Temperature dependence of antiferromagnetic susceptibility in ferritin

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We show that antiferromagnetic susceptibility in ferritin increases with temperature between 4.2 K and 180 K (i.e., below the Néel temperature) when taken as the derivative of the magnetization at high fields (30 x 10^4 Oe). This behavior contrasts with the decrease in temperature previously found, where the susceptibility was determined at lower fields (5 x 10^4 Oe). At high fields (up to 50 x 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 x 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 of magnetic moment with temperature,[3, 4, 5] and decrease of AF susceptibility (χ_{AF}) with temperature below the order temperature T_N and its enhancement compared to bulk [2, 3, 6, 7, 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 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 χ_{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-like 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 non-saturation of the magnetization associated to μ_{un} (M_{μ}) at the normally used high fields (5 x 10^4 Oe) and temperatures of interest. Again, 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 χ_{AF}(T)) quite difficult.

Despite all these questions, some steps were made towards the determination of χ_{AF}(T). In a first approach, M_{μ}(H) was modelled with a Langevin law,[2, 14] which enabled the first report on χ_{AF}(T) [2]. In Ref.[2] and in following ones,[3, 6] χ_{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 x 10^4 Oe was later reported in Ref.[8]. The model used for M_{μ}(H) was further refined by the use of a distribution and an Ising-like function that takes
into account the coupling between $\mu_{\text{un}}$ and the AF moments [7, 8]. Yet, these improvements did not change the observed decrease of $\chi_{\text{AF}}(T)$. A method for the separation between the $\chi_{\text{AF}}(T)$ and $\mu_{\text{un}}$ 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 $\chi_{\text{AF}}(T)$ arises when modelling $M_{\mu}(H)$ without considering anisotropy. This spurious contribution decreases with increasing temperature towards zero as anisotropy energy becomes small compared to $k_B T$ and $\mu_{\text{un}} H$.

Given this scenario, a better insight on $\chi_{\text{AF}}(T)$ 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 $\chi_{\text{AF}}(T)$ on the field at which it is considered and we discuss its origin. We compare $\chi_{\text{AF}}(T)$ 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 $50 \times 10^4$ Oe in terms of the random local anisotropy model.

II. EXPERIMENTAL

Ferritin consists of a hollow spherical shell composed of 24 protein subunits surrounding a ferrihydrite-like core. The diameter of the cavity is of 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 Company 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 mass Oe, using a MPMS-XL Quantum Design system. Magnetization was determined as a function of field i) up to $9 \times 10^4$ Oe at different temperatures using a PPMS system (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 $50 \times 10^4$ Oe at 4.2 K using pick up 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 $9 \times 10^4$, $29/30 \times 10^4$, and $50 \times 10^4$ 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 $6 \times 10^4$ Oe, the magnetization undergoes a slow approach to saturation. Clearly, $\mu_{\text{un}}$ is not yet saturated (i.e., magnetization is not yet linear with field) at fields of the order of those often used to estimate $\chi_{\text{AF}} (5 \times 10^4$ 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 $30 \times 10^4$ Oe [8] and at 1.52 K and up to $55 \times 10^4$ Oe [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 $\chi_{\text{AF}}$ with temperature, when $\chi_{\text{AF}}$ is estimated at different field values. In order to distinguish between $dM/dH$ taken at a given field and the real $\chi_{\text{AF}}$ obtained for complete $\mu_{\text{un}}$ 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 $\chi_{hf}$ decreases with temperature when taken at $5 \times 10^4$ Oe, in accordance with previous results [2, 7, 8, 15]. When taken at $9 \times 10^4$ Oe, $\chi_{hf}$ has a non-monotonic behavior, increasing and then decreasing.
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 $9 \times 10^4$ Oe (lines).

FIG. 3: (color online) Derivative of the magnetization curves taken up to $29 \times 10^4$ Oe (static fields, extraction magnetometer) as a function of field for selected temperatures. Dotted line shows $\chi_{AF}$ expected from bulk mean field at 0 K (termed $\chi_{AF,mf}$) and continuous lines represent the antiferromagnetic susceptibility considering superantiferromagnetism ($\chi_{SAF}$) 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 $50 \times 10^4$ Oe at 4.2 K (pulsed fields).

with temperature. For $H = 30 \times 10^4$ Oe, $\chi_{AF}$ is reduced about 3 times compared to the values at $5 \times 10^4$ Oe and increases with temperature from 4.2 to about 180 K. An even lower value of $\chi_{AF}$ is obtained at 4.2 K and $50 \times 10^4$ Oe. This clearly shows that the temperature dependence of the estimated $\chi_{AF}$ 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 $\chi_{AF}$ decreasing with temperature for $T < T_N$ almost vanishes when $\chi_{AF}$ 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].

FIG. 4: (color online) Above: high field susceptibility $\chi_{hf}$ as a function of temperature at selected field values, antiferromagnetic susceptibility estimated from mean field ($\chi_{AF,mf}(T)$, expected for bulk materials) and antiferromagnetic susceptibility estimated from mean field considering the contribution of superantiferromagnetism ($\chi_{SAF}(T)$, expected for nanoparticles) at $50 \times 10^4$ Oe. Below: $\chi_{hf}$ as a function of temperature and field obtained from magnetization curves taken up to $30 \times 10^4$ Oe.

B. The absence of a spin-flop transition

As previously reported [18] there is no evidence of a spin-flop transition up to $50 \times 10^4$ 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 $H_{sf} = (2H_EH_K)^{1/2}$ (where $H_E$ is the exchange field and $H_K$ the anisotropy field), which in ferritin is about $10 \times 10^4$ 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 $50 \times 10^4$ 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 ferromagnetic 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 $m_0 = 3.2 \ \mu_B/Fe_{ion}$ (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 $H_K$ in Sec. III C) in accordance with previous estimations [8, 20]. However, $E = KV$ does not hold in AF nanoparticles, where in nanoparticles with intraparticle ferromagnetic interactions $E < V^{p}$, 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

$$E' = K'V = EN^{1/2}. \tag{1}$$

$K'$ is the barrier that each moment experiences and so we can associated 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, $46 \times 10^4$ Oe, is close to the maximum field here used. Therefore, the experimental absence of a spin-flop in the field range here used 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 expected when considering superantiferromagnetism $\chi_{SAF}$ (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

$$\frac{\chi_{\perp 2N}}{\chi_{\perp}} = 2 - \frac{4h^2}{3} \tag{3}$$

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

$$\chi_{\perp SAF} = \frac{1}{2} \chi_{\perp} + \frac{1}{2} (\chi_{\perp} + \chi_{SA}) \tag{4}$$

C. Bulk antiferromagnetic and superantiferromagnetic susceptibilities

As one might expect, the study of the enhancement of $\chi_{AF}$ in nanoparticles and of the temperature dependence of $\chi_{AF}$ 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

$$\chi_{\perp} = \frac{M_0}{H_E} \tag{2}$$

$$H_E = \frac{3k_B T_N}{m_0}$$

where $m_0$ and $M_0$ are the magnetic moment and magnetization of an AF sublattice at 0 K, respectively, and $H_E$ the inter-sublattice exchange field. At $T = T_N$, $\chi_{AF}$ estimated from mean field $\chi_{AFmf}$ is equal to $\chi_{\perp}$, and at $T = 0$ K $\chi_{AFmf} = \frac{8}{3} \chi_{\perp}$. Eq. 2 disregards the anisotropy field, which is a good approximation for estimating $\chi_{AFmf}$ 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 ($330 \pm 30$ K in Ref. [23] and $\geq 350$ K in Ref. [3]). Neutron diffraction also gives an estimation of the magnetic moment: $m(5 K) = 3.2 \ \mu_B/Fe_{ion}$ [24]. This value is lower than that of isolated Fe ions $5\mu_B$ (previously used in the estimation of $\chi_{\perp}$ [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$_{Fe}$. $\chi_{AFmf}$ at 0 and $T_N$ thus estimated are plotted in Fig. 4.

Based on $\chi_{AFmf}$ estimation it is also possible to further estimate the antiferromagnetic susceptibility expected when considering superantiferromagnetism $\chi_{SAF}$ (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

$$\frac{\chi_{\perp 2N}}{\chi_{\perp}} = 2 - \frac{4h^2}{3} \tag{3}$$

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

$$\chi_{\perp SAF} = \frac{1}{2} \chi_{\perp} + \frac{1}{2} (\chi_{\perp} + \chi_{SA}) \tag{4}$$
where the extra susceptibility $x_a = x_{\perp 2N} - x_{\perp}$ is a function of $H$ and $T$ and can be expressed as $x_a = k(H, T) x_{\perp}$. The susceptibility of a set of randomly orientated nanoparticles can then be estimated as

$$x_{SAF}(H, T) = \frac{2}{3} \left( x_{\perp} + \frac{1}{2} k(H, T) x_{\perp} \right) + \frac{1}{3} x_{||}(T)$$  \hspace{1cm} (5)$$

In the frame of mean field, considering two sublattices with negligible intralattice exchange interaction, the temperature dependence of $x_{||}(T)$ is given by [24]

$$x_{||}(T) = \frac{N g^2 \mu_B^2 S^2 B_S(y)}{k_B(T + 3T_N S(S+1)^{-1}B_S'(y))}$$ \hspace{1cm} (6)$$

with

$$y = \frac{3T_NM}{(S+1)T} \hspace{1cm} (7)$$

Considering $S$ of Fe$^{3+}$, $x_{AFmH}(T)$ can be readily obtained (Fig. 4, upper panel). $x_{SAF}(H, T)$ 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 $2N = 15 \pm 5$ [8] and calculating $k(H, T)$ based on Eq.3 for $h < 0.3$, and on the tables presented in [11] for $h > 0.3$ and $T/T_N > 0.2$, one can estimate $x_{SAF}(H, T)$, plotted as a function of field for $T = 0K$ 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 Fig. 4 upper panel. It is clear from Fig. 3 that up to fields of the order of $25 \times 10^4$ dM/dH is higher than that expected from $x_{SAF}$ and $x_{AFmH}$, 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 $x_{SAF}$ and $x_{AFmH}$, and bulk antiferromagnetism and superantiferromagnetism are the relevant contributions for $dM/dH$ (Fig. 3, inset). At $50 \times 10^4$ Oe and 4.2 K, $dM/dH$ is of the order of $x_{SAF}$ and $x_{AFmH}$, being closer to $x_{SAF}$ than $x_{AFmH}$. Therefore, considering that at this temperature and field $\mu_{an}$ 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 $x_{HF}$ at $30 \times 10^4$ Oe is close to $x_{SAF}$, while it deviates in the intermediate temperature region, this deviation being higher than the difference between $x_{SAF}$ and $x_{AFmH}$. It is also noteworthy that, while $x_{\perp 2N}$ decreases with temperature, due to the approach of $x_{\perp}$ to $x_{\perp}$ at high fields, due to averaging particles with even and odd $2N$, averaging $x_{||}$ and $x_{\perp}$, and due to the temperature increase of $x_{||}$, $x_{SAF}$ at $50 \times 10^4$ 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 $x_{HF}$ is larger than $x_{AF}$ for $H < 28 \times 10^4$ neither for the decrease of $x_{HF}$ 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 non-saturation of $\mu_{an}$. In turn, this non-saturation is either due to small $\mu_{an}$ values or due to the role of anisotropy in the approach to saturation of $M_{||}$. 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 non-monotonic behavior observed in the temperature dependence of $x_{HF}$. Simple calculations of an hypothetical contribution of small moments to $x_{HF}$ 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.

![FIG. 5: (color online) $x_{HF} = dM/dH$ as a function of temperature and field obtained from magnetization curves simulated using the Langevin function and $\mu_{an} = 5 \mu_B$.](image)
to $k_BT$, leading to a decrease of the contribution of $M_\mu$ to $\chi_{hf}$. Considering only the $M_m$ component and two temperatures $T_2 > T_1$, there is a cross-over field below which $\chi_{hf}(T_2) < \chi_{hf}(T_1)$, so that $M_\mu$ gives a spurious contribution to the total $\chi_{hf}$ that decreases with temperature. This cross-over field increases in comparison to the Langevin law when uniaxial anisotropy is considered. When surface anisotropy is further taken into account, the increase of this cross-over field is quite dramatic: according to simulations shown in Ref. [26], the cross-over field is of the order of $8 \times 10^4$ 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 $M_\mu$ in a $H/T$ scale and ac susceptibility, since anisotropy does not affect the equilibrium linear susceptibility ($\chi'$ above blocking), affecting $M_\mu$ at intermediate fields whenever relevant. The in phase ($\chi'$) and out of phase ($\chi''$) components of the ac susceptibility (Fig. 6) show characteristic features of ferromagnetic superparamagnetic nanoparticles, namely frequency dependence below temperatures of the order of 40 K and a frequency dependent maximum at around 20 K [27]. From the frequency dependence of the maximum of $\chi''$ 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 $\chi'$, in order to study the temperature dependence of $\mu_{an}$ 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 $\chi'(T)$ and $\chi''(T)$ increase with temperature up to 40 K, the temperature at which $\chi''$ becomes zero, corresponding to an increase of the average $\mu_{an}$ due to the unblocking process (Fig. 6c). For $T > 40$ K, $\chi'(T)$ and $\chi''(T)$ decrease with temperature due to the decrease of the sublattice magnetization when approaching $T_N$, [8, 15] being this decrease more pronounced for $T > 90$ K. Due to the decrease of $\chi'(T)$, $M_\mu$ is not expected to scale in a $H/T$ plot, being expected lower values for $M_\mu$ in the curves taken at higher temperatures in all the $H/T$ range. 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, $M_\mu$ (and the slope of $M_\mu$) is higher in the curves taken at higher temperatures (Fig. 7, inset), unlike that expected from the slightly decrease of $\chi'(T)$. For $T > 91$ K, $M_\mu$ in a $H/T$ scale is always lower in the curves taken at higher temperatures, as expected from the decrease of $\chi'(T)$. In other words, the non-scaling of $M_\mu$

![Fig. 6](image-url) (color online) a. temperature dependence of the in phase component of the ac susceptibility $\chi'$ 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 $\chi''$ and c. temperature dependence of the $\chi'T$ product and temperature dependence of the product of temperature and susceptibility associated to $\mu_{an}$ determined as $\chi'(T)$ and $\chi''(T)$.

![Fig. 7](image-url) (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 the $38 < T < 91$ K temperature range and intermediate $H/T$ values where $M_{\mu}$ has higher values for curves taken at higher temperatures cannot be explained from the behavior of $\mu_{an}(T)$. Since $\mu_{an}(T)$ 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 non-scaling of $M_{\mu}$ (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 of $M_{\mu}(H/T)$ for curves taken at higher temperatures and for a given $H/T$ value in an intermediate range and scaling (or decrease) in the low $H/T$ range is, 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 non-saturation of $\mu_{an}$ 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 of the order of $5 \times 10^4$ Oe, $\chi_{AF}$ decreases with temperature, similarly to earlier studies [2, 7, 8]. This behavior is related to the influence of anisotropy in the approach to saturation of $\mu_{an}$ and probably due to the existence of small magnetic moments, that leads to the non saturation of $M_{\mu}$ at fields of the order of $5 \times 10^4$. On the contrary, when $\chi_{AF}$ is determined as $dM/dH$ at $30 \times 10^4$ Oe, it increases with temperature for $4.2 < T < 180$ K (i.e. below $T_N$) as in bulk AF. At fields of the order of $50 \times 10^4$ Oe and at $4.2$ K, $\chi_{AF}$ determined as $dM/dH$ is in good agreement to $\chi_{AF}$ estimated from mean field considering the effect of super-antiferromagnetism, and of the order of $\chi_{AF}$ estimated from mean field.

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