perimeter, and perimeter plus surface distributions. The authors concluded that the perimeter atoms were those relevant to the reversal process in the Co structures, i.e., E_a depends on the perimeter. Gilles *et al.*[7] also tried to use susceptibility curves to obtain the relation between μ_{un} and V in ferritin, but found out that their experimental curves were not very sensitive to the particular shape of distribution nor the value of q. In a different context, the luminosity and the size distributions of rare-earth-doped nanoparticles were used to establish the relation between luminosity and size through the size dependent optical detection probability.[8]

In this paper, we show that lognormal distributed nanoparticle samples are particularly useful to study the relation between a physical property and size. This is based on the fact that when two physical quantities are related by a power function, the power factor can readily be obtained by comparing the respective lognormal deviations, due to reproductive properties of the lognormal distribution function.[9] This method is of general use and can simply be applied to cases where the size of the system determines a given physical property by a power law relation, as in the optical properties of quantum dots.[10] In the present context of magnetism, we apply this approach to AF ferrihydrite nanoparticles grown in a hybrid matrix to investigate the relation between E_a and V.

II. MODEL

A. Relation between distributed quantities

As pointed out in the previous section, in AF nanoparticles there is no *a priori* established relation between V and μ_{un}. At the same time, E_a and V may also not be proportional. One may, however, expect that generally

$$E_a = \alpha V^p, \tag{1}$$

where p can be different from 1. In a given situation where the average values $\langle V\rangle$ and $\langle E_a\rangle$ of one sample are known, it is impossible to determine α and p simultaneously. Their determination is usually carried out by comparing samples with different $\langle V\rangle$, considering that α and p are constant in all of the samples. Here, we show how to determine α and p by using magnetic studies on a lognormal distributed sample. The probability distribution of E_a, $f(E_a)$, is a function of the V probability distribution $g(V)$ as follows:

$$f(E_a) = g(V)/(dE_a/dV). \tag{2}$$

If $g(V)$ is a lognormal distribution function with parameters s_V and n_V defined as

$$g(V) = \frac{1}{V s_V \sqrt{2\pi}} \exp - \left[\frac{[\log(V/n_V)]^2}{2 s_V^2} \right], \tag{3}$$

then $f(E_a)$ is given by

$$\begin{aligned} f(E_a) &= \frac{1}{\alpha p (E_a/\alpha)^{(p-1)/p}} \frac{1}{(E_a/\alpha)^{(1/p)} s_V \sqrt{2\pi}} \\ &\quad \times \exp - \left[\frac{\{\log[(E_a/\alpha)^{(1/p)}/n_V]\}^2}{2 s_V^2} \right] \\ &= \frac{1}{E_a s_E \sqrt{2\pi}} \exp - \left[\frac{[\log(E_a/n_E)]^2}{2 s_E^2} \right], \end{aligned} \tag{4}$$

with

$$n_E = \alpha n_V^p,$$

$$s_E = p s_V, \tag{5}$$

where s_E and s_V are the standard deviations of the distribution of $\log(E_a)$ and $\log(V)$, respectively, while $\exp(n_E)$ and $\exp(n_V)$ are the means of the distribution of $\log(E_a)$ and $\log(V)$ (which are normal distributions). From Eq. (4), it is evident that if V represents a lognormal distribution; all other physical quantities that can be related to V by a power relation [Eq. (1)] are also lognormal distributed. More importantly, when comparing V and E_a, the ratio between the distribution parameters s_E and s_V is a direct measure of the power p, while the relationship between n_E and n_V gives information about α [Eq. (5)]. Therefore, the relation between V and E_a in one sample can quantitatively be derived knowing the lognormal distribution of V and E_a. As one might expect, this method can be used to determine the relation between any two physical quantities related by a precise power law similar to Eq. (1).

The relations expressed in Eqs. (4) and (5) constitute a particular case of the reproductive properties of the lognormal distribution function.[9] In general, if X_i are independent random variables having lognormal distribution functions with parameters n_i and s_i [as defined in Eq. (3)], their product $Y=c\Pi X_i^{b_i}$ (with b_i and $c>0$ being constants) is also lognormal distributed, with $s_Y=\Sigma b_i s_i$ and $n_Y=c\Sigma n_i^{b_i}$.[9] In general, reproductive properties can be used in the analysis of an output whose inputs are lognormal distributed, as, for instance, in a quantitative analysis of human information processing during psychophysical tasks.[11] However, in this paper, they are used in the context of physical properties of nanoparticles.

Although many physical properties of interest such as size are often lognormal distributed, many others are better characterized by other functions. This is the case of the anisotropy energy, which is often described by a gamma distribution.[12–15] The gamma function can be expressed by

$$f(x) = \frac{b^{-a} x^{a-1}}{\Gamma(a)} \exp - \left(\frac{x}{b} \right), \tag{6}$$

with the average of x given by ab and the variance by $\sigma = ab^2$. For $a>1$, the gamma distribution is similar to the lognormal function, so that the use of the latter function, in the case where the gamma distribution is more suitable, may be a good approximation. Therefore, the use of Eq. (5) may also be a good approximation to find α and p. We are presently working on a method to find these values for any distribution function.[16]

B. Anisotropy energy distribution from ac susceptibility and viscosity measurements

The relation between the out-of-phase component of the ac susceptibility χ'' and the anisotropy energy barrier distribution was derived in the context of spin glasses[17] and ferromagnetic nanoparticles with negligible dipolar interactions.[12,18] In the latter case, χ'' is often expressed in terms of a volume distribution, which is the physical source of the observed distributions. At the same time, since E_a and V are proportional, χ'' can indistinctively be expressed as a distribution of E_a or V.[13] However, in the present case, the relation between E_a and V cannot be *a priori* established, so that further care must be taken.

In the cluster model, used for spin glasses, the material is considered as a set of superparamagnetic clusters, where each cluster has a relaxation time τ and a magnetic moment, which at a small constant applied field h_0 has a value $m_0(\tau)$ at $t=\infty$.[17] χ'' can then be written as

$$\chi''(\tau,T) \simeq -\frac{\pi}{2}\frac{m_0(\tau_m)}{h_0}f(\ln\,\tau), \tag{7}$$

where τ_m is the characteristic time of measurement. For systems following the Arrhenius law $E_a=k_BT\,\ln(\tau_m/\tau_0)$, Eq. (7) can be written as

$$\chi''(\tau,T) \simeq \frac{\pi}{2}\frac{m_0(E_a)}{h_0}k_bTf(E_a), \tag{8}$$

where τ_0 is a microscopic characteristic time. In Eq. (8), it is considered that the particles contributing to χ'' at a given τ and T are mainly those with energy equal to E_a,[17] and that the parallel susceptibility is well approximated by the equilibrium susceptibility[12] [i.e., $1/\ln(\tau_m/\tau_0)\ll 1$]. It follows from Eq. (8) that χ'' is a function of E_a and, therefore, curves taken at different frequencies should scale when plotted against E_a. By considering a system composed of moments m_0 with a negligible dependence of $m_0(E_a)$ on temperature, χ''/T is a measure of the anisotropy energy distribution $f(E_a)$. An equation similar to Eq. (8) is obtained for ferromagnetic nanoparticles as follows:

$$\chi''(\tau,T) \simeq \frac{\pi M_S^2}{6K}k_BT\,\ln[1/(f\tau_0)]f(E_a), \tag{9}$$

where M_S is the saturation magnetization and K the anisotropy constant.[1,13]

Measurements of the magnetization as a function of time t (viscosity measurements) at temperatures below the blocking temperature T_B are a complementary way to investigate the anisotropy energy barrier distribution of different nanoparticle systems,[1,19–21] including ferritin.[22] With such measurements, it is possible to determine the magnetic viscosity S, defined as the change in magnetization with $\ln(t)$ of a system held under a constant applied magnetic field h. As in the case of χ'', S primarily probes relaxation times and their distribution and, in systems where the Arrhenius law holds, $M(t)$ can be expressed as a function of $f(E_a)$ as follows:

$$M(t) = \int_0^\infty p(t,E_a)f(E_a)dE_a, \tag{10}$$

with

$$p(t,E_a) = \exp[-(t/\tau_0)\exp(-E_a/k_bT)]. \tag{11}$$

By considering $p(t,E_a)$ to be a step function centered at E_a, the critical energy approximation,[19,23] S, can be written as

$$S(t,T) \equiv \frac{\partial M}{\partial\,\ln\,t} = k_BTM_0f(E_a). \tag{12}$$

A similar result is obtained in Ref. 22 in the context of antiferromagnetic ferritin, where $q(E_a)=M_0f(E_a)$ is defined as the quantity of magnetic moment per unit mass of a specific element in the system that has an energy barrier equal to E_a. So, in the present case of antiferromagnetic materials, the main difference as compared to ferromagnetic materials is that the energy distribution cannot be straightforward normalized per volume but per magnetic moment. It follows directly from Eq. (12) that S/T is proportional to the anisotropy energy distribution, $f(E_a)$, in analogy to χ''/T. In fact, S and χ'' probe the same energy barrier at different time scales.

III. EXPERIMENTAL DETAILS

Ferrihydrite is a low-crystalline AF iron oxyhydroxide that typically forms after a rapid hydrolysis of iron at low *p*H and low temperatures.[24] The structure of ferrihydrite with domain sizes ranging from 2 to 6 nm was recently described as a single phase, based on the packing of clusters, constituted of one tetrahedrally coordinated Fe atom surrounded by 12 octahedrally coordinated Fe atoms.[25] The cell dimensions and site occupancies slightly and systematically change with average domain size, reflecting some disorder and relaxation effects. This picture homogeneously extends to the surface of the domains. This model is in contrast to previous ones, where multiple structural phases were considered,[26,27] and the existence of tetrahedrally coordinated Fe atoms was a matter of debate.[28,29]

The synthesis of the ferrihydrite nanoparticles in the organic-inorganic matrix (termed di-ureasil) has been described elsewhere.[30] The particles were precipitated by thermal treatment at 80 °C after the incorporation of iron nitrate in the matrix. The sample studied here has an iron concentration of 2.1 wt% and was structurally characterized in detail in Ref. 31.

Mössbauer spectra were measured at selected temperatures between 4.2 and 40 K. A conventional constant-acceleration spectrometer was used in transmission geometry with a ^{57}Co/Rh source, using a α-Fe foil at room temperature to calibrate isomer shifts and the velocity scale. ac and dc magnetic measurements were performed in a Quantum Design superconducting quantum interference device magnetometer.

IV. RESULTS AND DISCUSSION

A. Relationship between anisotropy energy and size

The Fourier transform high resolution transmission electron microscopy (FT-HRTEM) images and x-ray diffraction (XRD) patterns show the existence of low-crystalline six-line ferrihydrite nanoparticles. The nanoparticles are homogeneously distributed, separated from each other, and have a globular habit. The size (diameter D) distribution can be described by a lognormal function, with $n_D=4.7\pm0.2$ nm and deviation $s_D=0.43\pm0.05$ (see Fig. 2).[31] As expected from

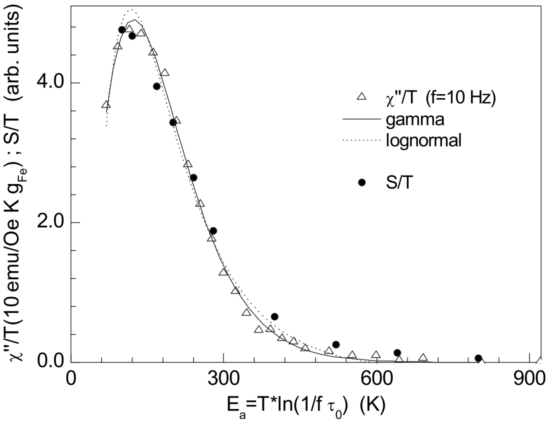

FIG. 1. Anisotropy energy distributions obtained by the out-of-phase component of ac susceptibility (χ''/T) and viscosity (S/T) measurements. Lognormal and gamma distribution fits to χ''/T data are shown.

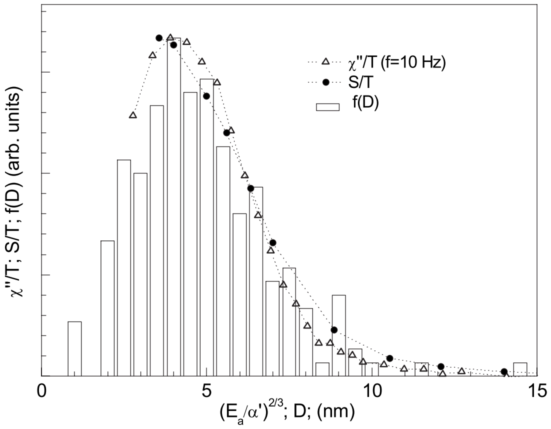

FIG. 2. Diameter distribution determined by TEM as compared to the anisotropy energy distributions obtained by χ''/T and S/T in a $(E_a/\alpha')^{2/3}$ scale, showing the scaling between $(E_a/\alpha')^{2/3}$ and D. Using other powers p' such as 3, 2, or 1 gives unsatisfactory scaling.

the reproductive properties, a lognormal size distribution results in a lognormal volume distribution.

The in-phase ac susceptibility χ' is frequency independent above T_F=30 K. The maxima of χ' follow a Néel–Arrhenius relation

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right). \qquad (13)$$

The extrapolated τ_0 is of the order of 10^{-12} s, as found in noninteracting or very weakly interacting nanoparticles.[32] As dipolar and exchange interactions become relevant, the extrapolated τ_0 decreases. For instance, similar ferrihydrite/hybrid matrix composites with more concentrated ferrihydrite nanoparticles (6.5% of iron in weight), have extrapolated $\tau_0 \approx 10^{-17}$ s.

Another evidence of the existence of negligible interactions is given by Mössbauer spectroscopy results, since interacting systems have a collapsed V-shaped pattern.[33–35] For temperatures around T_B, the spectra can be described by a simple sum of a sextet distribution and a doublet and no signs of a collapsed magnetic hyperfine field pattern. On the other hand, such a collapse is observed in the ferrihydrite/hybrid matrix sample with 6.5% of iron, where interactions are expected to be relevant. At 4.2 K, the Mössbauer spectrum of the sample studied here (2.1% of iron) shows a sextet, with a hyperfine field B_{hf}=48 T. This is characteristic of ferrihydrite nanoparticles of low crystallinity, in accordance with the FT-HRTEM and XRD results.

As described in Sec. II B, χ''/T and S/T constitute a direct measure of the anisotropy energy distribution, observed at different time scales. In Fig. 1, we can observe that the distribution obtained from χ''/T and S/T fairly superimpose, which means that Eqs. (8) and (12) are good approximations. Both χ''/T and S/T curves are well fitted by a gamma distribution function, with a=3.3 and b=53 (Fig. 1). As expected for $a>1$, the curves can also be satisfactorily fitted to a lognormal function, with $s_{\chi/T}=0.61\pm0.02$ and $\langle\chi/T\rangle=170\pm4$ K, and $s_{S/T}=0.65\pm0.02$ and $\langle S/T\rangle=176\pm4$ K, respectively. We therefore consider $s_E=0.63\pm0.04$ from the average of $s_{\chi/T}$ and $s_{S/T}$. Since $s_D=0.43\pm0.05$ and by using Eq. (5), we directly obtain the power relation between E_a and D, $p'=1.5\pm0.2$, which corresponds to $p'=3/2$, so that

$$E_a = \alpha' D^{3/2} \quad (\mathrm{K}). \qquad (14)$$

Equation (5) can be further used to determine the proportionality between E_a and $D^{3/2}$ ($\alpha'=18$ K nm$^{-3/2}$). As expected from the above equation, we observe that, in a $(E_a/\alpha')^{2/3}$ scale, distributions of both χ''/T and S/T superimpose on the diameter distribution (Fig. 2). This is a confirmation that describing χ/T and S/T by a lognormal function is a good approximation for the identification of p and α.

Equation (14) can be rewritten in terms of the particle volume as

$$E_a = \alpha V^{1/2}. \qquad (15)$$

This means that the anisotropy barriers are randomly distributed in volume. In each particle, the effective value of E_a is given by the fluctuation of local E_a. This requires that the local E_a is a random homogeneous quantity. Such homogeneity is supported by the recent structure model, (Ref. 25) since it is composed of a single phase with in-volume defects, where we can expected E_a to be locally different.

From Eq. (15), it is still possible to determine an effective anisotropy energy per volume, K_{eff}, that increases with decreasing V, following $V^{-1/2}$. In the 1–10 nm D range, K_{eff} ranges from 4.7×10^5 to 1.5×10^4 J/m^3, which are of the order of those found in the literature.[7,36] For the average size of the sample, $K_{\mathrm{eff}}=2.9\times10^4$ J/m^3.

B. Relationship between magnetic moment and size

Unlike the case of E_a, there is no direct measurement of the μ_{un} distribution. A way to obtain this distribution is to model the dependence of the magnetization on the field $M(H)$ to a given function of μ_{un} considering a μ_{un} distribution. A function usually applied to model $M(H)$ of nanoparticles is the Langevin function.[4–6,31] This is a good approximation when surface effects and anisotropy are negligible. Anisotropy effects are expected to be relevant in AF nanoparticles due to coupling between μ_{un} and the AF axis.[7,37] In AF nanoparticles, anisotropy effects have been taken into account using a Néel (Ising-type) model, considering that μ_{un} can have only the AF axis direction.[7] On the other hand, recent simulations show that $M(H)$ is greatly affected by surface effects, such that a one-spin approach as considered in the Langevin or Néel functions is a crude approximation.[38]

Despite this situation, we have previously modeled $M(H)$ by using a Langevin function[31] and found that the parameter s of the μ_{un} lognormal distribution is $s_{\mu}=0.9$, so that $q=0.7\pm0.1$ and $\mu_{un}\propto V^{2/3}$. We note that the value of q derived here is different from that estimated in Ref. 31 by comparing the average values of the equivalent number of uncompensated ions and the total number of ions ($q=1/3$). Both q values are obtained after the same fit procedure performed on the same $M(H)$ curves. The only difference is the approach for deriving q: using average values of the uncompensated moment and size or using the information about the distribution of both. This is an example of how the use of averages may lead to inaccurate estimations, since the prefactor of the power law cannot be ignored. In this scenario, the uncompensated moments were made to lie on the particle's surface, despite the fact that the energy barriers associated with the uncompensated moments are randomly distributed in volume.

At this point, one should highlight that the Langevin function with moment distribution may be too crude a description of $M(H)$ to yield a good estimation of s_{μ}, so that a different scenario is possible: having no reliable estimation of s_{μ}, we discuss the situation where the uncompensated moments are associated (proportional) with the energy barriers, so that $\mu_{un}\propto V^{1/2}$, i.e., they are randomly distributed in volume. In fact, the uncompensated moments are those contributing to the Curie-type ac susceptibility and those experiencing the blocking phenomena associated with the onset of χ'' and S. Therefore, uncompensated moments should be those relevant in determining the relation between E_a and V. Within this framework, $V^{1/2}$ may be regarded as the equivalent volume that contains the ferromagneticlike uncompensated moments. Such a relation between μ_{un} and $V^{1/2}$ was proposed for antiferromagnetic nanoparticles by Néel[3] and is consistent with magnetization measurements performed on ferritin.[4–6]

V. CONCLUSIONS

In this paper, we show that distributed samples can be used to investigate the relationship between the magnetic anisotropy barrier E_a and the nanoparticle volume V in a consistent manner. The relation is accessed by comparing the parameters of the lognormal distribution of both physical quantities. Size distribution was obtained by a transmission electron microscopy (TEM) study and E_a was obtained by two independent measurements: out-of-phase ac susceptibility and viscosity measurements. We have applied this method to a ferrihydrite nanoparticle system and found the relation between E_a and V in an antiferromagnetic material: $E_a\propto V^{1/2}$. This shows that the magnetic anisotropy barriers are randomly distributed in volume, in accordance with recent structure studies.

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