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In-field Mossbauer study of disordered surface spins in core/shell ferrite nanoparticles

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Magnetization and Mossbauer spectroscopy measurements are performed at low temperature under high field, on nanoparticles with a nickel ferrite core and a maghemite shell. These nanoparticles present finite size and surface effects, together with exchange anisotropy. High field magnetization brings the evidences of a monodomain ordered core and surface spins freezing in disorder at low temperature. Mossbauer spectra at 4.2 K present an extra contribution from the disordered surface which is field dependent. Field and size dependences of this latter show a progressive spin alignment along the ferrite core which is size dependent. The weak surface pinning condition of the nanoparticles confirms that the spin disorder is localized in the external shell. The underfield decrease in the mean canting angle in the superficial shell is then directly related to the unidirectional exchange anisotropy through the interface between the ordered core and the disordered shell. The obtained anisotropy field $H_{\text{EA}}$ scales as the inverse of the nanoparticle diameter, validating its interfacial origin. The associated anisotropy constant $K_{\text{EA}}$ equals $2.5 \times 10^{-4} \text{ J/m}^2$.

I. INTRODUCTION

A central challenge of new nanotechnologies is the production of magnetic nanoscale materials with controlled properties as well as for basic research issues and for devices production.1–3 Indeed the development of new technological applications require the deep knowledge of how the properties of magnetic materials differ from bulk ones when the size decreases down to the nanometric range.4,5

From the viewpoint of fundamental magnetism, much attention has been devoted to understanding the effect of nanoscaled confinement and the role of atoms lying at or near to the surface on the spin arrangement within a nanoparticle.4,6 More particularly, the reduced coordination and the large number of broken exchange bonds of surface atoms can give rise to surface anisotropy, frustration, and spin disorder.7,8 Among these effects, one of the most significant effects in ferrite nanoparticles is the observation of a unidirectional exchange anisotropy9–11 as in re-entrant spin-glasses12,13 and as exchange bias in magnetic multilayer sandwiches.14 It is usually attributed to the presence of canted spins either in the bulk for re-entrant spin-glasses or at the interfaces for nanoparticles and magnetic multilayer sandwiches.

In-field Mossbauer spectroscopy is able to reveal the existence of misaligned spins through the observation of an incomplete polarized spectrum when a magnetic field is applied parallel to the direction of the incident γ-rays.15–17 We propose here to follow, by Mossbauer spectroscopy under applied fields of up to 12 T, the evolution of the disordered surface spins of nickel ferrite nanoparticles. Such nanoparticles are indeed well known for presenting large surface effects and lack of reversibility under cyclic remagnetizing.7,8 These observations are standardly associated to a disordered surface layer of disordered spins with a spin-glass like structure.7,8 Our purpose here is to probe under field the exchange anisotropy experienced by the surface spins created by the interface between the magnetically ordered core of the nanoparticle and its external disordered shell.

The paper is organized as follows. Section II first gives some details about our samples and the performed experiments. Section III is devoted to the experimental results. First, the temperature dependence of the magnetization of well-dispersed particles is investigated allowing the contributions of the ferrimagnetic core and of the disordered surface spins to be separated. Second, we describe in detail the Mossbauer spectroscopy measurements under applied fields from 0 to 12 T. They are then discussed in Sec. IV in terms of surface pinning and anisotropy. Thereby it confirms the core-shell picture and quantifies the unidirectional exchange through the core-shell interface. To our knowledge, this is the first investigation on the evolution of the core-shell spin structure inside the nanoparticles as a function of the external field.

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II. SAMPLE DETAILS AND EXPERIMENTS

A. Magnetic fluids based on ferrite nanoparticles

Among the various ways of preparing ferrite nanoparticles, a fruitfull route is that of magnetic liquids.\textsuperscript{18,19} It brings a lot of innovative outputs in engineering or biotechnology, including biodetection, imaging, and therapy.\textsuperscript{3,20,21} From a more basic research point of view, it allows obtaining dilute dispersions of nanoparticles which as such are suitable model-systems to study anisotropy and magnetization of individual particles.\textsuperscript{10,22} In more concentrated systems, collective behaviors such as super spin-glasses are observed at low temperatures.\textsuperscript{23,24}

The aqueous magnetic fluids studied here stand out by relying only on electrostatic repulsion to stabilize the magnetic colloidal dispersion, without any added surfactant.\textsuperscript{20} Size sorted ferrite nanoparticles of various kinds are prepared by a wet chemistry method and dispersed in acidic medium using a chemical strategy that prevents the particles from dissolution.\textsuperscript{25} Their internal chemical composition is no longer homogeneous and they can be described as made of a stoichiometric ferrite core surrounded by a thin maghemite surface layer.\textsuperscript{26} At room temperature the dispersion state of our magnetic nanocolloids is controlled inside a well-known phase diagram, by using small angle scattering experiments combined with electrochemical measurements which allow a fine tuning of the electrostatic repulsion.\textsuperscript{27–30} Magnetization measurements performed on “gas-like” dilute dispersions of independent nanoparticles based on copper and manganese ferrite have recently shown that the spin structure of these particles is well accounted for by a magnetic core-shell model.\textsuperscript{10} In these nanoparticles based on copper ferrite, underfield Mossbauer experiments have also revealed the existence of canted spins, the relative fraction of which increases with decreasing particle size.\textsuperscript{31}

B. Elaboration of core-shell nanoparticles

The elaboration of the magnetic fluids is carried out in three steps, as described in more details elsewhere.\textsuperscript{25,26} Nickel ferrite nanoparticles are prepared by hydrothermal co-precipitation of aqueous solutions of a Ni(NO\textsubscript{3})\textsubscript{2}–FeCl\textsubscript{3} mixture in alkaline medium, after which the precipitate is thoroughly washed with water. In this step the mean particle size can be tuned by controlling the mixing velocity of the reagents. Next, the precipitate is hydrothermally treated with a 1 mol L\textsuperscript{−1} Fe(NO\textsubscript{3})\textsubscript{3} solution at 100 °C to ensure the stability of the particles and avoid their degradation in acidic medium. Finally, the particles are peptized by pH and ionic strength adjustment, in order to control the surface charge density and the screening of the electrostatic repulsion between particles to ensure colloidal stability. In order to improve the size tailoring, the solids are centrifuged so the precipitate and the supernatant present distinct crystalline sizes. Four samples of different mean particle sizes (named Ni1, Ni2, Ni3, and Ni4) were obtained by the above described procedure. Polydispersity can be reduced by means of a colloidal size sorting process based on a phase transition induced in the nanocolloid by increasing its ionic strength;\textsuperscript{27} such dispersions can be separated into a concentrated (bottom) phase containing larger particles than those in the dilute (upper) phase. Samples Ni5 and Ni6 were obtained from this size sorting procedure applied several times to the sample Ni1 in order to refine the size distribution.

The protective Fe(NO\textsubscript{3})\textsubscript{3} treatment introduces iron enrichment near the nanoparticle surface. To take this heterogeneity into account, we have recently proposed a chemical core-shell model supported by magnetization, x-ray diffraction, and liquid density measurements.\textsuperscript{25} Our synthesized nanoparticles are therefore described as a core of stoichiometric Ni ferrite (assumed to be spherical) surrounded by a shell of maghemite (γ-Fe\textsubscript{2}O\textsubscript{3}). The shell/particle volume ratio Φs/Φp can be calculated from the molar fraction \(X_M = [Ni]/([Ni]+[Fe])\) determined by atomic absorption spectroscopy and/or inductively coupled plasma atomic emission spectroscopy. It is expressed in terms of a shell thickness \(t_{sh}\). Pertinent data for our samples are summarized in Table I. \(X_M\) is always smaller than the stoichiometric value 0.33, confirming the Fe enrichment. In addition, \(X_M\) decreases as the particle size decreases, since the surface/volume ratio \(\Phi_s/\Phi_p\) becomes larger. It is also noteworthy that \(t_{sh}\) is smaller than one lattice parameter (i.e., 0.83 nm) for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symbol</th>
<th>(d_{SR}) (nm)</th>
<th>(d_0) (nm)</th>
<th>(s_d)</th>
<th>(X_M)</th>
<th>(\Phi_s/\Phi_p)</th>
<th>(t_{sh}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1</td>
<td>▼</td>
<td>8.9</td>
<td>8.3</td>
<td>0.17</td>
<td>0.19</td>
<td>0.45</td>
<td>0.80</td>
</tr>
<tr>
<td>Ni2</td>
<td>△</td>
<td>7.7</td>
<td>6.7</td>
<td>0.23</td>
<td>0.18</td>
<td>0.48</td>
<td>0.77</td>
</tr>
<tr>
<td>Ni3</td>
<td>◇</td>
<td>5.9</td>
<td>5.4</td>
<td>0.18</td>
<td>0.17</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>Ni4</td>
<td>⊙</td>
<td>4.3</td>
<td>3.5</td>
<td>0.15</td>
<td>0.17</td>
<td>0.51</td>
<td>0.46</td>
</tr>
<tr>
<td>Ni5</td>
<td>□</td>
<td>12.8</td>
<td>⋆⋆⋆</td>
<td>0.23</td>
<td>0.32</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Ni6</td>
<td>○</td>
<td>4.9</td>
<td>⋆⋆⋆</td>
<td>0.19</td>
<td>0.43</td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

C. Electron microscopy and x-ray diffraction

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-100 CX II microscope, while a JEOL JEM-2010 was used for high-resolution transmission electron microscopy. Figure 1(a) displays a typical micrograph obtained for sample Ni2 after evaporation of the liquid carrier. Nanocrystals are roughly spherical with a size distribution well accounted for by a log-normal law of median diameter \(d_0\) and polydispersity \(s_d\). \(d_0\) and \(s_d\) were obtained by fitting a histogram based on a 500 particles sampling. Results obtained for samples Ni2 to Ni4 are collected in Table I. Figure 1(b) presents for sample Ni2 a high-resolution image of a single nanoparticle that shows a set of reticular planes and demonstrates the good crystallinity of the synthesized nanomaterials. The lattice plane spacing, of the order of 2.95 Å, corresponds to the Miller indices (220), in good agreement with American Society for Testing and Materials (ASTM) (file 10-0325) data for NiFe\textsubscript{2}O\textsubscript{4}. X-ray powder diffraction (XRD) measurements were performed on D10B-XPD beam-line at the Brazilian Synchrotron Source [Laboratório Nacional de Luz Síncrona (LNLS)] with λ.
=0.1771 nm. The sample holder was rotated to improve the randomization of the crystallites and a graphite analyzer crystal was used to avoid fluorescence. XRD patterns were obtained typically within 15° < 2θ < 130° interval, with 0.05° step and 10 s counting time. The analysis was done by indexing of the diffracted lines and by comparing with bulk standard data. A typical result is presented in Fig. 1 and exhibits several peaks corresponding to interplanar spacings of the spinel structure. The nanocrystal mean size $d_{XR}$ was deduced by means of the Scherrer formula applied to the 311 diffraction line (see Table I).

D. Magnetization

Zero field cooled magnetization measurements were carried out on samples Ni5 and Ni6 on a Commercial Cryogenics S600 superconducting quantum interference device magnetometer in SPEC-CE Saclay, France, between 4.2 and 250 K and in a field $H=4 \times 10^3$ kA/m. The measured specimens were colloidal dispersions sufficiently dilute to ensure negligible interparticle interactions at room temperature.

E. Mossbauer spectroscopy

Mossbauer spectra of dry powder samples Ni1, Ni2, Ni3, and Ni4 were collected at $T=4.2$ K under fields up to 12 T, provided by a Cryogenic™ superconducting magnet and parallel to the γ-rays direction. A 50 mCi $^{57}$Co source was driven sinusoidally in a field-free region of the cryostat.

III. RESULTS

A. Effective Bloch law and surface spins freezing

The high field magnetization $m_s(T)$ of sample Ni5 is presented in Fig. 2(a). A smooth variation with temperature is observed above 70 K, while a steep upturn occurs below that temperature. Such behavior has been observed for other nanoparticle systems, and it can be understood as a superposition of two independent mechanisms according to the following equation:

$$m_s(T) = m_s(0)(1 - BT^a) + \Delta m_s(T).$$

The first term, the only one present in the high-temperature regime, is a modified form of Bloch’s law that describes the magnetization decrease caused by thermal excitation of spin waves in the magnetically ordered particle core. The exponent $\alpha$ was determined by fitting the log-log plots shown in the inset of Fig. 2(a). For the larger particles (Ni5, $d_{XR} = 12.8$ nm) $\alpha=1.5$, which corresponds accurately to the Bloch 3/2 exponent for a bulk ferromagnet. For the smaller particles (Ni6, $d_{XR}=4.9$ nm), on the other hand the fit yielded $\alpha=2$. Indeed, for very small particles the spatial confinement at nanoscale induces an energy gap in the spin wave spectrum and, as previously predicted and measured for small clusters and nanoparticles, the temperature dependence of the core magnetization is better described by an
effective Bloch law with an exponent larger than the bulk value.\textsuperscript{33,34} Furthermore, the $m_s(0)$ values found by extrapolation are 340 kA/m for sample Ni5 and 258 kA/m for sample Ni6, to be compared to 300 kA/m, the bulk saturation of Ni ferrite. For large particles, the magnetization $m_s(0)$ is found larger than the bulk saturation value, a result that suggests cation inversion at octahedral and tetrahedral sites of the nanocrystal core, the presence of nickel ions at A sites increasing the saturation value (this assumption will be confirmed by Mössbauer spectroscopy, to be discussed below). This mechanism does not explain the magnetization reduction for the smaller particles, which must be due to some less-understood finite size effect.

The second term in Eq. (1) represents the surface contribution to the total magnetization, rising at low temperatures as a consequence of the progressive freezing of disordered spins. Our data are accurately described by an exponential law:

$$\frac{\Delta m_s(T)}{m_s(0)} = A \exp\left(-\frac{T}{T_0}\right),$$

where $A$ and $T_0$ are parameters. Figure 2(b) displays the thermal variation in the surface magnetization for samples Ni5 and Ni6, normalized to their values at 5 K. All experimental points lie on the same master curve, given by Eq. (2) with $A \equiv 1.3 \Delta m_s(5\text{ K})/m_s(0)$. The characteristic temperature $T_0$ is nearly size independent and its mean value is $\langle T_0 \rangle \approx 18 \pm 5$ K, similar to values found for ferrofluids based on Cu and Mn ferrite nanoparticles and for $\gamma$-Fe$_2$O$_3$ nanoparticle dispersions.\textsuperscript{32,33} From the theoretical side, Monte Carlo simulations have yielded an exponential-like decrease in the magnetization, rising at low temperatures into a disordered spin-glasslike structure.\textsuperscript{6–8,36}

**B. Core-shell spin structure under external field**

Figure 3(a) exhibits Mössbauer spectra of samples Ni1 and Ni4 with and without a field of 8 T. The in-field spectra reveal two features. First, as a consequence of the antiparallel ordering of Fe$^{3+}$ spins at A and B sites, the external field adds to the magnetic hyperfine field ($B_{hf}$) at A site and subtracts from that at B site, yielding two well-resolved sextets. Lines 2 and 5 of these sextets have vanishing intensity since the spins are collinear to the $\gamma$-ray direction. Second, a third sextet, with an extra contribution of nonzero intensity at the second and fifth lines, is required to correctly fit the spectra. This contribution is attributed to Fe$^{3+}$ surface spins that are misaligned with respect to the field direction.\textsuperscript{8,9}

Thus, all experimental data were fitted in a core-shell scheme with the superposition of three subspectra henceforth denoted as A, B, and S. The ratio $I_{21}$ between the second and first line intensities was fitted independently for each sextet, while the third-line ratio $I_{31}$ was kept equal to 0.33. Only for the zero-field spectra, the ratio $I_{21}$ was constrained to be equal for the three sextets, the fits yielding a value close to 0.67. A small $B_{hf}$ distribution was allowed in order to account for the observed linewidth differences (larger for external lines) within each sextet.

The hyperfine fields of the A and B sextets at $H=0$ were around 50 and 53 T, respectively, and did not show any systematic variation with particle size. The B isomer shift is always larger than the A one by 0.10–0.15 mm/s. These two features allow the A and B sextets to be assigned to Fe$^{3+}$ ions in tetrahedral and octahedral sites of the spinel lattice, respectively. This result of two contributions corresponding to the ferrimagnetically ordered core of the nanoparticles is further confirmed by the small values obtained for the $I_{31}/I_{21}$ ratio: indeed, this quantity could be constrained to be 0 without affecting the quality of fit. The cation distribution between A and B sites can be determined from the relative areas of each corresponding sextets, and was found to be very similar for all four samples, with $I_A/I_B=1.25 \pm 0.05$. This result indicates a partially inverted spinel with 11% of the Ni$^{2+}$ ions occupying A sites, an inversion degree that could explain the large value of $m_s(0)$ as discussed above.

The relative area of S-sextet spectra, defined as $q = I_S/(I_A+I_B+I_S)$, gives the fraction of Fe ions belonging to the outer shell of canted spins. Figure 3(b) displays the $q$ values obtained at $\mu_0H=8$ T as a function of the mean particle; it clearly increases with decreasing size, reflecting the increase in the surface/volume ratio. The fitted $B_{hf}$ for S has

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** Mossbauer spectra at 4.2 K of samples Ni4 (4.3 nm) and Ni1 (8.9 nm) in null and 8 T applied fields. All spectra are fitted with three magnetic sextets. (b) Fraction of Fe ions belonging to the outer shell of canted spins (under 8 T) as a function of particle diameter. The dot-dashed line is a guide to the eyes.
the spin density of the shell structure matches the value typically found for maghemite particles. Nonzero clearly seen, the fractional area of sextet spectra. Because of the core-shell model, sextet cannot be experimentally distinguished for this component of the sequence, Fe spins at tetrahedral and octahedral sites cannot be identified by a sextet. As a consequence, Fe spins at tetrahedral and octahedral sites cannot be experimentally distinguished for this component of the spectra.

Figure 4(a) displays Mossbauer spectra of sample Ni3 (d_{XR}=5.9 nm), obtained at μ_0H=4, 8, and 12 T. As can be clearly seen, the fractional area of sextet S (identified by a nonzero I_{2/1} ratio)—i.e., the parameter q defined in the preceding paragraph—decreases as the field strength increases. Spectra are qualitatively similar for the other samples. In the framework of the core-shell model, q is the fractional number of iron ions of the disordered spin layer, which can be given a more geometrical expression in terms of the shell thickness e defined by the following equation:

\[ q = \frac{n_s \left[ 1 - \left(1 - \frac{2e}{d} \right)^3 \right]}{n_c \left(1 - \frac{2e}{d} \right)^3 + n_s \left[ 1 - \left(1 - \frac{2e}{d} \right)^3 \right]}, \]

where d is the particle diameter and n_s (respectively n_c) is the spin density of the shell structure (respectively of the core) taking into account the chemical inhomogeneity associated to the outer γ-Fe_2O_3 layer. The calculated e values for the studied samples are displayed in Fig. 4(b) as a function of field. It is observed that, at zero field, the shell thickness e amounts to roughly 30% of the particle radius, thus including both the outer maghemite layer t_{sh} and a fraction of the nickel ferrite core (see data in Table I). For increasing applied field the fraction of disordered spins steadily decreases, indicating an outward displacement of the magnetic core-shell interface due to progressive spin alignment along the field direction. The decrease rate is smaller for smaller particles, suggesting a larger local anisotropy field for the surface spins and/or exchange bond frustration for the latter.

As a further observation, the I_{2/1} ratio of the S sextet decreases for increasing field, though at a slower rate than the corresponding shell thickness. This quantity is related to the mean canting angle between Fe spins and field direction, as deduced from Mossbauer spectra, for increasing applied fields. (For symbols see Table I) The full lines are best linear fits.

Our results for this quantity are shown in Fig. 5. Note that the zero-field value is equal to sin^-1(√2/3), which corresponds to randomly oriented surface spins. For each sample the data can be roughly described by a linear field dependence, from the initial slope of which it can be estimated that the complete alignment of surface spins would require a field of 28 T for the largest particles and 61 T for the smallest ones. The decrease rate of θ scales as dθ/d(μ_0H)=−0.21d_{XR}(nm).

IV. DISCUSSION

Nickel ferrite nanoparticles are well known for their large surface spin disorder associated to a lack of reversibility under cyclic remagnetizing. The magnetic anisotropy of nickel ferrite nanoparticles, produced by the same way of synthesis as those studied here, has been previously quantified at room temperature by magneto-optical birefringence measurements in Ref. 37. It has been ascribed to a uniaxial surface anisotropy of Aharony type with an anisotropy constant K_s≈3×10^4 J/m^2, close to the value 1.2×10^4 J/m^2 adopted in Ref. 32 for the nickel ferrite nanoparticles of Ref. 8.
The localization of the spin disorder inside a nanoparticle and its influence on the magnetodynamics of such a nanosystem may be quantified by the parameter $p$, known as “the surface pinning parameter”\(^9,39\) which is given by the balance between local magnetic anisotropy and exchange stiffness. It is defined as:

$$ p = K_d/A_{Ea}, $$ \hspace{1cm} (5)

where $A_{Ea}$ is the exchange stiffness and $d$ the diameter of the particles. Setting $A_{Ea} \sim 10^{-11}$ $J/m$ (as in Ref. 40), $K_d$ to its experimental value from Ref. 37 and $d$ to 10 nm, we obtain $p \sim 0.3$. Thus for all the nanoparticles studied in the present work, the condition $p \leq 1$ is fulfilled, meaning that the experiments are performed in the so-called weak pinning limit.\(^9\)

This implies that the spin distortions are ousted from the magnetically ordered core to the surface, thus well justifying our magnetic core/shell model. These distortions are then localized in a thin surface shell, magnetically disordered as we observe here, in close contact with the magnetically ordered core. An interfacial anisotropy, related to the exchange interaction across the core-shell border, is then also entailed to the spatial border between the two magnetic materials (the core and the shell), which have two different kinds of magnetic ordering. Such an unidirectional (or rotatable) exchange anisotropy, first discovered by Meiklejohn and Bean\(^{36,41}\) and Meiklejohn\(^{41}\) at a ferromagnet/antimagnet border, is a customary effect for spin-glass films and superlattices. It has been also evidenced in maghemite nanoparticles through isotropic contributions to both linewidths and resonance fields in ferromagnetic resonance experiments.\(^9,10,11,39\)

Here, this exchange anisotropy experienced by the surface spins is probed in our Mossbauer experiment. Figure 5 expresses the elastic response of the surface spins to the stress exerted by the high applied field. In this context, the decrease rate of $\theta$ can be interpreted as:

$$ dH = -H_{Ea}d\theta, $$ \hspace{1cm} (6)

where the exchange anisotropy field equals $H_{Ea} = 4 \times 10^{-3}/d$ (in SI units). $H_{Ea}$ is related to the exchange anisotropy constant $K_{Ea}$ by the relation $H_{Ea} = 6K_{Ea}/\mu_0m_s d$ where $m_s$ is the magnetization of the core.\(^9\) Taking $m_s$ of the order of 300 kA/m as it is here extrapolated at $T=0$ K for Ni5 and Ni6 samples (on average), we obtain $K_{Ea} = 2.5 \times 10^{-4}$ $J/m^2$. This value is very close to the value of the constant $K_d$ associated to the surface anisotropy experienced by the core determined in a magnetodynamic experiment.\(^{37}\) Note that $K_{Ea}$ here exceeds by an order of magnitude that found for maghemite nanoparticles\(^9,10,11,39\) but well agrees with the order of magnitude inferred for a ferromagnetic/antiferromagnetic interface in Refs. 9 and 42.

Our underfield Mossbauer experiment also allows the measuring of the thickness $e$ of the disordered layer and its underfield evolution (see Figs. 4 and 6). We find that in zero field the thickness $e(H=0)$ is roughly proportional to the size of the particles. Moreover, whatever the values of the nanoparticle size and of the applied field in our experiment, the underfield evolution scales as

$$ e(H) = e(H=0)\exp\left((-9 \pm 0.3)10^{-2}H/H_{Ea}\right), $$ \hspace{1cm} (7)

If it seems basically natural to observe a decreasing of the thickness $e$ as the field increases, there is presently no model to relate the thickness $e$ to the surface pinning parameter $p$ and to describe theoretically their respective underfield evolutions. Such an underfield model is still to be done.

V. SUMMARY

In summary, our experiments reveal that the magnetization temperature dependence of gaslike diluted dispersions of independent nanoparticles is well described by a monodomain ordered core and a surface layer of disordered spins. The core magnetization, due to spatial confinement, follows an effective Bloch law. The freezing of the surface spins gives a contribution to the total magnetization, well accounted for by a reduced exponential behavior. The magnetic structure is investigated by Mossbauer spectroscopy at $T=4.2$ K in applied fields up to 12 T. Three distinct contributions to the spectra are found: two corresponding to Fe ions at tetrahedral and octahedral sites of the ferrimagnetic core, with spins collinearly aligned to the field, and a third one originating from randomly frozen spins of the particle surface shell. For increasing applied field the shell thickness deduced from the fraction of disordered spins steadily decreases, indicating the progressive alignment of spins at the border of the ferrimagnetic core. The mean canting angle relative to the field is also found to decrease for increasing fields, at a faster rate for larger particle sizes. This latter effect quantifies the delicate balance between exchange interaction and local anisotropy and allows to determine the unidirectional (or rotatable) exchange anisotropy field $H_{Ea}$ in our nickel ferrite nanoparticles. The associated constant $K_{Ea} = 2.5 \times 10^{-4}$ $J/m^2$ is close to the one expected for ferromagnetic/antiferromagnetic interface.

FIG. 6. Reduced variations in the magnetic shell thickness $e/e(H=0)$ as a function of $H/H_{Ea}$; $H_{Ea}$ was deduced from Eq. (6). The full line corresponds to Eq. (7) (symbols see Table I). Inset: Zero field thickness $e(H=0)$ as function of nanoparticle diameter $d_{SR}$, the full line has a slope 1.
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