Surface effects in maghemite nanoparticles

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Abstract

A consistent model is presented for the variation of saturation magnetization with particle size in maghemite nanoparticles, based on the existence of a magnetically disordered layer with a constant thickness of 1 nm. For particles smaller than 3 nm, layer thickness increases rapidly, and M_S is already zero for 2.5 nm particle size. Magnetization measurements have been performed on maghemite-polymer nanocomposites with low size dispersion and a regular distribution of particles in the matrix. A representative number of samples have been studied with a diameter size in the range from 1.5 to 15 nm and ±10% of size dispersion.

The magnetic properties of iron oxide nanoparticles have been of interest to paleontologists and geologists for a long time. Following the recent development of nanotechnology and nanoscience that interest has extended considerably over many other areas. Thus, these particles are especially attractive for ferrofluids and biomedical nanomaterials because they are easily dispersed in water, they can be covered with shells of different kinds, and they are biocompatible. Despite the number of studies on the magnetic properties of ferrimagnetic iron oxide nanoparticles, their magnetic behavior is not yet well understood. Magnetization of ferrimagnetic nanoparticles is lower than that of bulk materials, it does not saturate at rather high fields and it shows open and shifted hysteresis loops as well as irreversibility in ZFC–FC curves. Some of these features can be explained by anisotropy effects or finite size effects such as misalignment of antiferromagnetic sublattices and structural disorder [1–3]. However, a variety of experi- mental techniques and computer simulations have demon- strated that the incomplete coordination of superficial ions and the likely occurrence of surface structure defects are determinant for this kind of behavior [4–10]. These defects can lead to magnetic disorder extending into the core within a layer of a given thickness.

Thus, the most accepted theoretical model to explain the decrease of magnetization of nanoparticles with particle size is based on a bulk-like ferrimagnetic core and a shell composed of disordered moments [10–17]. Experimental determinations of shell thickness by Mössbauer, ZFC–FC measurements, or neutron techniques [4,8,13,14,17] are mostly based on just one sample, or on various samples within a narrow particle size range. A comparison of these values shows large variations for similar particle sizes and no correlation between shell thickness and particle size. Shell thickness can be calculated from the decrease of saturation magnetization, M_S, with respect to the bulk, using published values of M_S on series of samples with several average particle sizes [22–24]. This calculation also would lead to scattered values and inconsistency on the variation of shell thickness with particle size. Such a dispersion of values may come from differences in sample preparation and/or characterization, because the magnetization of nanoparticles is greatly influenced by a variety of factors related to sample quality (size dispersion, superficial and internal crystal defects [2], inter-phase chemical interactions [18], and interparticle magnetic interactions [19]).

In this article, we propose a simple model for the variation of saturation magnetization with particle size, based on the existence of a magnetically disordered layer with a constant thickness of 1 nm. For particles smaller than 3 nm, layer thickness increases rapidly, and M_S is already zero for 2.5 nm particle size. This model fits extraordinary well with obtained magnetization data, thanks to the use of nanocomposite samples containing isolated particles with narrow size distribution, high crystalline perfection, and regular inter-particle separation. It is shown that the model makes sense previous scattered data.

Magnetization against field measurements has been carried out on maghemite–polyvinylpyridine (PVP) nano-composites. The samples were prepared by basic treatment of PVP films containing Rb, Fe(II), Fe(III) and bromide ions. A representative number of samples covering a wide range of sizes from 1.5 to 15 nm were obtained by changing the iron/pyridine ratio. All the samples, herein designed as S1–S8, were produced following the same procedure. The samples were annealed at 250° C during 24 h in order to improve the crystallization of the particles. The composites contain isolated spherical particles that are uniformly distributed within the matrix, and that show a narrow size distribution (about 10% of the average value). TEM images of representative composite samples with low and high particle density are shown in Fig. 1. X-ray diffraction (XRD), electron diffraction ED, and electron energy loss spectroscopy (EELS) observations of the samples were consistent with maghemite crystal structure.
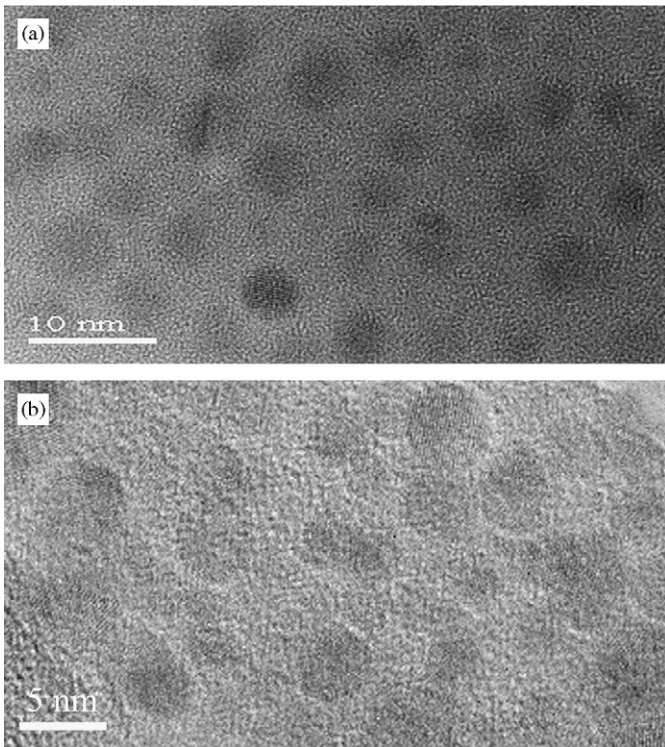

Fig. 1. Electron microscope image of (a) a 40 nm thick slice of sample S3, and (b) a grain of sample S7.

Infrared spectroscopy (IR) observations show band splitting in the region of Fe–O vibrations associated with cationic ordering and crystal perfection [25]. All the samples included in this study yield narrow single peaks in out-of-phase AC susceptibility measurements. This confirms that they are composed of a single type of particle with a narrow size distribution. Reliable particle size values have been obtained from small angle X-ray scattering (SAXS) data analysis. The characteristics of the samples are summarized in Table 1.

Fig. 2 shows plots of the magnetization against H/T for various maghemite nanocomposites with different particle sizes. It is clear that the magnetization decreases rapidly with particle size. For a particle size of 2.5 nm the $M(H/T)$ curve is a straight line. For samples with sizes above 2.5 nm, the curves show a component that saturates at about 20 Oe/K and a component almost linear up to 170 Oe/K. Deviations from this linear behavior are apparent for the larger particles. These two components can be assigned to the contribution from a bulk-like ferrimagnetic core and a shell composed of disordered moments, respectively. Assuming this core–shell model, the contribution of the core to the total magnetization of the particle must be negligible for a particle diameter, $D<2.5$ nm. In this framework, the saturation magnetization of the core, M_S, is the relevant parameter to observe the evolution of the core and shell sizes with particles size based on $M(H)$ curves. In a first approach, M_S can be estimated by a high field extrapolation (Table 1). This can be refined by fitting data to a modified Langevin equation:

$$M = M_S L\left(\frac{\mu H}{k_B T}\right) + \chi H, \tag{1}$$

where M_S is the saturation magnetization, m is the average magnetic moment of the core. The linear contribution to the magnetization, χH, is an additional term that is usually used for antiferromagnetic and ferrimagnetic nanoparticles [26,27]. In antiferromagnetic nanoparticles, such as ferritin, it is usually interpreted as bulk AF susceptibility [28], which is enhanced in nanoparticles [26]. However, the χ values found here (Table 1) are higher than typical values for antiferromagnetic nanoparticles, probably due to the contribution of non-collinear spins in the magnetic structure arising from surface effects [27]. In Fig. 2 differences between data and fits are observed, mainly due to a deficient model for surface. In fact, the surface spins have some saturation in the 20–160 Oe/K range, which is not accounted by the linear term. This small saturation arises since the surface ions are not paramagnetic and/or antiferromagnets, being probably better described as clusters with a magnetic moment much smaller than that of the core but higher than that of isolated paramagnetic Fe ions. Magnetic moment distributions are also contributing to these differences [20]. However, the extracted values of M_S are similar to those estimated from a high-field extrapolation and may serve as a guide to follow the influence of particle size.

Table 1
Characteristics of the nanocomposite samples

Sample	wt% Fe₂O₃	D(SAXS) (nm)	M_S extra (emu/g(Fe$_2$O$_3$))	M_S Lang (emu/g(Fe$_2$O$_3$))	χ Lang (emu/gOe)	d (nm)
S1	2.3	1.6	0	0		—
S2	7.6	2.5	0	0		(1.3)
S3	7.6	3.0	1.5	2.2	1.0×10^{-4}	1.0
S4	16.5	3.1	3	2.9	9.4×10^{-5}	1.0
S5	12.9	3.5	8.5	7.6	1.5×10^{-7}	0.9
S6	22.9	5.2	20	17.4	1.8×10^{-7}	1.0
S7	58.1	7.1	31	26.4	1.9×10^{-7}	1.0
S8	52.9	15	52	46.9	2.8×10^{-7}	1.1

D is particle diameter, M_S is the saturation magnetization derived from fitting to a modified Langevin equation and from high-field extrapolation, and d is the calculated thickness of the magnetically disordered layer.
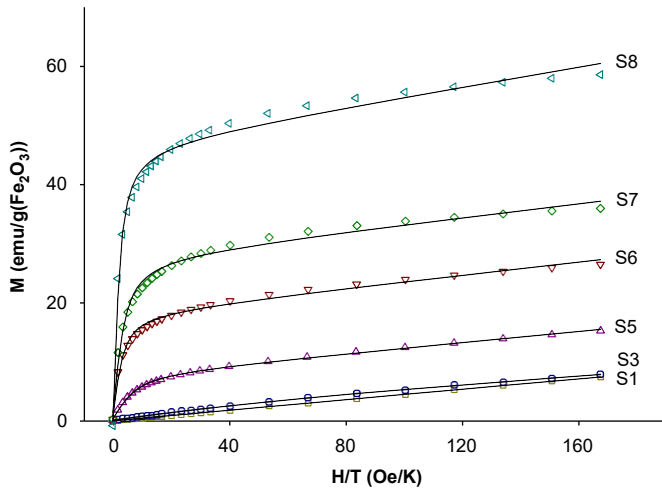

Fig. 2. (Color online) Magnetization per gram of iron oxide for a series of nanocomposite samples with different particle sizes, T = 300 K. Lines correspond to fittings to a modified Langevin equation.

Fig. 3a shows the variation of M_S with size. It is evident that the decrease of M_S is steeper as the particle size decreases. For a size of 3 nm the value approaches to zero, and for a size of 2.45 nm the M_S value is already zero (Table 1). In this core-shell model, M_S is proportional to the volume fraction of the maghemite-like core

$$M_S = M_{S0}\left(\frac{(D/2) - d}{D/2}\right)^3,$$

(2)

where M_{S0} should be close to the bulk saturation magnetization (76 emu/g) [21]. The validity of this relation can be confirmed observing a M_s versus $1/(D/2)$ plot (Fig. 3b). The results are surprisingly consistent: since this plot is quite linear, we conclude that the disordered layer d is almost constant in a 3–15 nm diameter range. A linear fit yields a magnetically death shell of thickness d=1 nm and M_{S0} = 73 emu/g, which is close to the bulk value and confirms the coherence of this model. We can also observe

that the thickness of the disordered layer slightly increases when approaching the limiting size value for total magnetic disorder, since M_S is already zero for sample S2 where D= 2.5 nm. Fig. 3b shows also series of M_S data for maghemite nanoparticles from different sources found in the literature [22–25,29–32]. One by one, these series do not show a clear and consistent tendency. However, the overall tendency is not far from the model proposed in this paper, in spite of a wide scattering. Deviations from the general tendency can be due to particle size dispersion, particle aggregation, interphase interactions, and different degrees of crystallization. It could also be caused by uncertainties in the determination of the particle size. In our case, the use of small angle X-ray scattering for size determination has guaranteed statistical representativity and no changes in particles due to specimen preparation.

In previous articles, shell thickness has also been estimated from the ratio of canted spins measured by Mössbauer spectroscopy. The shell thickness, d, would be 0.9 nm for D= 5.9 nm according to the Coey results [14], 0.5 nm for D= 9 nm according to the Hendriksen et al. [4], 0.9 nm for D = 7.5 nm according to the Linderoth et al. [17], and 0.35 nm for all the particle sizes in the range 2.7–7.1 nm (at T=7 K). From ZFC–FC measurements, Martinez et al. [13] suggest a spin-glass layer of 0.6 nm for D = 10–15 nm. Finally, Lin et al. [8] estimated a thickness of 1.2 nm for cobalt ferrite from polarized neutron experiments. Again, there is a disparity of values, though on average they are not far from the value found in this work. The degree of crystallinity on core and surface can have an important influence on the magnetic properties of maghemite nanoparticles [2]. Actually, it has been proposed that this is the only cause of decrease of magnetization in nanoparticles [33]. This conclusion is based on measurements of saturation magnetization on 7 nm size maghemite nanoparticles that yielded a value (80 emu/g) close to the bulk (76 emu/g). However, values from other authors [34] using a similar synthetic method show a decrease of saturation magnetization that fits well to Eq. (2). This disagreement could be partially explained by a presence of magnetite (M_S = 92 emu/g) in samples prepared with this method as found in ref. [35].
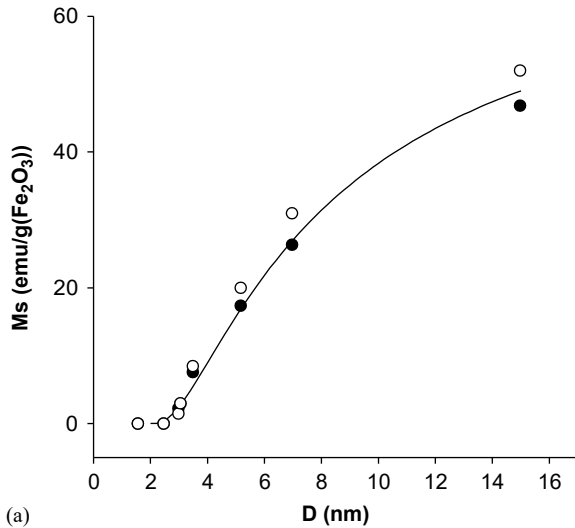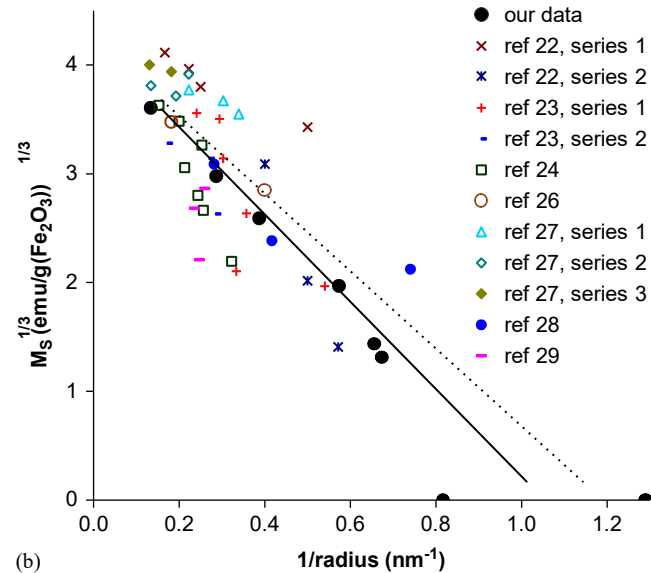
Fig. 3. (Color online) (a) Variation of the saturation magnetization, M_S, with the particle diameter. Full points correspond to values from fitting to Eq (1), and empty circles correspond to values from high-field extrapolation. The line corresponds to fit to Eq. (2); (b) linearization of the pervious plot, where the constancy of thickness of the magnetically disordered layer d with the particles size can be observed, and comparison with data from other authors. The full line corresponds to the fitting of the data here reported and the dashed line to the overall fitting of data included those from other authors.

Nanoparticle samples used here, showed a high crystalline perfection after annealing as revealed by IR observations.

There are no other experimental evidences on the limiting size at which the core disappears apart from this work. However, according to Monte Carlo simulations by Iglesias and Labarta [36], this should occur for a size around 3 nm. They also announce an increase of the shell thickness as the particle size approaches this value. These predictions are in very good agreement with the results of this work.

In conclusion, the decrease of magnetization in maghemite nanoparticles with respect to the bulk can be explained by a magnetically disordered surface layer with a thickness of 1 nm, in a size range of 3–15 nm that increases when approaching 3 nm. The core has a saturation magnetization close to the bulk.

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