Temperature dependence of antiferromagnetic susceptibility in ferritin

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We show that antiferromagnetic susceptibility in ferritin increases with temperature between 4.2 and 180 K (i.e., below the Néel temperature) when taken as the derivative of the magnetization at high fields (30×10^4 Oe). This behavior contrasts with the decrease in temperature previously found, where the susceptibility was determined at lower fields (5×10^4 Oe). At high fields (up to 50×10^4 Oe) the temperature dependence of the antiferromagnetic susceptibility in ferritin nanoparticles approaches the normal behavior of bulk antiferromagnets and nanoparticles considering superantiferromagnetism, this latter leading to a better agreement at high field and low temperature. The contrast with the previous results is due to the insufficient field range used ($< 5 \times 10^4$ Oe), not enough to saturate the ferritin uncompensated moment.

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I. INTRODUCTION

Antiferromagnetic (AF) nanoparticles have rich magnetic behavior that can be quite different from their bulk counterparts. This behavior is often termed "anomalous" and "unexpected" and includes enhanced magnetic moment and coercivity,[1] exchange bias,[1,2] increase in magnetic moment with temperature,[3–5] and decrease in AF susceptibility (χ_{AF}) with temperature below the order temperature T_N and its enhancement compared to bulk.[2,3,6–8] This last issue is the subject of the present report.

The enhancement of χ_{AF} below T_N in nanoparticles compared to bulk was predicted by Néel[9] and estimated to decrease with temperature.[10,11] The extra susceptibility (χ_a) is a finite-size effect termed superantiferromagnetism. In a simple picture, superantiferromagnetism arises in particles in which the AF easy axis is perpendicular to the external field, where surface spins rotate more in the field direction than inner ones since they have less neighbors. This corresponds to a progressive rotation of the AF easy axis from surface to surface across the particle, in particles with even number of ferromagnetic spin planes. Néel[9] also highlighted the first difficulty in finding experimental evidence of superantiferromagnetism: the need for magnetic particles with small sizes and controlled size distribution.[11] Other difficulties became apparent later and are related to the fact that AF nanoparticles have an uncompensated magnetic moment μ_{un} superposed to χ_{AF}. μ_{un} hinders the determination of $\chi_{AF}(T)$ based on low-field and high-field susceptibility measurements. In the case of low-field measurements, the difficulty arises since μ_{un} has an important Curie-type contribution that is not straightforward to model, due to the fact that the temperature

dependence of μ_{un} is not yet clear.[5,12,13] In the case of high-field measurements, the influence of μ_{un} is more subtle and is related to the nonsaturation of the magnetization associated to μ_{un} (M_μ) at the normally used high fields (5×10^4 Oe) and temperatures of interest. Again, neither the absence of a reliable model of the field dependence of M_μ nor even of its approach to saturation makes the separation between the contribution of χ_{AF} and μ_{un} to the total magnetization (and the subsequent determination of $\chi_{AF}(T)$) quite difficult.

Despite all these questions, some steps were made toward the determination of $\chi_{AF}(T)$. In a first approach, $M_\mu(H)$ was modeled with a Langevin law,[2,14] which enabled the first report on $\chi_{AF}(T)$.[2] In Ref. 2 and in Refs. 3 and 6, $\chi_{AF}(T)$ was found to decrease with temperature, and this decrease was associated to superantiferromagnetism.[2] Evidence of superantiferromagnetism based on a description of magnetization taken at 2 K up to 30×10^4 Oe was later reported in Ref. 8. The model used for $M_\mu(H)$ was further refined by the use of a distribution and an Ising-type function that takes into account the coupling between μ_{un} and the AF moments.[7,8] Yet, these improvements did not change the observed decrease in $\chi_{AF}(T)$. A method for the separation between the $\chi_{AF}(T)$ and μ_{un} components in the magnetization without the need of a model was also proposed;[15] however, this method does not take into account anisotropy effects, which are relevant in antiferromagnetic nanoparticles, as highlighted in Ref. 16. It also became clear in Ref. 16 that a spurious contribution to $\chi_{AF}(T)$ arises when modeling $M_\mu(H)$ without considering anisotropy. This spurious contribution decreases with increasing temperature toward zero as anisotropy energy becomes small compared to $k_B T$ and $\mu_{un} H$.
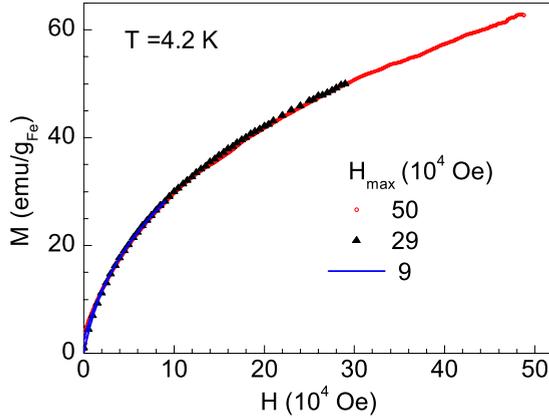
FIG. 1. (Color online) Magnetization curves of ferritin at 4.2 K taken up to 50×10^4 Oe (pulsed fields), 29×10^4 Oe (static fields, extraction magnetometer), and 9×10^4 Oe (static fields, VSM).

FIG. 2. (Color online) Magnetization curves of ferritin at selected temperatures, taken up to $29/30 \times 10^4$ Oe (points) and taken up to 9×10^4 Oe (lines).

Given this scenario, a better insight on $\chi_{AF}(T)$ depends on measurements of the susceptibility at fields higher than those used up to now. With this aim, we present measurements taken up to different maximum fields and different techniques of measuring magnetization in ferritin, a model system for nanoparticles with AF interactions where many of the above-cited studies where performed.[2,7,8,14,15] We study the dependence of the derived $\chi_{AF}(T)$ on the field at which it is considered, and we discuss its origin. We compare $\chi_{AF}(T)$ estimated at the highest measured fields to that estimated from mean field and from mean field considering superantiferromagnetism. We also discuss the absence of a spin-flop transition in ferritin up to 50×10^4 Oe in terms of the random local anisotropy model.

II. EXPERIMENT

Ferritin consists of a hollow spherical shell composed of 24 protein subunits surrounding a ferrihydrite-like core. The diameter of the cavity is on the order of 7–8 nm and average size of the core of horse spleen ferritin is 5 nm.[17] Horse spleen ferritin samples used in these experiments were obtained from Sigma Chemical Co. and prepared in powder samples by evaporation of the solvent at room temperature. The iron content (14.25 % in weight) was determined by inductively coupled plasma spectrometry. ac susceptibility was determined as a function of temperature after cooling in the absence of field, at selected frequencies (33, 476 and 1379 Hz) and a field amplitude of 4 Oe, using a magnetic property measurement system (MPMS) model XL, Quantum Design. Magnetization was determined as a function of field (i) up to 9×10^4 Oe at different temperatures using a physical properties measurement system (PPMS, Quantum Design) with a vibrating sample magnetometer (VSM) option, (ii) up to $29/30 \times 10^4$ Oe at different temperatures using an extraction magnetometer in a Bitter magnet (HFML facility, Nijmegen), and (iii) up to 50×10^4 Oe at 4.2 K using pickup coils and a pulsed field (LNCMP facility, Toulouse). Magnetization curves obtained in (ii) and (iii) were scaled with respect to those obtained in (i). Concerning curves obtained in (ii), scaling constitutes a small correction ($<5\%$) and all
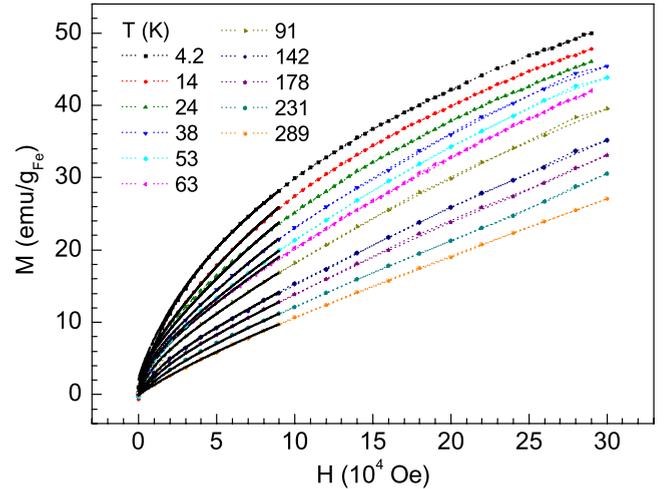
analysis and conclusions here presented do not depend on this scaling.

III. RESULTS AND DISCUSSION

A. Magnetization and high-field susceptibility

The scaled magnetization curves taken up to 9×10^4, $29/30 \times 10^4$, and 50×10^4 Oe at 4.2 K are shown in Fig. 1 (in emu per grams of iron). The magnetization curve and its derivative (see Fig. 3) have no signs of a spin-flop transition. On the contrary, after the initial fast saturation that occurs up to $\sim 6 \times 10^4$ Oe, the magnetization undergoes a slow approach to saturation. Clearly, μ_{un} is not yet saturated (i.e., magnetization is not yet linear with field) at fields of the order of those often used to estimate χ_{AF} (5×10^4 Oe). Both the slow approach to saturation and the absence of a spin flop are in accordance to the previous high-field measurements performed in horse spleen ferritin at low temperature [at 2 K and up to 30×10^4 Oe (Ref. 8) and at 1.52 K and up to 55×10^4 Oe (Ref. 18)].

The slow approach to saturation is also observed in $M(H)$ curves obtained at different temperatures (Fig. 2). However, as temperature increases, the magnetization approaches a linear regime at lower fields, i.e., at higher temperatures, the derivative of magnetization with respect to the field dM/dH approaches a nearly constant value for lower fields (Fig. 3).

With the values of dM/dH it is possible to study the different evolutions of χ_{AF} with temperature, when χ_{AF} is estimated at different field values. In order to distinguish between dM/dH taken at a given field and the real χ_{AF} obtained for complete μ_{un} saturation, we term the susceptibilities obtained at different (high) fields as high-field susceptibility $\chi_{hf} = dM/dH$. In Fig. 4 it is possible to observe that χ_{hf} decreases with temperature when taken at 5×10^4 Oe, in accordance with previous results.[2,7,8,15] When taken at 9×10^4 Oe, χ_{hf} has a nonmonotonic behavior, increasing and then decreasing with temperature. For $H = 30 \times 10^4$ Oe, χ_{hf} is reduced about three times compared to the
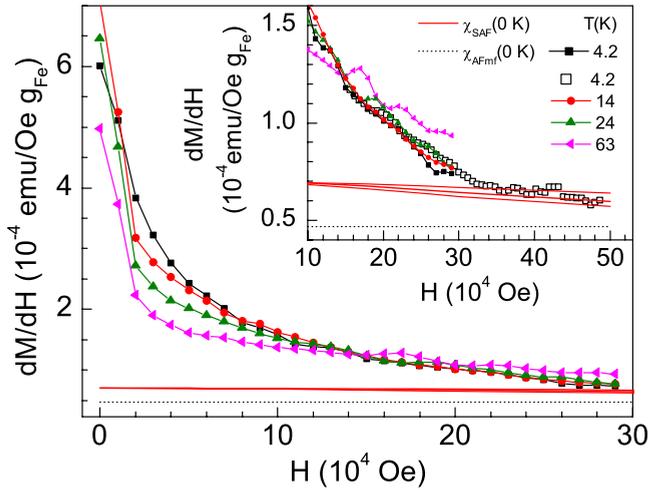
FIG. 3. (Color online) Derivative of the magnetization curves taken up to 29×10^4 Oe (static fields, extraction magnetometer) as a function of field for selected temperatures. Dotted line shows χ_{AF} expected from bulk mean field at 0 K (termed χ_{AFmf}) and continuous lines represent the antiferromagnetic susceptibility considering superantiferromagnetism (χ_{SAF}) also at 0 K, for $2N = 10$, 15, and 20. Inset shows zoom over the high-field region, including dM/dH values obtained up to 50×10^4 Oe at 4.2 K (pulsed fields).

values at 5×10^4 Oe and increases with temperature from 4.2 to about 180 K. An even lower value of χ_{hf} is obtained at 4.2 K and 50×10^4 Oe. This clearly shows that the temperature dependence of the estimated χ_{AF} depends on the field at which it is considered, with the trend to increase with temperature being more evident as the field increases. The anomalous behavior of χ_{AF} decreasing with temperature for $T < T_N$ almost vanishes when χ_{AF} considered at sufficiently high fields. This is in agreement with a recently published Monte Carlo simulation of AF nanoparticles with an even number of planes, where the simulated susceptibility increases with temperature.[19]

B. The absence of a spin-flop transition

As previously reported,[18] there is no evidence of a spin-flop transition up to 50×10^4 Oe in ferritin. In Ref. 18, a spin-flop transition was more likely to occur than in the present case since the temperature was lower and the field higher. From mean-field theory, at 0 K, the spin-flop field is $H_{sf} = (2H_E H_K)^{1/2}$ (where H_E is the exchange field and H_K is the anisotropy field), which in ferritin is about 10×10^4 Oe accordingly to estimations of H_E and H_K of Ref. 8. As discussed in Ref. 18, the experimental evidence of the absence of a spin flop up to 50×10^4 Oe implies an enhancement of H_K and/or H_E compared to that expected. The absence of a spin flop in this field range may also be due to the relatively large uncompensated moment of ferritin, as highlighted in Ref. 20, and both reasons are most probably related. In general H_K is estimated from the anisotropy constant K associated to the blocking process and from a saturation (or sublattice) magnetization as $H_K = K/M_0$. K is often estimated by dividing the activation energy E by the average nanoparticle volume since in nanoparticles with intraparticle ferromag-
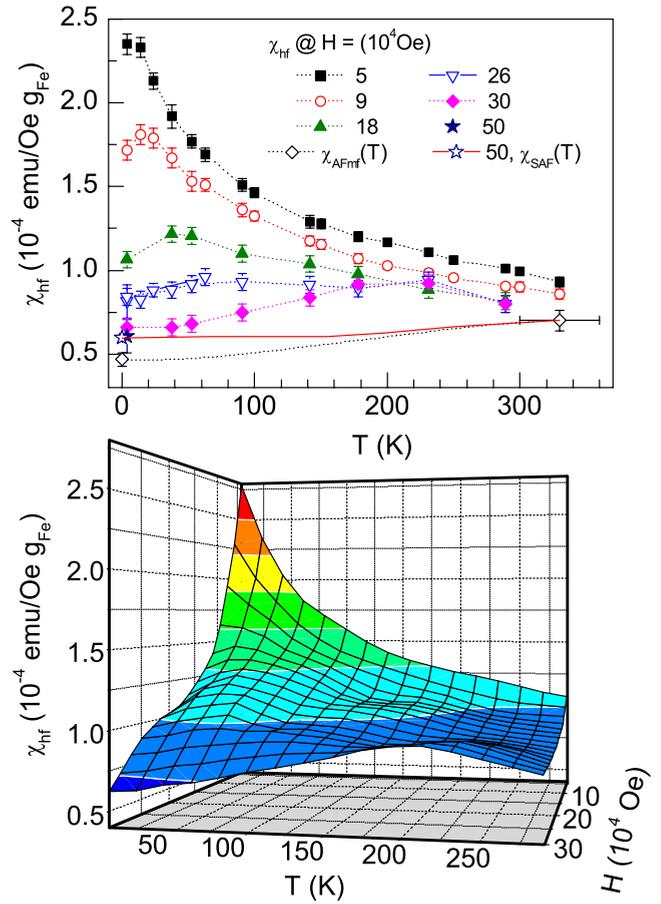
FIG. 4. (Color online) Top: high-field susceptibility χ_{hf} as a function of temperature at selected field values, antiferromagnetic susceptibility estimated from mean field ($\chi_{AFmf}(T)$, expected for bulk materials), and antiferromagnetic susceptibility estimated from mean field considering the contribution of superantiferromagnetism ($\chi_{SAF}(T)$, expected for nanoparticles) at 50×10^4 Oe. Bottom: χ_{hf} as a function of temperature and field obtained from magnetization curves taken up to 30×10^4 Oe.

netic interactions $E = KV$. Since $E = 255$ K (see Sec. III D) and the average ferritin core has $N = 2500$ Fe ions,[17] the average anisotropy constant per Fe ion of the average core is $K = 1.4 \times 10^{-17}$ erg/Fe$_{ion}$. Taking the sublattice magnetization $m_0 = 3.2$ μ_B/Fe$_{ion}$ (see Sec. III C) the anisotropy field is $H_K = K/m_0 = 470$ Oe and so $H_{sf} = 7 \times 10^4$ Oe (see estimation for H_E in Sec. III C) in accordance with previous estimations.[8,20] However, $E = KV$ does not hold in AF nanoparticles, where in general $E \propto V^p$, with $p < 1$. In fact, it was recently shown that in ferrihydrite the energy barrier is proportional to the square root of the total volume (i.e., $p = 1/2$), corresponding to a random distribution of energy barriers and probably of uncompensated ions.[21] This means that in each particle, the effective value of E is given by the fluctuation of the local anisotropy energy such that the local anisotropy constant K' is higher than the average value calculated by $K = E/V$, being higher by a factor of $N^{1/2}$ where N is the number of Fe ions. In other words, the energy of a nanoparticle with N Fe ions and the same local anisotropy energy of ferritin but without a random distribution of anisotropy barriers would be

$$E' = K'V = EN^{1/2}. \qquad (1)$$

K' is the barrier that each moment experiences, and so we can associate it to the spin-flop process. By doing so, we can define a local anisotropy field $H'_K = H_K N^{1/2}$ and a local spin-flop field $H'_{sf} = (2H_E H'_K)^{1/2}$ whose estimated value, 46×10^4 Oe, is close to the maximum field used here. Therefore, the experimental absence of a spin flop in the field range used here can be, at least, partially explained in the frame of the mean field considering that $E \propto V^{1/2}$. We also emphasize that while the blocking is primarily probing the anisotropy energy experienced by the uncompensated moments in their process of crossing the energy barrier between easy directions, the flopping process is primarily associated to the anisotropy experienced by the AF coupled moments, and the anisotropy field associated to AF moments can be significantly different from that of the uncompensated moments.

C. Bulk antiferromagnetic and superantiferromagnetic susceptibilities

As one might expect, the study of the enhancement of χ_{AF} in nanoparticles and of the temperature dependence of χ_{AF} benefits from comparing to bulk results. This is not possible for ferritin since ferrihydrite exists only in the form of nanoparticles.[22] However a comparison to mean-field estimations can be made. In the mean-field context, the perpendicular AF susceptibility $\chi_\perp$ is

$$\chi_\perp = \frac{M_0}{H_E},$$

$$H_E = \frac{3k_B T_N}{m_0}, \qquad (2)$$

where m_0 and M_0 are the magnetic moment and magnetization of an AF sublattice at 0 K, respectively, and H_E the intersublattice exchange field. At $T = T_N$, χ_{AF} estimated from mean field χ_{AFmf} is equal to $\chi_\perp$, and at $T = 0$ K $\chi_{AFmf} = \frac{2}{3}\chi_\perp$. Equation (2) disregards the anisotropy field, which is a good approximation for estimating χ_{AFmf} of ferritin since it is about 2 orders of magnitude lower than H_E. Concerning the values to be used in Eq. (2), there is a broad range of T_N estimated for ferritin and ferrihydrite (typically from 300 to 500 K), depending on the used technique.[2,3,8,15,23] Using magnetization measurements, T_N is always obtained by extrapolation[2,8,15] and is higher than that obtained as a direct result with neutron diffraction for ferrihydrite (330 ± 30 K in Ref. 23 and $\simeq 350$ K in Ref. 3). Neutron diffraction also gives an estimation of the magnetic moment: $m(5 \text{ K}) = 3.2 \ \mu_B/\text{Fe}_{\text{ion}}$.[23] This value is lower than that of isolated Fe ions $5\mu_B$ [previously used in the estimation of $\chi_\perp$ (Ref. 8)] but is reasonable for a compound where magnetic exchange interactions are influenced by a high degree of structural disorder.[23] m_0 can be further obtained by extrapolation to 0 K using the mean-field temperature dependence for the magnetic moment. Using the neutron-diffraction results $H_E = 456 \pm 40 \times 10^4$ Oe and $\chi_\perp = 7.0 \pm 0.6 \times 10^{-5}$ emu/Oe g_{Fe}. χ_{AFmf} at 0 and T_N thus estimated are plotted in Fig. 4.

Based on χ_{AFmf} estimation it is also possible to further estimate the antiferromagnetic susceptibility expected when considering superantiferromagnetism χ_{SAF} (both temperature and field dependent). At zero field, and considering only first neighbor exchange, the perpendicular susceptibility of particles with even number of ferromagnetic spin planes $2N$ is $\chi_{\perp 2N} = 2\chi_\perp$, and considering n^{th} neighbor interactions would increase this estimation.[8,11] By increasing the field, $\chi_{\perp 2N}$ approaches $\chi_\perp$, being this approach dependent on a characteristic field given by $h = H_E/2N$. For low h values the relation between $\chi_{\perp 2N}$ and $\chi_\perp$ is

$$\frac{\chi_{\perp 2N}}{\chi_\perp} = 2 - \frac{4h^2}{3}. \qquad (3)$$

For h around unity, $\chi_{\perp 2N}/\chi_\perp$ can be obtained by solving an integral equation,[8,11] whose results are given in tables in Ref. 11. The perpendicular susceptibility of a set of nanoparticles with half of them having $2N$ even can be written as

$$\chi_{\perp SAF} = \frac{1}{2}\chi_\perp + \frac{1}{2}(\chi_\perp + \chi_a), \qquad (4)$$

where the extra susceptibility $\chi_a = \chi_{\perp 2N} - \chi_\perp$ is a function of H and T and can be expressed as $\chi_a = k(H,T)\chi_\perp$. The susceptibility of a set of randomly oriented nanoparticles can then be estimated as

$$\chi_{SAF}(H,T) = \frac{2}{3}\left(\chi_\perp + \frac{1}{2}k(H,T)\chi_\perp\right) + \frac{1}{3}\chi_\parallel(T). \qquad (5)$$

In the frame of mean field, considering two sublattices with negligible intralattice exchange interaction, the temperature dependence of $\chi_\parallel(T)$ is given by[24]

$$\chi_\parallel(T) = \frac{Ng^2\mu_B^2 S^2 B'_S(y)}{k_B[T + 3T_N S(S+1)^{-1}B'_S(y)]}, \qquad (6)$$

with

$$y = \frac{3T_N M}{(S+1)T},$$

$$M = SB_S(y). \qquad (7)$$

Considering S of Fe^{3+}, $\chi_{AFmf}(T)$ can be readily obtained (Fig. 4, upper panel). $\chi_{SAF}(H,T)$ can be further calculated by estimating $k(H,T)$, which depends on h (i.e., on $2N$ and H_E) and on T/T_N. Using $2N = 15 \pm 5$ (Ref. 8) and calculating $k(H,T)$ based on Eq. (3) for $h < 0.3$ and on the tables presented in Ref. 11 for $h > 0.3$ and $T/T_N > 0.2$, one can estimate $\chi_{SAF}(H,T)$, plotted as a function of field for $T = 0$ K in Fig. 3 (using the average value of $2N$ and its upper and lower limits) and as a function of temperature for $H = 50 \times 10^4$ Oe in upper panel of Fig. 4. It is clear from Fig. 3 that up to fields of the order of 25×10^4 dM/dH is higher than that expected from χ_{SAF} and χ_{AFmf}, having thus contribution from mechanisms other than bulk antiferromagnetism and superantiferromagnetism. For $H > 29 \times 10^4$ Oe and at 4.2 K, dM/dH approaches χ_{SAF} and χ_{AFmf}, and bulk antiferromagnetism and superantiferromagnetism are the relevant contributions for dM/dH (Fig. 3, inset). At 50×10^4 Oe and 4.2 K,
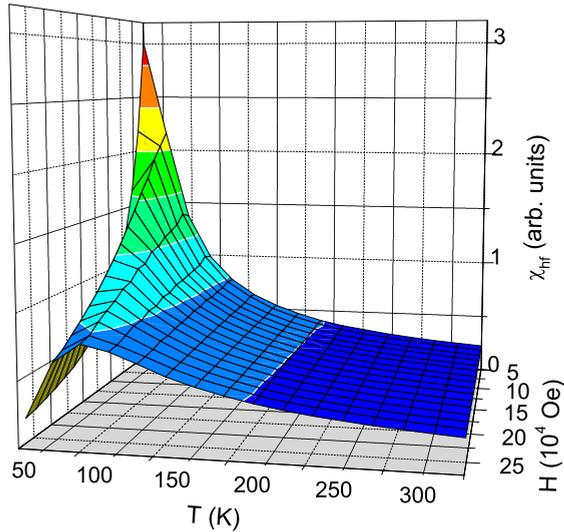
FIG. 5. (Color online) $\chi_{hf}=dM/dH$ as a function of temperature and field obtained from magnetization curves simulated using the Langevin function and $\mu_{un}=5$ μ_B.

dM/dH is on the order of χ_{SAF} and χ_{AFmf}, being closer to χ_{SAF} than χ_{AFmf}. Therefore, considering that at this temperature and field μ_{un} is already saturated the AF susceptibility has a contribution from superantiferromagnetism. Concerning the temperature dependence of the susceptibilities, (Fig. 4, upper panel), it is clear that for lower and higher temperatures χ_{hf} at 30×10^4 Oe is close to χ_{SAF} while it deviates in the intermediate temperature region, this deviation being higher than the difference between χ_{SAF} and χ_{AFmf}. It is also noteworthy that while $\chi_{\perp 2N}$ decreases with temperature due to the approach of $\chi_{\perp 2N}$ to $\chi_{\perp}$ at high fields, due to averaging particles with even and odd $2N$, averaging $\chi_{\parallel}$ and $\chi_{\perp}$, and due to the temperature increase in $\chi_{\parallel}$, χ_{SAF} at 50×10^4 Oe estimated for ferritin is roughly constant up to $T=150$ K increasing then with temperature up to T_N.

D. The role of anisotropy and small magnetic moments

From the above discussion, it is clear that superantiferromagnetism is not the most relevant mechanism responsible for the fact that χ_{hf} is larger than χ_{AF} for $H<28\times10^4$ neither for the decrease in χ_{hf} with temperature below T_N. It is therefore interesting to investigate the origin of this enhancement and decrease with temperature, which is expected to be related to the nonsaturation of μ_{un}. In turn, this nonsaturation is either due to small μ_{un} values or due to the role of anisotropy in the approach to saturation of M_{μ}. The existence of such small moments, in particular paramagnetic Fe^{3+} ions, is in fact expected from relaxometry results.[25] These small moments may in fact be related to the nonmonotonic behavior observed in the temperature dependence of χ_{hf}. Simple calculations of a hypothetical contribution of small moments to χ_{hf} based on dM/dH with $M(H)$ being given by the Langevin law show that dM/dH increases and then decreases with temperature at a given field, with the temperature at which that maximum occurs increasing with the field (Fig. 5). This behavior is qualitatively similar to that observed in Fig. 4.

Concerning the role of anisotropy, although for fields on the order of 10×10^4 Oe, for the typical average μ_{un} of ferritin (~ 100 μ_B) and $T\sim 5$ K, M_{μ} would be close to saturation accordingly to the Langevin law, anisotropy retards saturation to higher fields so that the typical average μ_{un} still gives an important contribution to χ_{hf} in the above-mentioned conditions. As temperature increases, the relevance of anisotropy energy decreases compared to k_BT, leading to a decrease in the contribution of M_{μ} to χ_{hf}. Considering only the M_{μ} component and two temperatures $T_2>T_1$, there is a crossover field below which $\chi_{hf}(T_2)<\chi_{hf}(T_1)$ so that M_{μ} gives a spurious contribution to the total χ_{hf} that decreases with temperature. This crossover field increases in comparison to the Langevin law when uniaxial anisotropy is considered. When surface anisotropy is further taken into account, the increase in this crossover field is quite dramatic: accordingly to simulations shown in Ref. 26, the crossover field is on the order of 8×10^4 Oe for Co nanoparticles (515 spins) and temperatures between ~ 0.5 and ~ 10 K.

The existence of a relevant anisotropy contribution to $M(H)$ curves can be qualitatively evaluated combining information from M_{μ} in a H/T scale and ac susceptibility since anisotropy does not affect the equilibrium linear susceptibility (χ' above blocking), affecting M_{μ} at intermediate fields whenever relevant. The in phase (χ') and out of phase (χ'') components of the ac susceptibility (Fig. 6) show characteristic features of ferritin superparamagnetic nanoparticles, namely, frequency dependence below temperatures on the order of 40 K and a frequency-dependent maximum at around 20 K.[27] From the frequency dependence of the maximum of χ'' it is possible to estimate an energy barrier associated to the blocking process as 255 K. The antiferromagnetic susceptibility $\chi_{SAF}(T)$ and $\chi_{AFmf}(T)$ can be subtracted to χ' in order to study the temperature dependence of μ_{un} based on a susceptibility temperature product plot since interparticle interactions are negligible.[27] $[\chi'-\chi_{SAF}(T)]T$ corresponds also to the slope of $M_{\mu}=M-\chi_{SAF}(T)H$ in a H/T scale at $H=0$. Both $[\chi'-\chi_{SAF}(T)]T$ and $[\chi'-\chi_{AFmf}(T)]T$ increase with temperature up to 40 K, the temperature at which χ'' becomes zero, corresponding to an increase in the average μ_{un} due to the unblocking process [Fig. 6(c)]. For $T>40$ K, $[\chi'-\chi_{SAF}(T)]T$ and $[\chi'-\chi_{AFmf}(T)]T$ decrease with temperature due to the decrease in the sublattice magnetization when approaching T_N,[8,15] being this decrease more pronounced for $T\gtrsim 90$ K. Due to the decrease in $[\chi'-\chi_{SAF}(T)]T$ with temperature for $T>40$ K (above blocking), M_{μ} is not expected to scale in a H/T plot, being expected lower values for M_{μ} in the curves taken at higher temperatures in all the H/T ranges. In Fig. 7 it is clear that above blocking $M_{\mu}=M-\chi_{SAF}(T)H$ does not scale in H/T for $H/T>100$ Oe/K. In particular, in the $38<T<91$ K range and $H/T>100$ Oe/K, M_{μ} (and the slope of M_{μ}) is higher in the curves taken at higher temperatures (Fig. 7, inset) unlike that expected from the slightly decrease in $(\chi'-\chi_{SAF}(T))T$. For $T>91$ K, M_{μ} in a H/T scale is always lower in the curves taken at higher temperatures, as expected from the decrease in $[\chi'-\chi_{SAF}(T)]T$.

In other words, the nonscaling of M_{μ} in the $38<T<91$ K temperature range and intermediate H/T values
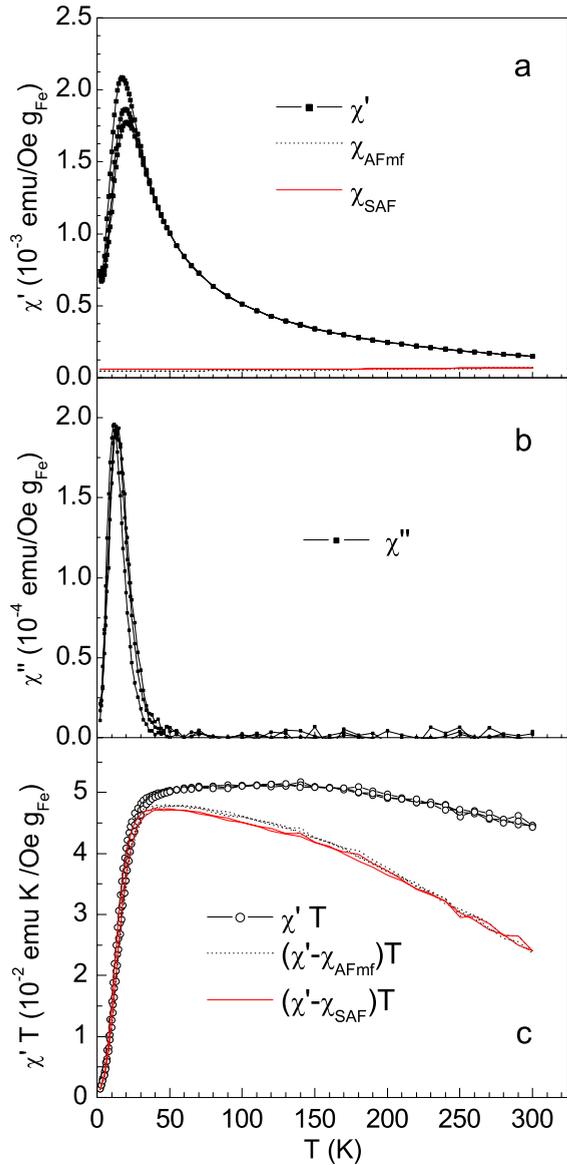
FIG. 6. (Color online) (a) Temperature dependence of the in phase component of the ac susceptibility χ' for different field frequencies (33, 476, and 1379 Hz), $\chi_{SAF}(T)$ estimated considering superantiferromagnetism, and $\chi_{AFmf}(T)$ estimated from mean field; (b) temperature dependence of the out of phase component of the ac susceptibility χ''; and (c) temperature dependence of the $\chi'T$ product and temperature dependence of the product of temperature and susceptibility associated to μ_{un} determined as $[\chi' - \chi_{AFmf}(T)]T$ and $[\chi' - \chi_{SAF}(T)]T$.

where M_μ has higher values for curves taken at higher temperatures cannot be explained from the behavior of $\mu_{un}(T)$. Since $\mu_{un}(T)$ cannot account for the behavior of $M_\mu(H/T)$, since interparticle interactions in ferritin are negligible[27] and a distribution of uncompensated moments for itself does not produce a nonscaling of M_μ (the sum of functions of H/T is also a function of H/T), the only reason left for the behavior of $M_\mu(H/T)$ in the $38 < T < 91$ K temperature range is anisotropy. In fact, the increase in $M_\mu(H/T)$ for curves taken at higher temperatures and for a given H/T value in a intermediate range and scaling (or decrease) in the low H/T range is,
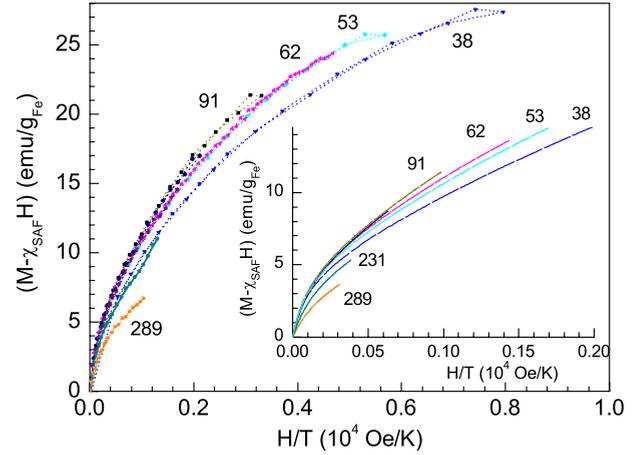
FIG. 7. (Color online) Saturation component of the magnetization, obtained after subtracting $\chi_{SAF}(T)H$ to the total magnetization, in a H/T scale. Inset shows a zoom over a lower field region, concerning data obtained with VSM.

in fact, a fingerprint of anisotropy, as found for instance in Co nanoparticles[28] and in simulations.[16,26] Therefore anisotropy has a relevant contribution to the $M(H)$ curves of ferritin, being one of the causes to the nonsaturation of μ_{un} at the applied fields normally used.

IV. CONCLUSIONS

We show that the derived $\chi_{AF}(T)$ depends critically on the maximum field at which it is determined. When it is determined at fields on the order of 5×10^4 Oe, χ_{AF} decreases with temperature, similar to earlier studies.[2,7,8] This behavior is related to the influence of anisotropy in the approach to saturation of μ_{un} and probably due to the existence of small magnetic moments, which leads to the nonsaturation of M_μ at fields of the order of 5×10^4. On the contrary, when χ_{AF} is determined as dM/dH at 30×10^4 Oe, it increases with temperature for $4.2 < T < 180$ K (i.e., below T_N) as in bulk AF. At fields on the order of 50×10^4 Oe and at 4.2 K, χ_{AF} determined as dM/dH is in good agreement with χ_{AF} estimated from mean field considering the effect of superantiferromagnetism and on the order of χ_{AF} estimated from mean field.

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