Nonmonotonic field dependence of the zero-field cooled magnetization peak in some systems of magnetic nanoparticles

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We have performed magnetic measurements on a diluted system of γ-Fe_2O_3 nanoparticles ($d\sim 7$ nm), and on a ferritin sample. In both cases, the zero-field cooled (ZFC) peak presents a nonmonotonic field dependence, as has already been reported in some experiments, and discussed as possible evidence of resonant tunneling. Within simple assumptions, we derive expressions for the magnetization obtained in the usual ZFC, field cooled (FC) and thermoremanent magnetization (TRM) procedures. We point out that the ZFC-peak position is extremely sensitive to the width of the particle-size distribution, and give some numerical estimates of this effect. We propose to combine the FC magnetization with a modified TRM measurement, a procedure which allows a more direct access to the barrier distribution in a field. The typical barrier values that are obtained in this procedure show a monotonic decrease for increasing fields, as expected from the simple effect of anisotropy barrier lowering, in contrast with the ZFC results. From our measurements on γ-Fe_2O_3 particles, we show that the width of the effective barrier distribution is slightly increasing with the field, an effect that is sufficient for causing the observed initial increase of the ZFC-peak temperatures. [S0163-1829(97)03746-6]

I. INTRODUCTION

A rapid characterization of ensembles of small magnetic particles (like ferrofluids) is very commonly achieved by ''zero-field cooled'' (ZFC) magnetization measurements. The ZFC curve is measured by cooling the sample in zero field, applying the field at low temperature and then measuring the magnetization while raising the temperature by steps. The ZFC curve peaks at a temperature that is related to a typical scale of the anisotropy energy barriers in the system; it is commonly referred to as the ''blocking temperature'' of the sample. For ZFC curves measured under increasing field amplitudes, the peak is expected to reflect the lowering of the anisotropy barriers, and hence should shift towards lower temperatures (as observed, e.g., in Ref. 1).

However, in several experiments,[2–5] an astonishing increase of the ZFC-peak temperature with the field amplitude has been reported. In the first papers,[2,3] no explanation was proposed for this apparent barrier increase under the effect of the applied field. In very recent works on antiferromagnetic particles of ferritin,[4,5] interestingly, the effect has been discussed as a possible indication of a resonant spin tunneling phenomenon.[6] In brief, if the magnetic moment of the particles can flip by quantum tunneling through the anisotropy barrier (a process that should be favored in antiferromagnetic particles[7]), then the flipping rate should be enhanced by a resonance effect when the up and down energy levels coincide. In Mn-12 magnetic molecules, where the energy levels can be well defined, the resonances have been recently observed for the corresponding values of the field.[8,9] In a system of size-distributed particles, there can be no coincidence of the various up and down energy levels in the different particles, except in the symmetrical situation of zero field. Resonant tunneling has thus been suggested to produce an increase of the relaxation rate around zero field,[6] which could (among other evidences, see Refs. 4 and 5) show up as the observed anomalous increase of the ZFC-peak temperature for increasing fields.

In the present paper, we want to address the question of the origin of this anomalous behavior, and to argue in favor of characterization procedures other than the ZFC measurement. We first present a series of experiments on a sample of γ-Fe_2O_3 particles, which do indeed exhibit the ZFC anomaly in the $\sim$65 K region, a rather high temperature range for expecting evidences of quantum effects. Under some simple approximations, we discuss the expression of the ZFC magnetization, and point out that the peak temperature is strongly influenced by the width of the barrier distribution. We propose as a possible explanation of the anomaly that this width increases under the influence of increasing field.

In comparison with the ZFC-peak results, we use another experimental procedure, which also gives access to a characteristic temperature depending on the applied field amplitude. This other characteristic temperature can be expected to be much less sensitive to the width of the barrier distribution (and even insensitive in an ideal log-normal case). Our measurements on γ-Fe_2O_3 particles indeed show that this characteristic temperature decreases for increasing fields, without any anomaly. We also extract from the γ-Fe_2O_3 measurements an approximate width of the barrier distribution, which we find to slightly increase with field; the effect has

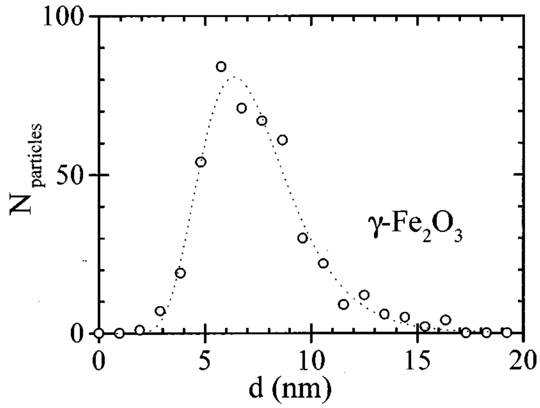

FIG. 1. Histogram of the γ-Fe_2O_3 particle diameters, as observed in TEM imaging (symbols). 454 particles have been sampled. The dotted line is a fit to a log-normal distribution, with $d_0=7.05$ nm and $\sigma_d=0.32$.

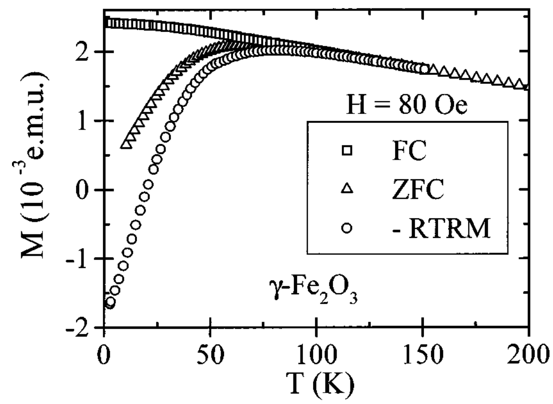

FIG. 2. Example magnetization curves from the γ-Fe_2O_3 particles ($H=80$ Oe), obtained following the different experimental procedures: Field-cooled, zero-field cooled, and reversed thermoremanent magnetization (the R-TRM curve has been multiplied by -1 in the figure).

the correct order of magnitude for reproducing the observed ZFC anomaly.

The majority of the present paper (Secs. III and IV) is devoted to the γ-Fe_2O_3 sample, which we have studied in more detail.[10–12] We use these results as an example for discussing the physical information which can be extracted from the various experimental procedures. Finally, in Sec. V, we apply the same procedures to a ferritin sample. The anomaly is found in the ZFC measurements around 3000 Oe (in agreement with the other works[3–5]), and disappears with the other procedure, making likely our ''classical'' explanation of the ZFC anomaly.

II. EXPERIMENTAL PROCEDURE AND SAMPLES

Our first sample consists in small ferrimagnetic particles of γ-Fe_2O_3 (maghemite), which have been embedded in a silica matrix obtained by a room-temperature polymerization process.[13] Other samples of the same batch have recently been used for studying the features of the magnetic relaxation in the limit of very low temperatures.[10,11] Here, the particles are diluted to the very low volume fraction of $f_v=2\times10^{-4}$, in order to favor independent relaxation processes of the particles. In a saturated sample (all particle moments being aligned, which is far from our case), the corresponding dipolar field would be of order 1 Oe.

We could not directly observe the γ-Fe_2O_3 particles in the TEOS matrix. However, TEM imaging of the particles before their incorporation in silica has been made; Figure 1 displays the resulting diameter histogram, which can be tentatively fitted (as is usually done in the literature) to a log-normal shape,

$$f(d)=\frac{1}{\sqrt{2\pi}\sigma_d d}\exp\left(-\frac{\ln^2\frac{d}{d_0}}{2\sigma_d^2}\right), \qquad (1)$$

yielding $d_0=7$ nm and $\sigma_d=0.3$.

We have performed the magnetization measurements with a commercial SQUID magnetometer (from Cryogenic Ltd, U.K.). Figure 2 presents example curves from the γ-Fe_2O_3 sample, obtained at a given field amplitude along various procedures. The ZFC curve is measured as explained above. The FC (field-cooled) curve is obtained by cooling the sample in the field, and measuring while increasing the temperature. We have used in addition a less common measurement procedure, which we denote as R-TRM (reversed thermoremanent magnetization); it consists in cooling the sample in the field, reversing the field at low temperature, and then measuring upon increasing the temperature. Compared to the more usual TRM procedure, in which the field is cutoff instead of being reversed, it presents the advantage that the field conditions for the initial and final states of the particle relaxation are identical; the effect of the field amplitude on the barrier distribution can be studied more directly, as we argue below.

Our second sample in this study is made of horse-spleen commercial ferritin (Sigma Chimie). Ferritin is an iron-storage protein; it consists in a protein shell of outer and inner diameters 12 and 7.5 nm, which is partially or completely filled with an antiferromagnetic iron oxide core (maximum of $\sim$5000 Fe ions per ferritin molecule).[14] The concentration of our solution is 100 mg/ml, which again corresponds to a dipolar field of order 1 Oe (at saturation of the noncompensated moments). As an example of antiferromagnetic nanoparticles, ferritin is considered a good candidate for the observation of quantum tunneling of the Néel vector,[7] and has been the subject of numerous studies at low temperatures these last years (see Refs. 3–5, 15 and 16 and references therein).

Throughout the paper, we have chosen as a convention to present the results in terms of magnetic moments, in cgs electromagnetic units; we have not divided the measured magnetic moments by the sample volume, which we estimate for the γ-Fe_2O_3 particles to $V_{tot}=2.1\times10^{-5}$ cm^3. For ferritin, we only know the total mass, which amounts to 8.4×10^{-3} g of ferritin particles. Coherently, in the following equations, we do not divide by integrals over the particle volumes.

III. ZFC MEASUREMENTS: ANOMALOUS FIELD DEPENDENCE

We present now the ZFC measurements that we have performed on our sample of γ-Fe_2O_3 particles, for field ampli-

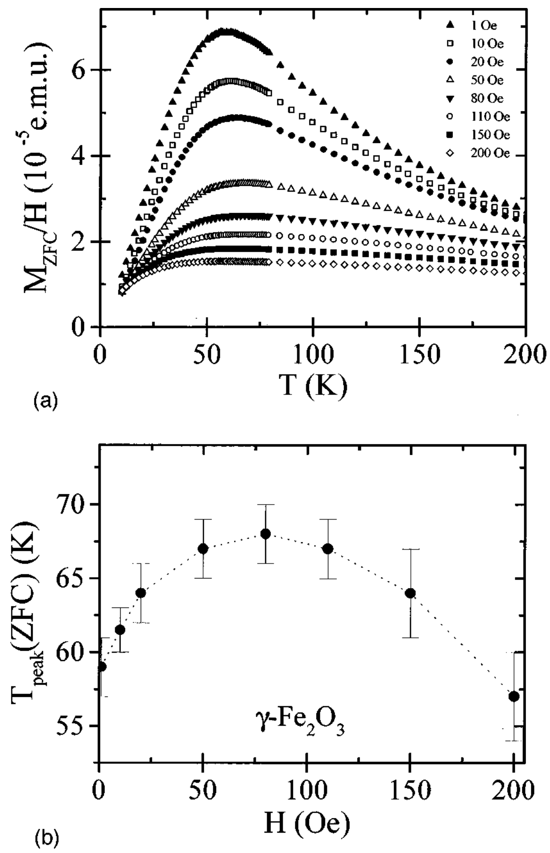

FIG. 3. (a) Measured ZFC magnetizations on the γ-Fe_2O_3 sample, normalized to the field amplitude. From top to bottom, the field values are 1, 10, 20, 50, 80, 110, 150, and 200 Oe. (b) Peak temperatures of the measured ZFC magnetization curves for γ-Fe_2O_3.

tudes ranging from 1 to 200 Oe [in this sample, the effective coercive field which brings the total magnetization to zero after saturation is $\sim$300 Oe at 2 K (Ref. 12)]. The curves are displayed in Fig. 3(a), and the peak temperature variation with the field is shown in Fig. 3(b). Surprisingly, the peak temperature increases with the field up to $\sim$80 Oe, before decreasing for larger values as expected.

The initial increase of a ZFC curve reflects the additive contributions of larger and larger particles, which are deblocked as the temperature is raised; the maximum is obtained when these contributions are compensated by the superparamagnetic reduction of already deblocked moments. It is therefore clear that the peak temperature has no simple relation with the peak of the size distribution. One may, however, consider that it is related to some typical anisotropy barrier; in that case, the effect of an increasing field amplitude should be to lower the anisotropy barrier, in contradiction with our result in Fig. 3(b).

A similar observation has already been reported for magnetite particles,[2] and also in ferritin;[3] no explanation was proposed. Again in ferritin, the phenomenon has recently been quoted,[4,5] and discussed as a possible indication of a resonant tunneling process at zero field.[6] In our present sample, the temperature range of the ZFC peak ($\sim$65 K) does not favor an explanation of quantum origin. In the following, we write in more detail the $M_{\rm ZFC}$ expression under simple assumptions, and propose a semiquantitative explanation of a nonmonotonic behavior of the peak temperature in terms of the field influence on the barrier distribution.

The ZFC data being taken in a field H, deblocking of particles with anisotropy barrier $U(H)$ occurs at a temperature T_b such that the typical time for crossing the barrier $U(H)$ is equal to the measurement time $t_m \sim 100$ s, namely

$$k_B T_b = \frac{U(H)}{\ln t_m/\tau_0} \tag{2}$$

where the attempt time τ_0 is of order 10^{-10} s, giving $\ln t_m/\tau_0 \simeq 28$. We assume that the anisotropy barrier U of a particle is proportional to its volume V; in zero field, $U = KV$, where K is the energy density for uniaxial anisotropy [from other measurements, $K \simeq 6\,10^5$ erg/cm^3 (Ref. 12)]. In the general case of random orientations of the easy axes of the particles, the question of the field dependence $U(H)$ of the anisotropy barriers cannot be solved analytically (approximations are discussed in Ref. 17). If the easy axes are parallel to the field, in contrast, it is straightforward to derive exactly

$$U(H) = KV\left(1 - \frac{H}{H_c}\right)^{\alpha} \tag{3}$$

with $\alpha = 2$. H_c is the coercive field, at which the given barrier vanishes. In Ref. 18, it has been observed that the disorder of the easy axes orientations yields a distribution of the H_c values. We restrict ourselves to simply considering that we can approximate the orientational disorder by Eq. (3) with $\alpha = 1.5$ instead of $\alpha = 2$,[19] keeping the same H_c for all particles.

At a given temperature T, the magnetization $M_{\rm ZFC}$ is the sum of the superparamagnetic contributions of the particles for which $T_b < T$, or, in other words, of volume smaller than a blocking value V_b such that

$$V_b(T,H) = \frac{k_B T \ln t_m/\tau_0}{K(1 - H/H_c)^{\alpha}}. \tag{4}$$

For the sake of simplicity, we approximate here the superparamagnetic behavior by an $1/T$ Curie shape, and do not include a temperature dependence of the saturated magnetization M_s. We do not expect these approximations to significantly affect the present discussion (see more detailed analysis in Ref. 12).

Within this framework, $M_{\rm ZFC}$ reads

$$M_{\rm ZFC}(T) = M_r(H) + \frac{M_s^2}{3k_B T} H \int_0^{V_b(T,H)} f(V) V^2 dV, \tag{5}$$

where M_r stands for the reversible contribution that is due to the canting of the moments from the easy axes towards the field direction. This term equals $M_r = M_s^2 V_{\rm tot} H/3K$ in the $T = 0$ limit; at nonzero temperatures, it is a correction to the main term, which accounts for the fact that the moments are not exactly lying along the easy axes. As is usually done, we neglect it in the present discussion of the ZFC peak; we show below that this term disappears to first order in some other quantities.

First, one sees in Eq. (5) that the temperature dependence of $M_{\rm ZFC}$ occurs (at least) via $V_b(T,H)$ and the Curie term.

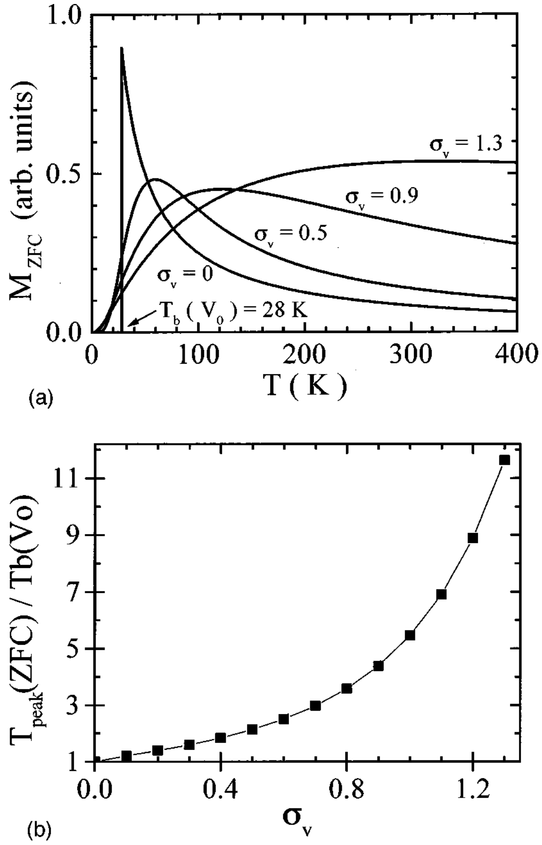

FIG. 4. (a) Calculated ZFC curves, using a log-normal volume distribution, for various values of the standard deviation σ_v. (b) Ratio of the calculated ZFC-peak temperatures to the blocking temperature corresponding to V_0 (reference volume of the log-normal distribution), for different values of the standard deviation σ_v.

The temperature derivative cannot be written in simple terms, and there is no explicit expression of the peak temperature (which, however, obeys a simple first-order differential equation[20]). Second, the $f(V)$ distribution is here involved through a $V^2 f(V)$ contribution, which clearly emphasizes the effect of the largest particles; the sensitivity of M_{ZFC} to the standard deviation $\sigma_v = 3\sigma_d$ is stronger than that of other quantities that involve lower powers of V, like the one that we propose below.

In order to quantitatively estimate the sensitivity of M_{ZFC} to σ_v, we have performed numerical calculations of Eq. (5), which are shown in Fig. 4(a). The K and V_0 parameters have been adjusted to the values of the experiment; in this elementary calculation, due to the various approximations, the shape of the ZFC curves is not completely realistic. However, one sees clearly in Fig. 4(a) that the ZFC peaks shifts extremely rapidly towards higher temperatures when σ_v is increased. In Fig. 4(b), we present the ratio of the ZFC-peak temperature to the blocking temperature for the typical volume V_0. For our sample ($\sigma_v \sim 0.9$), the calculation yields a ratio of 4.4 [neglecting the $M_s(T)$ variation should produce a slight overestimate]. In most cases found in the literature, the standard deviation of the volume distribution is of this same order of magnitude; the particle volume that is commonly deduced from the ZFC peak must, therefore, be divided by a non-negligible factor before being compared with V_0.

In our opinion, the result in Fig. 4(b) opens the way to a possible explanation of the $T_b(H)$ increase at low fields, which could be due to a slight enlargment of the barrier distribution under the influence of the field. A simple reason for that can be the disorder of orientations. For randomly oriented particles of a unique size, the applied field lowers differently the barriers with respect to their orientation, thus enlarging the barrier distribution. One may also imagine that, in relation with the defects of a particle, an increasing field results in different coupling energies of the field to various parts of the particle, thus yielding several energy barriers. Whatever its origin, which remains an open question, an enlargement of the barrier distribution can indeed be found in our R-TRM data (see below).

IV. OTHER MEASUREMENT PROCEDURES FOR PROBING THE BARRIER DISTRIBUTION

A TRM measurement corresponds to the inverse field history of the ZFC procedure; the sample is cooled in the field, the field is cut at low temperature, and deblocking is measured for increasing temperatures in zero field. Keeping the same assumptions as above, the TRM can be written as the sum of the moments which are still blocked in the field-cooled state:

$$M_{\mathrm{TRM}}(T) = \frac{M_s^2}{3k_B} H \int_{V_b(T,0)}^{\infty} \frac{f(V)V^2}{T_b(V,H)} dV. \tag{6}$$

Contrary to the ZFC case, no M_r term appears, and now the $1/T$ term is replaced by $1/T_b$, since each particle has kept a magnetization that is equal to the superparamagnetic value at the blocking temperature $T_b(V,H)$. T_b is obtained from Eqs. (2) and (3), where t_m now corresponds to the time scale τ_c of blocking during the field-cooling process. An estimate of τ_c can be obtained from the cooling rate $v_c = dT/dt$ ($\simeq 0.04$ K/s). As the temperature decreases, the Arrhenius relaxation time τ for a given barrier abruptly increases, and freezing occurs when $\partial\tau(t)/\partial t \sim 1$. One finds that τ_c satisfies

$$\tau_c \ln^2 \frac{\tau_c}{\tau_0} = -\frac{U}{k_B v_c}, \tag{7}$$

which yields $\tau_c \sim 30s \sim t_m$ for $U = KV_0$; the $\ln t_m/\tau_0$ term that is involved in T_b for the TRM procedure is almost the same as above. Replacing now $T_b(V,H)$ in Eq. (6), we obtain

$$M_{\mathrm{TRM}}(T) = \frac{M_s^2 \ln t_m/\tau_0}{3K(1-H/H_c)^{\alpha}} H \int_{V_b(T,0)}^{\infty} f(V) V dV. \tag{8}$$

The only temperature dependence of the TRM occurs in the lower bound $V_b(T,0)$ of the integral; this allows us to take very simply the temperature derivative of M_{TRM},[21] which reads

$$\frac{\partial M_{\mathrm{TRM}}}{\partial T} = -\frac{M_s^2 k_B H}{3K^2} \frac{\ln^2 t_m/\tau_0}{(1-H/H_c)^{\alpha}} V_b(T,0) f(V_b(T,0)). \tag{9}$$

Thus, the TRM derivative gives a direct access to the quantity $Vf(V)$; if $f(V)$ is log normal, then $Vf(V)$ peaks at $V = V_0$, independently of the width of the distribution. This makes a crucial difference with the ZFC case, for which the peak rapidly shifts as σ_v increases. However, the blocking volume $V_b(T,0)$ that is involved in $\partial M_{\text{TRM}}/\partial T$ is the blocking volume in zero field, because the measurement is performed in zero field. The effect of the field amplitude only appears through a multiplicative factor in Eq. (9); in other words, $\partial M_{\text{TRM}}/\partial T$ does not give access to the field-modulated barrier distribution.

This is our motivation for using another experimental procedure, which allows the study of the effect of the field amplitude on the barrier distribution. We have performed a series of R-TRM measurements for various field values; after field cooling in $+H$, the field is reversed to $-H$ at low temperature, and the magnetization is measured while increasing the temperature. An example of such a curve has been given in Fig. 2. Within the same framework as above, the magnetization $M_{\text{R-TRM}}$ at a given temperature T can be written as the sum of the contributions of the smaller particles, already deblocked at T in $-H$, plus that of the larger ones, still blocked in the $+H$ field-cooled state; again using the $T_b(V,H)$ expression for the blocked term, one obtains

$$M_{\text{R-TRM}}(T,H) = M_r(-H) + \frac{M_s^2 H}{3}\left[-\frac{1}{k_B T}\int_0^{V_b(T,H)} f(V)V^2 dV + \frac{\ln(t_m/\tau_0)}{K(1-H/H_c)^\alpha}\int_{V_b(T,H)}^{\infty} f(V)V dV \right]. \tag{10}$$

This expression looks rather complicated; but it is almost the same as that of the field-cooled magnetization M_{FC}, up to the respective signs of the superparamagnetic contributions (also, the reversible parts M_r are just of opposite sign). In a $+H$ field, M_{FC} reads

$$M_{\text{FC}}(T,H) = M_r(+H) + \frac{M_s^2 H}{3}\left[\frac{1}{k_B T}\int_0^{V_b(T,H)} f(V)V^2 dV + \frac{\ln(t_m/\tau_0)}{K(1-H/H_c)^\alpha}\int_{V_b(T,H)}^{\infty} f(V)V dV \right]. \tag{11}$$

The idea is to consider the sum $M_{\text{R-TRM}}+M_{\text{FC}}$ of both magnetizations, and thus get rid of the superparamagnetic contribution (and of M_r), which presents the most intricate temperature dependence:

$$M_{\text{R-TRM}}(T,H) + M_{\text{FC}}(T,H) = 2\frac{M_s^2 H}{3}\,\frac{\ln(t_m/\tau_0)}{K(1-H/H_c)^\alpha}\int_{V_b(T,H)}^{\infty} f(V)V dV. \tag{12}$$

As in the TRM case [Eqs. (6) and (8)], the temperature derivative can easily be taken:

$$\frac{\partial(M_{\text{R-TRM}}+M_{\text{FC}})}{\partial T} = -2\frac{M_s^2 H k_B \ln^2 t_m/\tau_0}{3K^2(1-H/H_c)^{2\alpha}} V_b(T,H) f(V_b(T,H)). \tag{13}$$

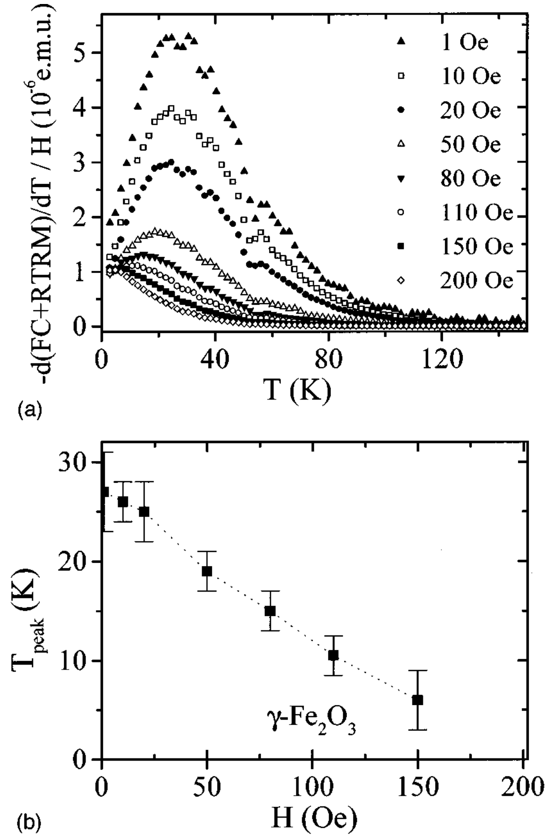

FIG. 5. (a) Temperature derivative of the sum of the measured magnetizations $M_{\text{FC}}+M_{\text{R-TRM}}$, divided by the field amplitude, for different fields (γ-Fe_2O_3 sample). (b) Peak temperatures of the curves in (a), for different fields; these temperatures do not show the nonmonotonic behavior that is found using the ZFC peaks.

In this quantity, the blocking volume corresponds to blocking in a field H, a quantity that was not involved in simple TRM measurements. Using our R-TRM and FC measurements, we have estimated the derivatives [Eq. (13)] for our 1–200 Oe measurement fields; the resulting curves are displayed in Fig. 5(a). If the $f(V)$ distribution is log normal, then $Vf(V)$ is a simple Gaussian of $\ln V/V_0$, which peaks at V_0 whatever the distribution width. One may, therefore, argue that the peak of this quantity in different fields corresponds to the same objects. Obviously, the assumption of a log-normal $f(V)$ remains questionable (see below); however, within this assumption that is the most commonly used, our procedure allows a clearly more direct characterization of the barrier distribution than the ZFC measurement.

The peak temperatures of Fig. 5(a) are plotted versus H in Fig. 5(b), which can be compared with the ZFC data in Fig. 3(b). The peak temperatures monotonically decrease with increasing field, whereas the ZFC results were exhibiting a striking nonmonotonic behavior. The peak temperatures can be fitted to the expected field dependence, Eq. (3); fixing $\alpha=1.5$ (Ref. 19) and $V_0=180$ nm^3 from TEM (Fig. 1), we obtain $H_c\simeq 250$ Oe and $K=6.4\ 10^5$ erg/cm^3, in good agreement with other estimates.[12]

Another combination of R-TRM and FC data can be used for checking the overall coherence of our data and analysis. According to Eqs. (5), (10), and (11), the three kinds of experiments are related:

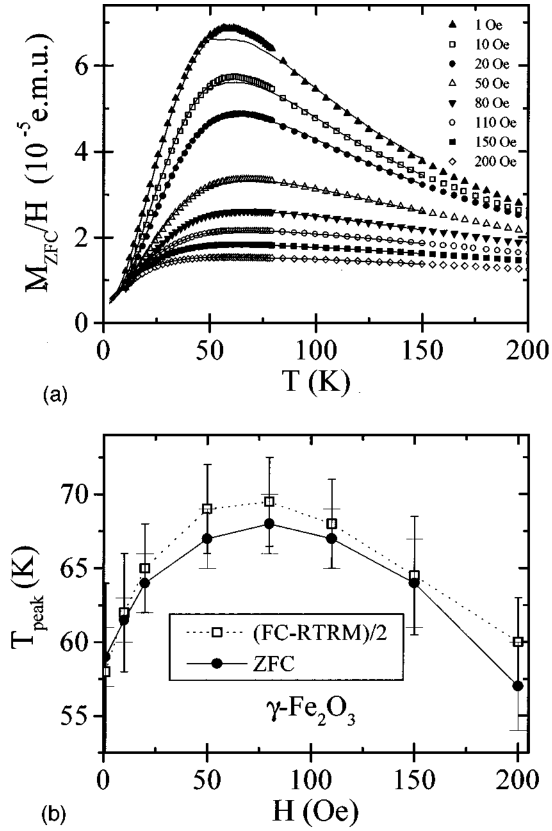

FIG. 6. (a) Comparison for the γ-Fe_2O_3 sample of the measured ZFC magnetizations (symbols) with the combination of measured magnetizations $(M_{FC}-M_{R\text{-}TRM})/2$ (solid lines), showing the consistency of the data and of our description (the magnetizations are normalized to the field amplitude). The field values are the same as in Fig. 3(a). (b) Comparison of the peak temperatures of the measured ZFC curves (full circles) with the peak temperatures of the combination $(M_{FC}-M_{R\text{-}TRM})/2$ of other measured magnetizations (open squares).

$$M_{ZFC}=\tfrac{1}{2}\,(M_{FC}-M_{R\text{-}TRM}), \tag{14}$$

or, in other words, given two of the measurements, the third one can be deduced. Equation (14) is thus the generalization to the situation of a non-negligible field of the well-known relation $M_{ZFC}=M_{FC}-M_{TRM}$. Following a remark by Fiorani, we note that Eq. (14) allows the reader who prefers to avoid the R-TRM measurements to use, in place of the sum $M_{R\text{-}TRM}+M_{FC}$, the equivalent quantity $2(M_{FC}-M_{ZFC})$. We have checked the validity of Eq. (14) with our γ-Fe_2O_3 data. Figure 6(a) compares the measured ZFC magnetizations (symbols) with the ones that are obtained by combining FC and R-TRM through Eq. (14). They are in rather good agreement, except for a slight amplitude difference in the vicinity of the peak for the lower field curves. In Fig. 6(b), we compare the field variation of the ZFC peaks obtained in both direct and indirect ways; they are fully compatible within the errors bars, and, in particular, the nonmonotonic behavior is found in both cases, whereas it does not show up in the FC+R-TRM analysis of Fig. 5(b).

The fact that the anomalous behavior of the ZFC peak does not appear in a (FC+R-TRM) measurement, which is less sensitive to the $f(V)$ width, prompts us to propose that

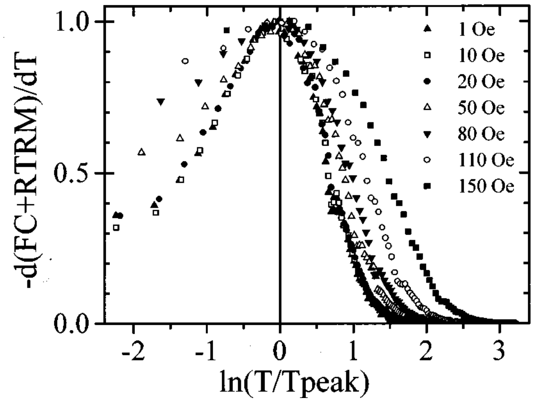

FIG. 7. Temperature derivative (normalized to the peak amplitude) of the combination $(M_{FC}+M_{R\text{-}TRM})$ of measured magnetizations, as a function of the neperian logarithm of the temperature (normalized to the peak position), for the γ-Fe_2O_3 sample.

the initial increase of the ZFC peak with increasing field be related to an increase of the distribution width. This effect can be searched in the $V_b f(V_b)$ data that were presented in Fig. 5(a); in Fig. 7, we present differently this same data, in a way that favors the comparison of the various curves. If $f(V_b)$ is log normal, all $V_b f(V_b)$ curves are simple Gaussians of $\ln T$; their peak temperature corresponds to blocking V_0 in a field H, that is the peak temperatures are deduced from each other by a multiplicative factor (which is the effect of the field on the anisotropy barrier). In Fig. 7, the data is presented as a function of $\ln T$, and the peaks are superposed by a T affinity; also, for clarity, the peak amplitudes have been normalized to one.

A slight but systematic asymmetry of the curves can be noted; they are a little bit more spread out on the low-T side. The derivative estimate of the first points can be less accurate; apart from that difficulty, the effect suggests that the log-normal approximation is not completely correct. This may indicate a difference between the geometrical sizes which are seen by TEM and the effective magnetic sizes. However, the accuracy with which the size histogram of Fig. 1 suggests a log-normal shape is less than that of Fig. 7. The universal success of the log-normal shape for particle size distributions could be more related to practical reasons than really scientifically grounded.

Even though they are slightly asymmetric, the curves in Fig. 7 show that the width of the effective distribution increases for increasing field. Within the present assumptions, we do not intend to reproduce in detail the observed ZFC-peak temperature variation, but we can roughly quantify the effect. For example, when H goes from 1 to 50 Oe, the approximative σ_v that can be read in Fig. 7 increases from 0.8 to 1.1. For $H_c=250$ Oe as obtained above, and using Eq. (3) with $\alpha=1.5$ for the field influence on the barriers, we have computed the corresponding ZFC curves; the curve with ($H=50$ Oe, $\sigma=1.1$) peaks at a 1.3 times higher temperature than the one with ($H=1$ Oe, $\sigma=0.8$). Hence, for increasing field, the observed distribution enlargment is enough for producing an increase of the ZFC-peak temperature, despite the lowering of the barriers.

V. FERRITIN RESULTS

In ferritin, a nonmonotonic variation of the ZFC peak, together with other particular features of the magnetization

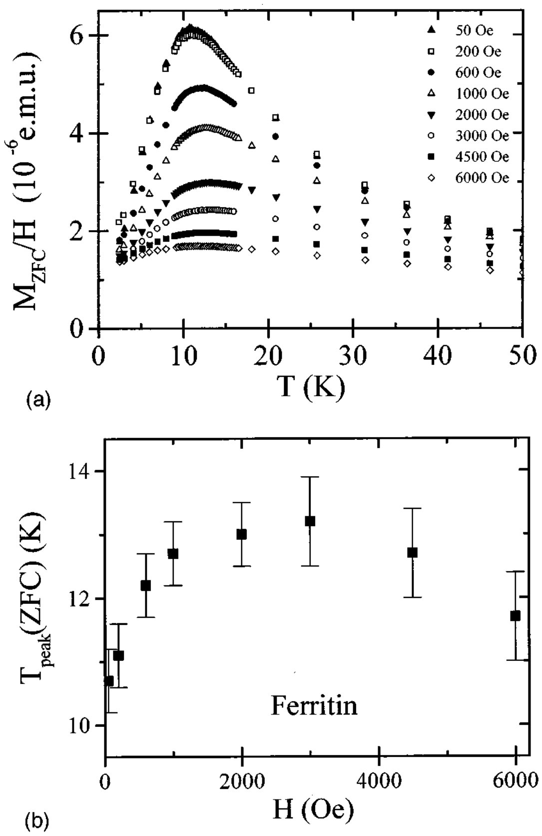

FIG. 8. (a) Measured ZFC magnetizations on the ferritin sample, normalized to the field amplitude. From top to bottom, the field values are 50, 200, 600, 1000, 2000, 3000, 4500, and 6000 Oe. (b) Peak temperatures of the measured ZFC magnetization curves for ferritin [more data than in (a)].

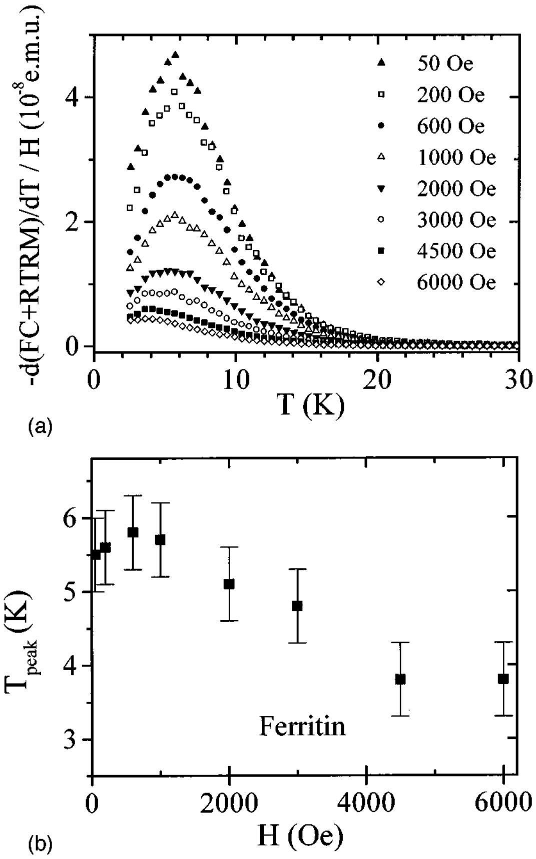

FIG. 9. (a) Temperature derivative of the sum of the measured magnetizations $M_{\mathrm{FC}}+M_{\mathrm{R\text{-}TRM}}$, divided by the field amplitude, for different fields [ferritin sample]. (b) Peak temperatures of the curves in (a) [ferritin sample, more data than in (a)] for different fields, which do not confirm the nonmonotonic behavior observed for the ZFC peak.

relaxation, has been discussed in terms of resonant tunneling at zero field.[4,5] A ''pinch'' of the hysteresis loop is observed around $H=0$;[4,5] viscosity data can be interpreted as showing an anomaly[5] (not yet clear in Ref. 4), but this latter point still raises the question of a relevant normalization for the comparison of viscosity data at various fields, which is not yet completely solved.[4,22] The observation of resonant tunneling is more plausible in ferritin than in the γ-Fe_2O_3 particles, because of the antiferromagnetic character of the particles, which makes their resultant moment smaller ($\sim$50 iron moments); the energy level spacing is thus larger, making wider the field range around zero where the effect can be visible.[6] Prompted by discussions with some of the authors of Refs. 4 and 5, we have measured a commercial ferritin sample and applied the same analysis as above for γ-Fe_2O_3 particles.

We have performed the measurements for fields ranging from 50 to 6000 Oe. The ZFC curves are shown in Fig. 8(a), together with the field dependence of the peaks in Fig. 8(b). Here again a nonmonotonic variation is found, in agreement with previous works.[3–5] Following the procedure of Sec. IV, we have also measured the FC and R-TRM curves at the same fields, and estimated the temperature derivative of the sum, which is shown in Fig. 9(a) [peak values in Fig. 9(b)]. The result is qualitatively similar to the case of the γ-Fe_2O_3 particles. In the region of $\sim$3000 Oe where the ZFC-peak data show a clear maximum, the peak values of the derivative monotonically decrease for increasing field. An anomalous behavior still remains possible within the error bars below 1000 Oe, but it is located far below the anomaly which is seen in the ZFC results, and more accurate data would be needed for discussing this point. Thus, on both samples that we have studied, the same nonmonotonic behavior is obtained from the ZFC peak temperatures, and the anomaly is not confirmed in the other procedure. The analysis of $\partial(M_{\mathrm{FC}}+M_{\mathrm{R\text{-}TRM}})/\partial T$ seems, therefore, able to provide physical information that is of much more direct interpretation than that extracted from ZFC measurements.

VI. CONCLUSIONS

In this paper, we have discussed the physical interpretation of standard magnetic measurement procedures in systems of nanometric magnetic particles, on the basis of experiments performed with two very different samples. One is made of ferrimagnetic particles (γ-Fe_2O_3), highly diluted, with a ZFC-peak temperature of $\sim$65 K, and the other of antiferromagnetic particles of ferritin, less diluted but with much lower magnetic moment, with a ZFC peak in the $10-15$ K range.

In both samples, the ZFC-peak temperature is found to initially increase with field, at variance with the commonsense expectation of an anistropy barrier lowering due to the field. From a very simple description of the blocking and deblocking processes, we recall that the ZFC-peak temperature is not simply related to the typical volume of the distribution $f(V)$; it is influenced by the $1/T$ behavior of the deblocked particles, and involves a $V^2f(V)$ term that enhances the contribution of the larger volumes. The ZFC curve is thus extremely sensitive to the distribution width; the peak rapidly shifts to higher temperatures when the width increases, an effect that we have quantified under simple approximations.

We propose to understand the ZFC anomaly in the light of another experimental procedure. As a first example, the temperature variation of the TRM, which is measured in zero field, does not involve the $1/T$ superparamagnetic contribution, and contains a $Vf(V)$ term that yields a weaker sensitivity to the distribution width. But the TRM does not bring information about the effective distribution of anisotropy barriers in a field. This point can be studied using a reversed-TRM procedure, in which the field is reversed to its opposite value at low temperature. In the sum of the FC magnetization and the R-TRM, the $1/T$ term is eliminated (together with the reversible magnetization), and $f(V)$ comes in through $Vf(V)$ (weak sensitivity to the width), in which V now stands for the volume that is deblocked in the field, thence the access to the field-modulated barrier distribution. Note that one may also use the equivalent combination $M_{\rm FC}-M_{\rm ZFC}$, which presents the same property.

The temperature derivative $\partial(M_{\rm FC}+M_{\rm R\text{-}TRM})/\partial T$ of this sum is proportional to $Vf(V)$, which peaks to a typical volume in the distribution, and our point is the following: for different experiments with various field amplitudes, the magnetic objects that correspond to the peak value remain almost the same (exactly the same in the log-normal case), which is far from being the case for ZFC measurements. Indeed, our measurements on both samples show that the peak of $\partial(M_{\rm FC}+M_{\rm R\text{-}TRM})/\partial T$ decreases for increasing field, in contrast with the peak of the ZFC curves.

The effect of the field on the distribution of anisotropy barriers is not easily described in detail,[17] mainly for two reasons. On the one hand, for random orientations of the particle easy axes, there is no general analytical treatment of the problem. On the other hand, the usual assumptions that are commonly made for describing systems of small particles might become less applicable in the presence of higher fields: Is each particle a single fixed macromoment, or do some parts couple selectively to the field? Are the particles relaxing independently, or do they become influenced by the field of their neighbors? On the γ-Fe_2O_3 sample, which we have studied in more detail than the ferritin, the examination of the measured $\partial(M_{\rm FC}+M_{\rm R\text{-}TRM})/\partial T$ shows that, for increasing field, $Vf(V)$ naturally peaks to lower values, but also becomes wider, as already expected from the only effect of orientational disorder. The observed effect has the correct order of magnitude for compensating the barrier decrease at low fields, and hence for producing the observed anomalous increase of the ZFC peak temperature. We therefore consider that the nonmonotonic variation of the ZFC-peak temperature is related to an enlargment of the effective barrier distribution under the influence of the field; no anomaly is found using the other procedure.

There has been these last years a renewed interest in the low-temperature dynamics of systems of small particles, motivated by a search for quantum tunneling phenomena in these quasimacroscopic objects.[7] Evidencing the quantum effects from viscosity measurements is hindered by the lack of knowledge of the effective barrier distribution, which modulates the temperature variation of the measured relaxation rates.[10,18] Very recently, observations of the nonmonotonic field dependence of the ZFC-peak temperature in ferritin[4,5] have been discussed in terms of possible resonant tunneling effects in zero field.[6] This has prompted us to extend the present work, mainly centered on γ-Fe_2O_3 particles, to a ferritin sample. It appears that the same ''classical'' explanation of the ZFC anomaly should work in both cases. This conclusion does not concern other possible evidences of the resonant tunneling effects in ferritin, such as e.g. the astonishingly pinched hysteresis cycles.[4,5] Here again, as is the case for viscosity, it appears that the barrier distribution plays a non-negligible role, and that the choice of physically meaningful quantities for characterizing the low-temperature dynamics of magnetic nanoparticle systems remains a delicate matter.

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