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

N. J. O. Silva, V. S. Amaral, and L. D. Carlos
Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

B. Rodríguez-González and L. M. Liz-Marzán
Departamento de Química Física, Universidade de Vigo, 36310 Vigo, Spain

T. S. Berquó and S. K. Banerjee
Institute for Rock Magnetism, University of Minnesota, Minneapolis 55455-0128

V. de Zea Bermúdez
Departamento de Química, Universidade de Trás-os-Montes e Alto Douro and CQ-VR, Quinta de Prados, Apartado 1013, 5001-911 Vila Real, Portugal

A. Millán and F. Palacio
Instituto de Ciencia de Materiales de Aragón, CSIC - Universidad de Zaragoza, 50009 Zaragoza, Spain
(Dated: February 2, 2008)

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.

I. INTRODUCTION

The relation between structural and magnetic properties is of importance from the point of view of applied and fundamental research. This relation is not straightforward in systems with antiferromagnetic (AF) interactions, reduced dimensionality or size such as nanoparticles. In these systems, surface effects and disorder play an important role and therefore deviations to the superparamagnetic (SP) canonic behavior are expected. Such effects change the relation between anisotropy energy, $E_a$, volume, V, and magnetic moment, $\mu$, found for typical SP systems for which $E_a$ and $\mu$ are proportional to $V^q$. This is also the case of ultrathin films, where anisotropy energy is proportional to surface area, leading to perpendicular magnetization. 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 non-proportionality between $E_a$ and V is two-dimensional Co nanostructures, where $E_a$ was found to depend on the perimeter [2].

The deviations to the proportionality between V and $\mu$ found in AF nanoparticles are associated to the fact that, in these systems, the net magnetic moment arises from the uncompensated and/or canted moments, $\mu_{un}$, that can be present at the surface, throughout the volume, or both. The relation between $\mu_{un}$ and V reflect the origin of the moments. In particular, Néel has shown that $\mu_{un}$ 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 $1/3$ [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 $\mu_{un}$, or by the usual comparison of systems with different average sizes [3]. The latter approach is limited by the possibility of synthesizing identical systems with different average volumes, that usually covers less that one order of magnitude. An alternative approach that takes advantage from 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. An approach reminiscent of this approach was first used by Luis and co-workers for the determination of the origin of magnetic anisotropy in gaussian size-distributed Co nanoparticles [1]. 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 later used to study two-dimensional Co
structures by Rusponi et al. [2]. The idea was based on the fact that the shape of the in-phase component of the ac susceptibility $\chi'$ was critically dependent on the chosen distribution, namely surface, perimeter and perimeter plus surface distributions. The authors concluded that perimeter atoms were those relevant to the reversal process in the Co structures, i.e., $E_a$ depends on the perimeter. Gilles and co-workers have also tried to use susceptibility curves to obtain the relation between $\mu_{un}$ and $V$ in ferritin [7] but found that their experimental curves were not very sensitive to the particular shape of distribution nor the value of $q$ [3]. 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 report we show that lognormal distributed nanoparticle samples are particularly useful to study the relation between a physical property and size. This is based in the fact that when two physical quantities are related by a power function, the power factor can be readily obtained by comparing the respective lognormal deviations, due to reproductive properties of the lognormal distribution function [3]. Moreover we generalize this concept to any distribution function. This method is of general use and can be simply applied in cases where the size of the system determined 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 $\mu_{un}$. At the same time, $E_a$ and $V$ can also be not proportional. One may however expect that, in general

$$E_a = \alpha V^p$$  \hspace{1cm} (1)

where $p$ can be different than 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 $\alpha$ and $p$ simultaneously. Their determination is usually carried out comparing samples with different $\langle V \rangle$, considering that $\alpha$ and $p$ are constant in all samples. Here we show how to determine $\alpha$ and $p$ using magnetic studies on one lognormal distributed sample. The probability distribution of $E_a$, $g(E_a)$, is a function of the $V$ probability distribution $g(V)$:

$$g(E_a) = f(V)/(dE_a/dV)$$  \hspace{1cm} (2)

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

$$f(V) = \frac{1}{V s_V \sqrt{2\pi}} \exp\left(-\frac{(\log(V/n_V))^2}{2 s_V^2}\right)$$  \hspace{1cm} (3)

then $g(E_a)$ is given by:

$$g(E_a) = \frac{1}{\alpha p (E_a/\alpha)^{(p-1)/p}} \frac{1}{(E_a/\alpha)^{(1/p)/p} s_V \sqrt{2\pi}} \exp\left(-\frac{[\log((E_a/\alpha))^{(1/p)/n_V}]^2}{2 s_V^2}\right) =$$

$$= \frac{1}{E_a s_E \sqrt{2\pi}} \exp\left(-\frac{[\log(E_a/s_E)]^2}{2 s_E^2}\right)$$  \hspace{1cm} (4)

with:

$$n_E = \alpha n_V$$

$$s_E = p s_V$$  \hspace{1cm} (5)

This means that if $V$ presents a lognormal distribution, all other physical quantities that can be related to $V$ by a power relation (Eq. 1) are also lognormal distributed. More important, when comparing $V$ and $E_a$, the ratio between the distribution parameters $s$ is a direct measure of the power $p$, while the relationship between $n$ values gives information about $\alpha$. Therefore, the relation between $V$ and $E_a$ in one sample can be quantitatively 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. 1 and 5 are 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 $Y = c \prod X_i^{b_i}$ (with $b_i$ and $c > 0$ being constants) is also lognormal distributed, with $s_Y = \sum b_i s_i$ and $n_Y = c \sum n_i b_i$ [9]. In general, reproductive properties can be used in the analysis of an output whose inputs are lognormal distributed, as for instance in quantitative analysis of human information processing during psychophysical tasks [11]. However, to the best of our knowledge, here is the first time that they are used in the context of physical properties of nanoparticles.

Although many physical properties of interest 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, 13, 14, 15]. The gamma function can be expressed by:

$$f(x) = \frac{b^{-a} x^{a-1}}{\Gamma(a)} \exp\left(-\frac{x}{b}\right)$$  \hspace{1cm} (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. 6 may also be a good approximation to find $\alpha$ and $\rho$. These values may also be found in the general case of a different or an unknown distribution, by searching for a scaling plot or numerically [?] but, as seen, the validity of the lognormal distribution makes this task quite straightforward.

B. Anisotropy energy distribution from ac susceptibility and viscosity measurements

The out-of-phase component of the ac susceptibility $\chi''$ is usually used to obtain the anisotropy energy barrier distribution of different nanoparticles systems and is given by [1, 13, 14, 15, 16]:

$$\chi''(f, T) \approx \frac{\pi M_S^2}{6K} k_B T \ln(1/(f \tau_0)) f(E_a)$$

(7)

where $\tau_0$ is a microscopic characteristic time and $E_a = k_B T \ln(1/(f \tau_0))$ is the activation energy of the particles having $\tau$ equal to the characteristic time of measurement $1/f$. It follows from Eq. 7 that $\chi''$ is a function of $E_a$ and that therefore curves taken at different frequencies should scale when plotted against $E_a$. At the same time, $\chi''/T$ is a measure of the anisotropy energy distribution $f(E_a)$. In Eq. 7 it is considered that the particles contributing to $\chi''$ at a given $f$ 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. $1/\ln(1/(f \tau_0)) \ll 1$). It is also considered that dipolar interactions are negligible.

Measurements of the magnetization as a function of time $t$ (viscosity measurements) at temperatures below the blocking temperature $T_B$ is a complementary way to investigate the anisotropy energy barrier distribution of different nanoparticles systems [1, 13, 14, 15, 16], including ferritin [21]. 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, $h$, and may be written as:

$$S(t, T) = \frac{\partial M}{\partial \ln t} = k_B T M_{eq} f(E_a)$$

(8)

considering that the function $(t/\tau) \exp(-t/\tau)$ is narrower than the distribution function $f(E_a)$ [18]. In ferromagnetic materials $M_{eq}/h = M_S^2/3K$, where $M_S$ is the saturation magnetization and $K$ the anisotropy constant. It follows directly from Eq. 8 that $S/T$ is proportional to the anisotropy energy distribution, $f(E_a)$, in analogy with $\chi''/T$. In fact, $S$ and $\chi''$ are probing the same energy barrier at different time scales.

III. EXPERIMENTAL DETAILS

Ferrihydrite is a low-crystalline AF iron oxide-hydroxide that typically forms after rapid hydrolysis of iron at low pH and low temperatures [22]. 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 by one tetrahedrally coordinated Fe atom surrounded by 12 octahedrally coordinated Fe atoms [23]. The cell dimensions and site occupancies change slightly and systematically with average domain size, reflecting some disorder and relaxation effects. This picture extends homogeneously to the surface of the domains. This model contrasts with previous ones, where multiple structural phases were considered [24, 25], and the existence of tetrahedrally coordinated Fe atoms was a matter of debate [26, 27].

The synthesis of the ferrihydrite nanoparticles in the organic-inorganic matrix (termed di-ureasil) has been described elsewhere [28]. The particles are 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. [29]. Mössbauer spectroscopy was measured at selected temperatures between 4.2 K and 40 K. A conventional constant-acceleration spectrometer was used in transmission geometry with a $^{57}$Co/Rh source, using a $\alpha$-Fe foil at room temperature to calibrate isomer shifts and 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 images (FT-HRTEM) and XRD diffraction patterns show the existence of low crystalline 6-line ferrihydrite nanoparticles. The nanoparticles are homogeneously distributed, separated from each other, and have globular habit. The size (diameter, $D$) distribution can be described by a lognormal function, with $n_D = 4.7 \pm 0.2$ nm and deviation $s_D = 0.43 \pm 0.05$ [29] (see Fig. 2). As expected from the reproductive properties, a lognormal size distribution results in a lognormal volume distribution.

The in-phase ac susceptibility, $\chi'$, is frequency independent above $T_F = 30$ K. The maxima of $\chi'$ follow a Néel-Arrhenius relation:

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

(9)

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

Another evidence of the existence of negligible dipolar interactions is given by Mössbauer spectroscopy results, since interacting systems have a collapsed V-shaped pattern \cite{31,32,33}. For temperatures around $T_B$ the spectra can be described by the simple sum of a sextet distribution and a doublet and no signs of a collapsed magnetic hyperfine field pattern. On the other hand, such collapse is observed in the ferrihydrite/hybrid matrix sample with 6.5% of iron, where dipolar interactions are expected to be relevant. At 4.2 K, the Mössbauer spectrum of the sample here studied (2.1% of iron) shows a sextet, with a hyperfine field $B_{hf} = 48$ T. This is characteristic of ferrihydrite nanoparticles low crystallinity, in accordance with the FT-HR TEM and XRD results.

As described in Sec. II B $\chi''/T$ 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 $\chi''/T$ and $S/T$ fairly superimpose, meaning that Eq. 4 and 8 are good approximations. Both $\chi''/T$ 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 $s_{\chi''/T} = 0.61 \pm 0.02$ and $\langle \chi/T \rangle = 170 \pm 4$ K, and $s_{S/T} = 0.65 \pm 0.02$ and $\langle S/T \rangle = 176 \pm 4$ K, respectively. We therefore consider $s_{E} = 0.63 \pm 0.04$ from the average of $s_{\chi''/T}$ and $s_{S/T}$. Since $s_{D} = 0.43 \pm 0.05$, and using Eq. 5 we directly obtain the power relation between $E_a$ and $D$, $p' = 1.5 \pm 0.2$, which corresponds to $p' = 3/2$, so that:

$$E_a = \alpha' D^{3/2} \text{ (K)}$$

Eq. 5 can be further used to determine the proportionality between $E_a$ and $D^{3/2}$, $\alpha' = 18$ Knm$^{-3/2}$. As expected from the above equation, we observe that, in a $(E_a/\alpha')^{2/3}$ scale, both distributions of $\chi''/T$ and $S/T$ superimpose to the diameter distribution (Fig. 2). This is a confirmation that describing $\chi/T$ and $S/T$ by a lognormal function is a good approximation for the identification of $p$ and $\alpha$. Eq. 10 can be rewritten in terms of the particle volume as:

$$E_a = \alpha V^{1/2}$$

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 structure model, since it is composed of a single phase with in-volume defects, where we can expected $E_a$ to be locally different.

From Eq. 11 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 $4.7 \times 10^5$ to $1.5 \times 10^4$ J/m$^3$, which are of the order of those found in the literature \cite{2,3,4}. For the average size of the sample, $K_{eff} = 2.9 \times 10^4$ J/m$^3$.

B. Relationship between magnetic moment and size

Unlike the case of $E_a$, there is no direct measurement of the $\mu_{un}$ distribution. A way to obtain this distribution is to model the dependence of the magnetization with the field $M(H)$ to a given function of $\mu_{un}$ considering a $\mu_{un}$
distribution. A function usually applied to model $M(H)$ of nanoparticles is the Langevin function [4, 5, 6, 29]. 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 $\mu_{un}$ and the AF axis [3, 32]. In AF nanoparticles, anisotropy effects have been taken into account using a Néel (Ising-like) model, considering that $\mu_{un}$ 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 are crude approximations [30].

Despite this situation, we have previously modelled $M(H)$ using a Langevin distributed function [21] and found that the parameter $s$ of the $\mu_{un}$ lognormal distribution is $s_\mu = 0.9$, so that $q = 0.7 \pm 0.1$ and $\mu_{un} \propto V^{2/3}$. We note that the value of $q$ here derived is different to that estimated in Ref. [21] 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 pre-factor of the power law cannot be ignored. In this scenario the uncompensated moments were to lie on the particles surface, despite the fact that the energy barriers associated to the uncompensated moments are randomly distributed in volume.

At this point one should highlight that the Langevin distributed function may be a too crude description of $M(H)$ to yield a good estimation of $s_\mu$, so that a different scenario is possible: having no reliable estimation of $s_\mu$, we discuss the situation where the uncompensated moments are associated (proportional) to the energy barriers, so that a $\mu_{un} \propto V^{1/2}$, i.e. they are randomly distributed in volume. In fact, the uncompensated moments are those contributing to the Curie-like ac susceptibility and those experiencing the blocking phenomena associated with the onset of $\chi''$ 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 ferromagnetic-like uncompensated moments. Such relation between $\mu_{un}$ and $V^{1/2}$ was proposed for antiferromagnetic nanoparticles by Néel [2] and is consistent with magnetization measurements performed on ferritin [4, 3, 29].

V. CONCLUSIONS

In this report we show that distributed samples can be used to investigate the relationship between the magnetic anisotropy barrier $E_a$ and the nanoparticles 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 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 nanoparticles 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 the volume, in accordance to recent structure studies.

Acknowledgments

The authors would like to acknowledge E. Lythgoe for critical reading the manuscript. The financial support from FCT, POCTI/CTM/46780/02, research grant MAT2004-03395-C02-01 from the Spanish CICYT. Bilateral projects GRICES-CSIC and Acción Integrada Luso-Espaňola E-105/04, and are gratefully recognized. N. J. O. S. acknowledges a grant from FCT (Grant No. SFRH/BD/10383/2002), CSIC for a I3P contract, and financial support from IRM visiting fellowship program. L.M.L.M. acknowledges support from the EU Network of Excellence SoftComp. Institute for Rock Magnetism (IRM) is funded by the Earth Science Division of NSF, the W. M. Keck Foundation and University of Minnesota. This is IRM publication # 0616.

[1] F. Luis, J. M. Torres, L. M. García, J. Bartolomé, J. Stankiewicz, F. Petroff, F. Fettar, J. L. Maurice, and A. Vaurès, Phys. Rev. B. 65, 094409 (2002).
[2] S. Rusponi, T. Cren, N. Weiss, M. Epplle, P. Buluschek, L. Claude, and H. Brune, Nature Mater. 2, 546 (2003).
[3] L. Néel, C. R. Hebdo. Seances Acad. Sci. 252, 4075 (1961).
[4] S. A. Makhlof, F. T. Parker, and A. E. Berkowitz, Phys. Rev. B. 55, R14717 (1997).
[5] J. G. E. Harris, J. E. Grimaldi, D. D. Awschalom, A. Chichelow, and D. Loss, Phys. Rev. B. 60, 3453 (1999).
[6] N. J. O. Silva, V. S. Amaral, and L. D. Carlos, Phys. Rev. B. 71, 184408 (2005).
[7] C. Gilles, P. Bonville, K. K. Wong, and S. Mann, Eur. Phys. J. B 17, 417 (2000).
[8] D. Casanova, D. Giaume, E. Beaurepaire, T. Gacoin, J.-P. Boilot, and A. Alexandrou, Appl. Phys. Lett. 89, 253103 (2006).
[9] E. L. Crow and K. Shimizu, Lognormal distributions theory and applications (Marcel Dekker, New York, 1988).
[10] L. Brus, J. Phys. Chem. 90, 2555 (1986).
[11] T. O. Kvalseth, IEEE Trans. Inform. Theory 6, 963 (1982).
[12] M. I. Shliomis and V. I. Stepanov, J. Magn. Magn. Mater. 122, 176 (1993).
[13] T. Jonsson, J. Mattsson, P. Nordblad, and P. Svedlindh, J. Magn. Magn. Mater. 168, 269 (1997).
[14] P. Svedlindh, T. Jonsson, and J. L. García-Palacios, J. Magn. Magn. Mater. 169, 323 (1997).
[15] F. Luis, E. del Barco, J. M. Hernández, E. Remiro, J. Bartolomé, and J. Tejada, Phys. Rev. B. 59, 094409 (1999).
[16] F. Luis, J. Bartolomé, J. Tejada, and E. Martínez, J. Magn. Magn. Mater. 157-158, 266 (1996).
[17] L. Lundgren, P. Svedlindh, and O. Beckman, J. Magn. Magn. Mater. 25, 33 (1981).
[18] A. Labarta, O. Iglesias, L. Balcells, and F. Badia, Phys. Rev. B. 48, 10240 (1993).
[19] O. Iglesias, F. Badia, A. Labarta, and L. Balcells, J. Magn. Magn. Mater. 140-144, 399 (1995).
[20] L. C. Sampaio, C. Paulsen, and B. Barbara, J. Magn. Magn. Mater. 140-144, 391 (1995).
[21] T. G. St. Pierre, N. T. Gorham, P. D. Allen, J. L. Costa-Krämer, and K. V. Rao, Phys. Rev. B 65, 024436 (2001).
[22] J. L. Dormann, F. D’Orazio, F. Lucari, E. Tronc, P. Prené, J. P. Jolivet, D. Fiorani, R. Cherkaoui, and M. Noguès, Phys. Rev. B. 53, 14291 (1996).
[23] S. Morup, C. Frandsen, F. Bødker, S. N. Klausen, P. Lindgård, and M. F. Hansen, Hyp. Inter. 144-145, 347 (2002).
[24] J. L. Dormann, D. Fiorani, R. Cherkaoui, E. Tronc, F. Lucari, F. D’Orazio, L. Spinni, M. Noguès, H. Kachkachi, and J. P. Jolivet, J. Magn. Magn. Mater. 203, 23 (1999).
[25] J. Dormann, S. Morup, and M. F. Hansen, J. Magn. Magn. Mater. 305, 95 (2006).
[26] H. Kachkachi, J. Magn. Magn. Mater. 316, 248 (2007).