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Effects of magnetic interactions in antiferromagnetic ferrihydrite particles

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Abstract

The effects of magnetic interactions in the magnetic properties of six-line ferrihydrite particles were investigated by studying the behavior of aggregated versus coated particles. Four different coating agents (sugar, alginate, lactate and ascorbate) were employed in order to obtain dispersed particles and prevent particle agglomeration; one sub-sample was allowed to dry with no coating agent. The five sets of ferrihydrite particles were from the same batch and the size was estimated as 3.6 ± 0.4 nm in length. Low temperature magnetization, ac susceptibility and Mössbauer spectroscopy data showed contrasting blocking temperatures for uncoated and coated samples with a decrease of T_P from about 50 K to 12 K, respectively. The contributions from magnetic interactions were recognized in magnetic measurements and the effective anisotropy constant for non-interacting ferrihydrite was estimated as $(100 \pm 10) \times 10^3 \text{ J m}^{-3}$. Overall, employing sugar and alginate as coating agents was more successful in preventing particle aggregation and magnetic interactions. In contrast, ascorbate and lactate were unsuitable due to the chemical reaction between the coating agent and ferrihydrite surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanoparticles of magnetic materials have been the focus of intense research since their properties may differ from those of their bulk counterpart materials [1]. In the case of ferrihydrite there is no corresponding bulk material. Ferrihydrite particle sizes are described in the range 3–6 nm, its crystals are mainly spherical in shape, and the x-ray diffraction pattern shows two or six reflections as the structural order increases [2, 3]. Recently, the magnetic behavior of unusually large particles (23 nm) with seven sharp lines from Si ferrihydrite was reported [4]. This antiferromagnetic (AF) iron oxyhydroxide is described by a single-phase model with the hexagonal space group $P6_3mc$ and a unit cell with average dimensions of $a = 5.95 \text{ \AA}$ and $c = 9.06 \text{ \AA}$ [5].

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Due to the limited small size of ferrihydrite, its magnetic properties frequently have been determined by considering reduced particle size effects such as magnetic interactions, the hypothetical core/shell structure, and the presence of uncompensated moments as described by Néel for AF materials [6]. Moreover, for the ferrihydrite a resulting net magnetic moment was observed and it was explained by many authors as being related to a ferromagnetic-like moment due to the presence of surface uncompensated spins [7, 8]. Despite the fact that bulk AF materials are not expected to present a resulting magnetization it has been suggested that it is possible to use AF nanoparticles to stabilize the magnetization direction of ferrimagnetic particles for applications as in magnetic recording media [9]. Ferrihydrite also has a known contribution to environmental problems since it is an adsorber of various trace elements and can act as a control on the concentration of iron in surface waters [2].

Furthermore, AF iron oxide nanoparticles have also been the subject of interest in magnetic interaction studies in order

to understand its nature and contribution to magnetic data [1]. Among these studies focusing on magnetization of AF phases it is possible to cite the studies with NiO [10] hematite [11] ferrihydrite [12, 13] and ferritin [14–17]. Ferritin is an iron-storage mammalian protein [18] that is an ensemble of magnetically non-interacting particles of ferrihydrite. In this case, ferrihydrite appears to be encapsulated in protein cages as ferritin's core. The nature of magnetic interactions in AF nanoparticles was explored by Mørup *et al* [1] who claim that it is important to consider surface electronic exchange coupling as the main contribution. Dipolar interactions are typically observed for ferromagnetic and ferrimagnetic nanoparticles; [19, 20] for AF nanoparticles, on the other hand, they are not expected to contribute significantly to superparamagnetic relaxation [1].

Thus, ferrihydrite nanoparticles are an ideal system for investigating the contributions/effects of exchange coupling between the surfaces of magnetic AF nanoparticles due to their reduced particle size. The usual way to understand the contribution of magnetic interactions in AF materials is the use of different strategies of sample preparation, such as ferrihydrite dispersed in a polymeric matrix [13], in order to mimic ferritin's behavior. The effects of interactions in ferrihydrite and how their contributions play a role in ferrihydrite's intrinsic properties still deserve further investigation.

Here we report a systematic study with synthetic ferrihydrite samples of aggregated (clumped) particles and dispersed particles by using coating agents. In the absence of surface active agents to prevent particle agglomeration they are expected to be magnetically interacting. To investigate the effects of magnetic interactions in AF material we compare the magnetic data obtained from ferrihydrite particles coated with multiple organic agents (sugar, alginate, lactate and ascorbate) with aggregated particles of ferrihydrite. In this paper the particles studied are smaller than the ones found in ferritin core. The efficiency of the organic coating procedure is also considered here.

2. Experimental details

Six-line ferrihydrite samples were prepared using the method of Erbs *et al* [21] with synthesis temperatures of 25 °C. After dialysis of the suspensions, each sample was separated into five equal volumes. No additional treatment was required for the uncoated sample (Fh_{UC}). For each coated sample, a pH-adjusted solution of alginate (Fh_{AL}), sugar (Fh_S), ascorbate (Fh_{AS}) or lactate (Fh_L) was added to the ferrihydrite suspension after dialysis. Coating agents were added with 5–10 molecules per nm² of particle surface depending on molecular size to produce a minimum of a monolayer of coverage. The mass of alginate added was equal to the mass of sugar due to the absence of a well-defined molecular weight and structure for alginate. Estimated surface areas and the mass loading of the ferrihydrite suspensions from previous experiments were used. Each sample was allowed to air-dry for five days, ground gently into a powder using an agate mortar and pestle, and stored in glass vials.

Powder x-ray diffraction (XRD) was performed using a PANalytical X-Pert PRO MPD x-ray diffractometer equipped with a cobalt source and an X-Celerator detector. Data were collected over the range of 10°–90° 2 θ at a scan rate of 0.6° min⁻¹. The diffraction patterns were compared to the reference powder diffraction files (PDF) for six-line ferrihydrite (#29-713), goethite (#29-712), and hematite (#33-664). The sample of the uncoated ferrihydrite for transmission electron microscopy (TEM) was prepared by diluting one drop of suspension into 3 ml of Milli-Q water. A drop of the resulting diluted suspension was placed onto a 3 mm 200 mesh holey carbon coated copper grid (Structure Probe, Inc.) and then allowed to air-dry. Using forceps, the coated ferrihydrite TEM samples were prepared by rubbing the TEM grid into finely ground powder, then gently tapping the sample to remove excess powder. Images with Ångstrom spatial resolution were collected using an FEI Tecnai T12 TEM, operated at 120 kV, and a Gatan CCD camera. A commercial SQUID magnetometer (MPMS-XL-Quantum Design) was employed to perform static (ZFC/FC susceptibility curves, hysteresis loops), and dynamic (ac susceptibility curves) measurements made as a function of magnetic field, temperature and driving frequency. Susceptibility measurements in a magnetic field $H = 50$ Oe were performed while heating the sample from 2 up to 300 K in zero-field-cooled (ZFC) and field-cooled (FC) procedures. Hysteresis loops were obtained by using maximum applied fields up to 50 kOe in the temperature range 2–25 K. The ac susceptibility (in-phase χ' and out-of-phase χ'' components) curves were measured for variable frequencies in the temperature range 2–300 K. Mössbauer spectra were measured at selected temperatures between 4.2 and 300 K. A conventional constant-acceleration spectrometer was used in transmission geometry with a ⁵⁷Co/Rh source, using a α -Fe foil at room temperature to calibrate isomer shifts and velocity scale.

3. Results and analysis

3.1. X-ray diffraction and TEM

The XRD obtained for sample Fh_{UC} (figure 1) showed the usual six-line pattern of ferrihydrite reported in the literature [2, 3]. For the other four samples (not shown) attenuated peaks were prominent in the positions corresponding to the main peaks of sample Fh_{UC}. In addition, the XRD patterns for samples Fh_S and Fh_{AL} exhibited broad amorphous peaks at low angle. Sample Fh_{AS} also presented a few extra and unknown peaks and for sample Fh_L calcium lactate extra peaks were observed. The XRD for these last two samples suggests that the lactate and ascorbate coating procedure was not ideal since it produced undesirable additional phases which could be due to surface chemical reactions of ferrihydrite particles. The magnetic data of these two samples also indicate a phase other than ferrihydrite, thus, they will not be discussed here.

The TEM images of dispersed samples (figure 2) are not easy to obtain since the organic coating surrounding the ferrihydrite makes identification difficult for individual particles. The average size estimated by using TEM for

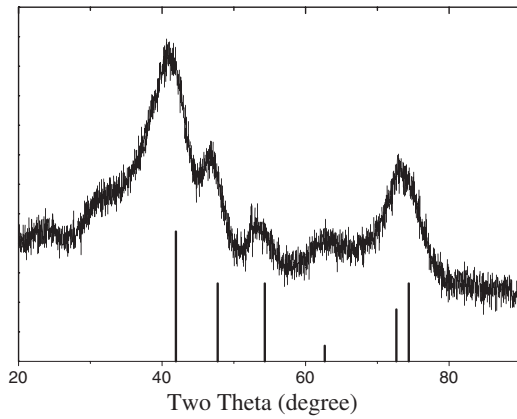


Figure 1. The x-ray diffraction (XRD) pattern obtained for sample Fh_{UC} . The PDF for six-line ferrihydrite (#29-712) is shown as a stick pattern.

particles without coating and synthesized at 25°C is about 3.6 ± 0.4 nm in length. It is assumed that all particles in this preparation batch have the same mean size and, therefore, particles used in the coating procedure are expected to have the same size. The images obtained showed that the coated particles are not completely aggregated (figure 2) suggesting that the use of organic coating was very effective in preventing particle agglomeration.

3.2. DC magnetization and hysteresis loops

The temperature dependence of dc susceptibility for all three ferrihydrite samples is presented in figure 3, and it is possible to observe that the ZFC peak (T_P) occurs at the highest temperature (about 55 K) for Fh_{UC} . Interestingly, the ZFC peaks for Fh_S and Fh_{AL} were at much lower temperature (about 12 K). Another important feature observed from dc magnetization curves is the FC branch. For sample Fh_{UC} magnetization seems to saturate at temperatures below T_P while for samples Fh_S and Fh_{AL} the magnetization increases steadily with decreasing temperature.

At first glance, the shift in T_P for coated samples may be associated with volume changes as described by the relation $T_P = KV/25k_B$ between peak temperature and volume as derived from Néel–Arrhenius law,

$$\tau = \tau_0 e^{\frac{KV}{k_B T}}, \quad (1)$$

where $T = T_B$ for $\tau = \tau_m$, and τ_m is the measuring time (for $\tau = \tau_m T_P$ is known as blocking temperature, T_B), τ_0 is characteristic of the material (10^{-9} – 10^{-11}), K is anisotropy constant, V is volume and k_B is Boltzmann's constant. However, the particles used for coating experiments are from the same batch and the size of all three ferrihydrite samples are the same, around 3.6 nm in length as measured from TEM images. Thus, we conclude that the changes in peak temperature for Fh_S and Fh_{AL} samples must be associated with an effect other than volume changes.

In order to investigate effects related to the field dependence of the T_P , a series of ZFC curves were obtained

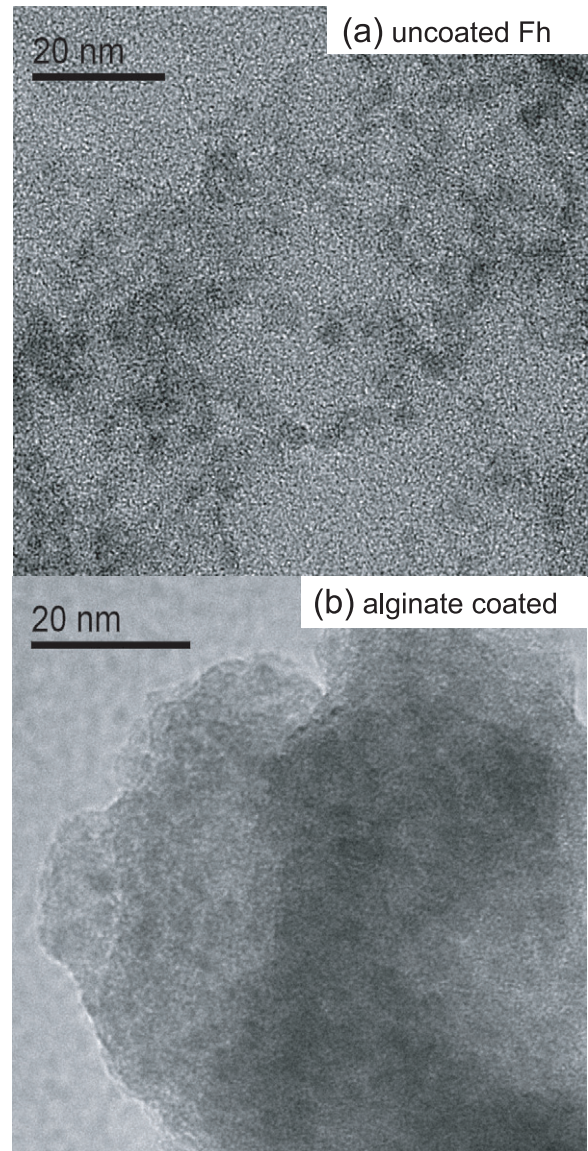


Figure 2. Transmission electron microscopy for samples (a) uncoated (Fh_{UC}) and (b) alginate coated (Fh_{AL}). The sample prepared with the coating agent resulted in submicron particles composed of the coating agent and distributed ferrihydrite nanoparticles. The ferrihydrite particles appear uniformly distributed throughout the matrix material.

with variable applied fields. Figure 4 shows the data obtained for samples Fh_{UC} and Fh_S . It is clear that in small fields Fh_{UC} has a large T_P and it decreases with high fields since the magnetic Zeeman energy overcomes the average superexchange interaction energy as noted for an interacting system. In contrast, sample Fh_S (and also Fh_{AL} , not shown here) present an almost constant T_P with increasing magnetic field. Only at high fields, when the magnetic Zeeman energy dominates over the anisotropy energy, do we observe a modest decrease in T_P .

The hysteresis loops obtained at 2 K (figure 5) show exchange bias (shift in H_C) after field cooling treatment. For sugar (Fh_S) and alginate (Fh_{AL}) coated ferrihydrite the exchange bias was less pronounced when compared with

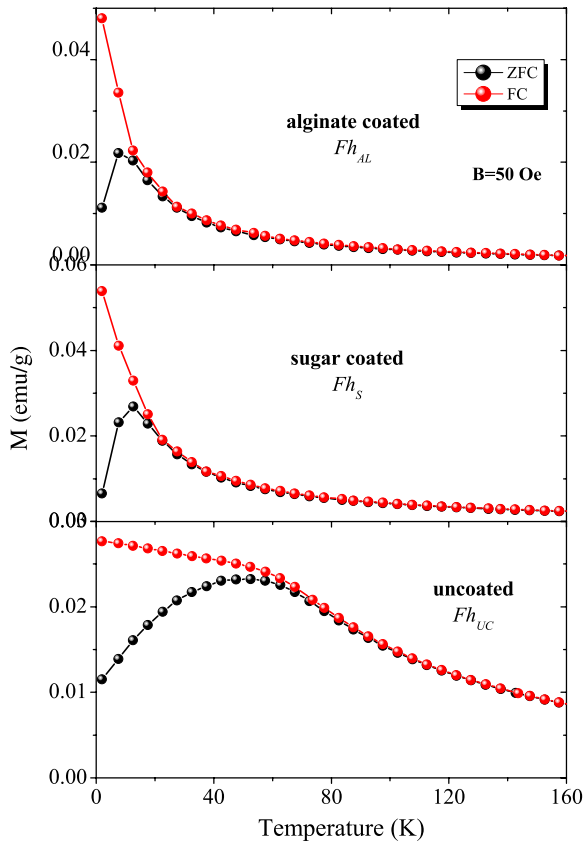


Figure 3. ZFC/FC curves from all three sub-samples prepared. The T_p shift from about 50 K (for uncoated) to 12 K (for alginate and sugar coated samples) can be readily observed. The FC branches also show characteristic behavior differences for uncoated and coated ferrihydrite particles. The lines shown are only guides for the eyes.

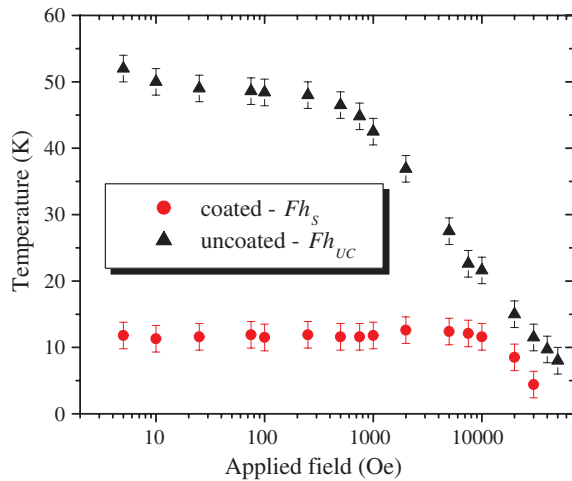


Figure 4. Field dependence of T_p from ZFC curves obtained at various applied magnetic fields. Circles represent coated particles with an almost constant T_p at low magnetic fields and triangles represent uncoated particles. At high fields magnetic energy is high and both samples show the same trend.

ferrihydrite without coating (see figure 5 inset). The exchange bias is usually related to surface spin canting or surface spin disorder and modeled as surface spins freezing at low

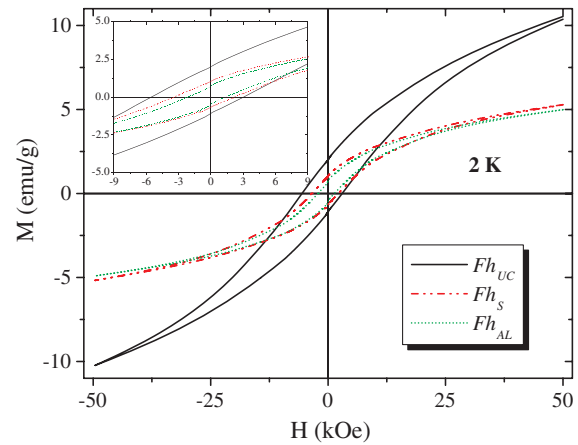


Figure 5. Hysteresis loops at 2 K show an exchange bias behavior (loop shift) for three ferrihydrite samples (uncoated, sugar coated, alginate coated).

temperature and behaving as highly anisotropic ‘spin glass like’ layers at the nanoparticle surface. Nogués *et al* [22] have suggested that the spin glass surface layer in nanoparticles acts as an antiferromagnet in the case of ferrimagnetic particles while it can act as a ferrimagnetic layer on the surfaces of AF materials. In our case the exchange bias feature is not yet fully understood but it seems to be a very important feature for the uncoated sample (Fh_{UC}). Besides the exchange bias, another feature observed in these hysteresis loops at 2 K is the decrease of saturation magnetization (in this case the magnetization at 50 kOe) for ferrihydrite coated with sugar and alginate as compared with uncoated ferrihydrite (Fh_{UC}). The decrease in saturation magnetization for coated samples may be associated with the decrease in the amount of iron in our sample.

3.3. ac susceptibility

The in-phase (χ') and out-of-phase (or quadrature) (χ'') ac susceptibility components as a function of temperature are shown in figure 6 for frequencies in the range 1–1000 Hz for samples Fh_{UC} (uncoated) and Fh_S (sugar). The insets show χ'' components. Both ac susceptibility components, in-phase and out-of-phase, exhibit the expected and well-known behavior of a superparamagnetic system; that is to say, the occurrence of a maximum at a temperature T_m . These samples follow the Néel–Arrhenius law at temperatures above T_m , and χ' is frequency independent, indicating thermodynamic equilibrium as expected in a temperature range at which all the particles are in a superparamagnetic state. However, at $T < T_m$, χ' is frequency dependent, indicating a nonequilibrium situation, as expected when a fraction of particles are in the blocked state. Since T_m depends on the measurement frequency the corresponding peak occurs at different temperatures. The general behavior observed is the shift of this maximum towards higher temperatures with an increase of the driving frequency. The ac susceptibility curves obtained agree with dc magnetization (ZFC curve), and they do not show any evidence of shoulders or additional peaks related to a hypothetical bimodal distribution of particle size as a secondary product of coating procedure.

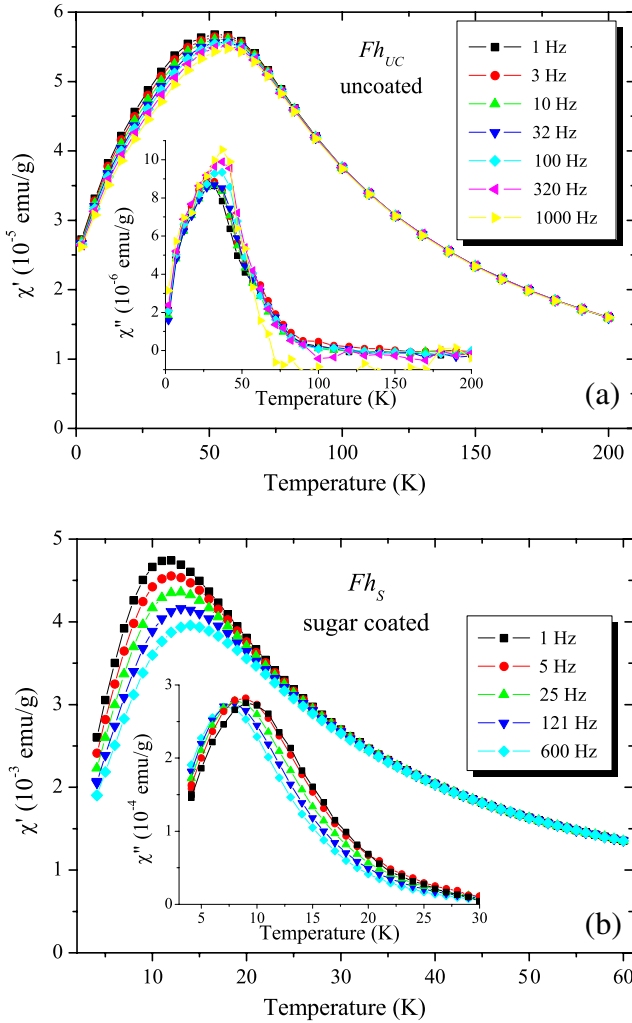


Figure 6. ac susceptibility curves for in-phase χ' , and out-of-phase χ'' (inset) with variations in temperature and variable frequencies shown for uncoated (a) and sugar coated (b) particles. The lines shown are only guides for the eyes.

Considering the samples Fh_S and Fh_{AL} as non-interacting particle systems, the ac susceptibility data and Mössbauer spectroscopy (see below) was used to derive parameters related to the frequency (τ_m) dependence of T_m ($\tau_m = 1/\omega$, where $\omega = 2\pi f$) [17]. By plotting $\ln(\omega)$ versus $1/T_p$ (figure 7) it was possible to observe a linear dependence of the above parameters and estimate the energy barrier for magnetic relaxation, E_a/k_B . In the absence of an external magnetic field the energy barrier, E_a , is assumed to be proportional to the particle volume V through the expression $E_a = K_{\text{eff}}V \sin^2\theta$, where K_{eff} is an effective magnetic anisotropy constant and θ is the angle between the magnetic moment of the particle and its easy magnetization axis. Obtaining E_a and using the particle diameter estimated with TEM, the effective anisotropy constant was estimated to be $(100 \pm 10) \times 10^3$ and $(80 \pm 10) \times 10^3$ erg cm^{-3} for samples Fh_S and Fh_{AL} , respectively. In addition, from the experimental data of figure 7 τ_0 was estimated to be 1.4×10^{-11} and 0.5×10^{-11} s for samples Fh_S and Fh_{AL} , respectively. On the other hand, a large effective

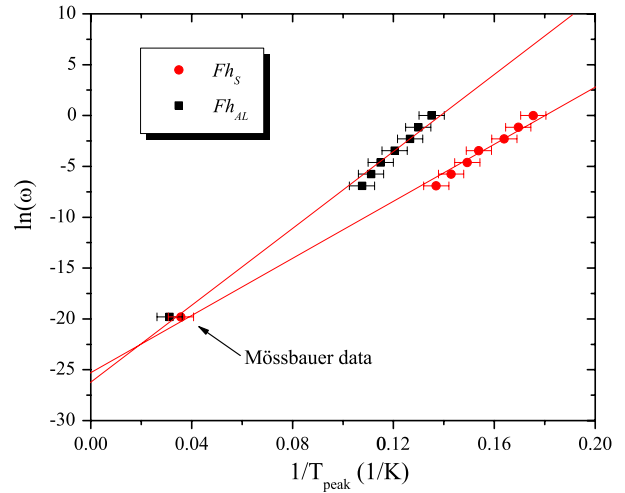


Figure 7. Néel–Arrhenius plot for ferrihydrite samples coated with sugar (Fh_S) and alginate (Fh_{AL}). The solid line is the fitting of the ac susceptibility data and Mössbauer measurements.

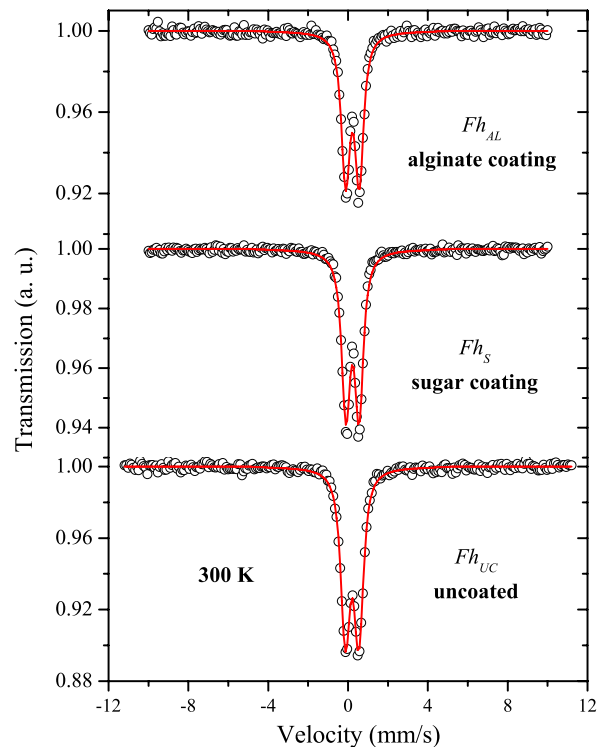


Figure 8. Mössbauer spectra at room temperature represented by Fe^{3+} for all three ferrihydrite samples. Open circles are experimental data and lines are the best fitting.

anisotropy constant (three fold the value of Fh_S) and a non-physical τ_0 was obtained for sample Fh_{UC} .

3.4. Mössbauer spectroscopy

Mössbauer spectra at room temperature for all three samples are shown in figure 8. The spectra at room temperature are represented by Fe^{3+} doublets, which is consistent with a superparamagnetic ensemble of ferrihydrite particles.

Table 1. Magnetic hyperfine parameters at room temperature and 4.2 K for ferrihydrite samples coated with sugar, alginate and uncoated. (Note: maximum hyperfine field (B_{HF}), quadrupole splitting (QS), isomer shift (IS). Errors are quoted within parentheses.)

	300 K			4.2 K		
	Fh _{UC}	Fh _S	Fh _{AL}	Fh _{UC}	Fh _S	Fh _{AL}
B_{HF} (T)	—	—	—	49.0(1)	48.0(1)	47.8(1)
QS (mm s ⁻¹)	0.66(1)	0.67(1)	0.68(1)	-0.07(1)	-0.07(1)	-0.08(1)
IS (mm s ⁻¹)	0.33(1)	0.35(1)	0.35(1)	0.54(1)	0.54(1)	0.53(1)
%	100	100	100	100	100	100

Parameters fitted for sample Fh_{UC}, Fh_S and Fh_{AL} are presented in table 1 and the magnetic hyperfine parameters obtained are similar to the ones previously reported for ferrihydrite [23].

At 4.2 K the spectra for samples Fh_{UC}, Fh_S and Fh_{AL} are represented, exclusively, by sextets. For Fh_S, Fh_{AL} and Fh_{UC} the Mössbauer magnetic hyperfine parameters (magnetic hyperfine field (B_{HF}), quadrupole splitting (QS) and isomer shift (IS)) fitted at 4.2 K are similar to each other and are in agreement with the literature [23]. Mössbauer spectra at temperature ranging from 4.2 to 120 K are shown in figure 9 for samples Fh_{UC} and Fh_S. The spectra for sample Fh_{UC} showed collapsed sextet with increasing temperature and a broad doublet was reached at 120 K. In contrast, the spectra for sample Fh_S (and also Fh_{AL}, not shown) are represented by the coexistence of a sextet and a doublet for spectra obtained with increasing temperature. The relative area of the doublet increases with increasing temperature and consequent decrease of sextet contribution. The median blocking temperature is obtained when each component (sextet and doublet) is fifty per cent of the spectral area. These data were also plotted in figure 7 in order to estimate K_{eff} and τ_0 for samples Fh_S and Fh_{AL}. It is noticed in figure 9 that the temperature at which sample Fh_S reached a doublet is dramatically lower than the temperature observed for sample Fh_{UC}.

4. Discussion

The magnetic data of the ferrihydrite samples studied here presented two different behaviors that are closely related to the surface treatments used. Two samples prepared with coating agents (Fh_S, Fh_{AL}) showed a magnetic behavior corresponding to monodispersed particles without magnetic interactions and one sample, Fh_{UC}, the one without any surface treatment showed characteristic features of a magnetic interacting system.

Interparticle magnetic interactions effects reported in the literature for agglomerated ferrimagnetic nanoparticles usually discuss changes in T_p of ZFC curves [24]. For our samples a dramatic change in T_p was also observed but for a different reason. For ferrimagnetic particles variable T_p is associated with an increasing concentration of particles with consequent decrease in their interparticle distances. Thus, more concentrated samples have a greater chance to exhibit the effects of magnetic interaction while increasing the distance between particles decreases the chance of magnetic interactions. For our ferrihydrite samples the data for Fh_{UC} sample with aggregated ferrihydrite particles resulted in a

large value of T_p when compared with the T_p observed for samples Fh_S and Fh_{AL}. The effects of coating ferrihydrite that resulted in a decrease of T_p is associated with suppressing magnetic interactions in an antiferromagnetic system. Thus, the experimental procedure of simply drying the particles after exposure to sugar or alginate solution was effective in preventing such aggregation. The FC curve also yields a clue about magnetic interactions. Careful examination of the FC branch, before it merges with the ZFC branch, reveals a steep trend of increasing magnetization with decreasing temperature for coated particles (Fh_S, Fh_{AL}), whereas, for uncoated sample (Fh_{UC}) the FC branch displays only weakly increasing magnetization with decreasing temperature. This observation is also consistent with data previously reported in the literature for ferrimagnetic particles with variable concentration resulting in different interparticle separations that produce variable magnetic interactions response.

A very important feature that was investigated for coated and aggregated samples was the behavior of T_p from ZFC curves under variable applied fields. For ferrimagnetic magnetite with different concentrations (and variable magnetic interactions) Luo *et al* [24] showed that magnetic interactions play a role in observed T_p values. The nature of magnetic interactions investigated in their samples, however, is different from ours since the ferrihydrite particles are antiferromagnetic. On the other hand, Luis *et al* [14] explored this same feature for ferritin, a non-interacting system. A close inspection of the data from Luis *et al*, [14] for a system with similar characteristics as the coated particles studied here, shows that T_p was almost constant with increasing magnetic field. Our data provides an addition to the behavior reported by Luis *et al* [14] by showing the contrasting behavior of T_p of coated and non-interacting particles versus the T_p behavior for aggregated and magnetically interacting particles of antiferromagnetic particles.

There is a well-known lack of accurate information about the anisotropy constant for ferrihydrite and many contrasting values have been estimated. We believe that variable magnetic exchange interactions (i.e. increasing the energy barrier) as well as an enhanced anisotropy constant related to nanoparticle surface and its internal stress may be responsible for the large range of magnetic anisotropy constant (K) values obtained. The coated ferrihydrite samples Fh_S and Fh_{AL} presented high quality and very consistent results. The data used here to obtain more accurate values of effective anisotropy were obtained from out-of-phase (χ'') ac susceptibility component [25] and from Mössbauer spectroscopy.

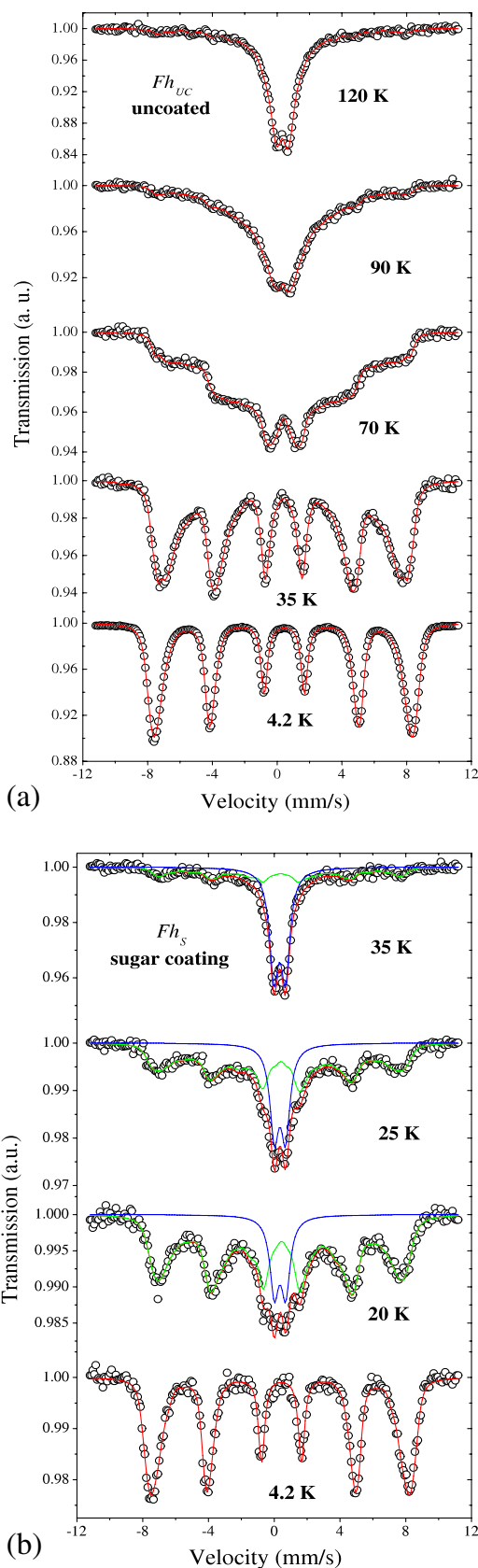


Figure 9. Mössbauer spectra evolving from 4.2 K until reaching a doublet, at indicated temperatures, for ferrihydrite uncoated particles (a) and ferrihydrite coated with sugar (b). For sample Fh_{UC} the sextet pattern at intermediate temperatures collapses while for sample Fh_S the coexistence of sextet and doublet is observed. Open circles are experimental data and lines are the best fitting.

For the two ferrihydrite samples, Fh_S and Fh_{AL} , studied with Mössbauer spectroscopy, we attribute the progression from sextet to doublet over a small temperature range, from 4.2 to 35 K, for Fh_S (as compared to the large temperature range, from 4.2 to 120 K, for Fh_{UC}), to the suppression of particle–particle exchange interactions due to the coating procedure. This result is strongly supported by the data of ZFC/FC curves already discussed above. The Mössbauer spectra at variable temperatures of ferritin, the mammalian protein with a core of ferrihydrite, showed a trend similar to the one found here for sample Fh_S and Fh_{AL} [7]. In their case they did not have a counterpart aggregated system to observe the effects of ferrihydrite magnetic interactions. On the other hand, for our two sets of ferrihydrite samples, aggregated and coated particles, a conspicuous change was observed in the Mössbauer spectral pattern due to the contribution of magnetic interactions and its suppression by coatings.

5. Summary

Different organic coating agents (sugar, alginate, ascorbate and lactate) were employed to prevent iron oxide nanoparticle agglomeration in order to avoid magnetic superexchange interactions, and for comparison one sub-sample was allowed to dry with no coating agent and became aggregated. The method for coating AF ferrihydrite particles with sugar and alginate seems to have been successful. A non-interacting system of coated particles could be recognized by a downward shift in T_p from ZFC curves and ac susceptibility (from 55 K to aggregated sample to 12 K to sugar and alginate coated) and a characteristic T_p behavior was presented with variable applied fields. The ferrihydrite system also showed a characteristic Mössbauer pattern evolution with temperature, during transition from a magnetically ordered to a thermally relaxed state. The data obtained with these samples strongly support our view that interparticle interactions is an issue for these ferrihydrite particles. Since the uncompensated magnetic moment is small in such antiferromagnetic material, interparticle exchange interactions are suggested. The magnetic anisotropy constant estimated ($100 \times 10^3 \text{ erg cm}^{-3}$) from coated non-interacting 3.6 nm particles should be very reliable and accurate since the system studied here is close to an ideal one (non-interacting ensemble of coated, single particles and, predominantly, spherical in shape). It was also observed that ascorbate and lactate were unsuitable coating agents due to chemical reaction between the coating agent and the ferrihydrite particles.

Acknowledgments

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