Journal of Magnetism and Magnetic Materials 384 (2015) 148–154

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic relaxation and correlating effective magnetic moment with particle size distribution in maghemite nanoparticles

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form
2 February 2015
Accepted 16 February 2015
Available online 17 February 2015

Keywords:
Maghemite nanoparticles
Magnetic properties
Magnetic relaxation
Particle size distribution
Magnetic moment distribution
Interparticle interaction

ABSTRACT

The role of particle size distribution inherently present in magnetic nanoparticles (NPs) is examined in considerable detail in relation to the measured magnetic properties of oleic acid-coated maghemite (γ-Fe_2O_3) NPs. Transmission electron microscopy (TEM) of the sol–gel synthesized γ-Fe_2O_3 NPs showed a log-normal distribution of sizes with average diameter $\langle D\rangle = 7.04$ nm and standard deviation $\sigma = 0.78$ nm. Magnetization, M, vs. temperature (2–350 K) of the NPs was measured in an applied magnetic field H up to 90 kOe along with the temperature dependence of the ac susceptibilities, χ' and χ'', at various frequencies, f_m, from 10 Hz to 10 kHz. From the shift of the blocking temperature from $T_B = 35$ K at 10 Hz to $T_B = 48$ K at 10 kHz, the absence of any significant interparticle interaction is inferred and the relaxation frequency $f_o = 2.6 \times 10^{10}$ Hz and anisotropy constant $K_a = 5.48 \times 10^5$ erg/cm^3 are determined. For $T < T_B$, the coercivity H_C is practically negligible. For $T > T_B$, the data of M vs. H up to 90 kOe at several temperatures are analyzed two different ways: (i) in terms of the modified Langevin function yielding an average magnetic moment per particle $\mu_p = 7300(500)\ \mu_B$; and (ii) in terms of log-normal distribution of moments yielding $\langle\mu\rangle = 6670\ \mu_B$ at 150 K decreasing to $\langle\mu\rangle = 6100\ \mu_B$ at 300 K with standard deviations $\sigma \simeq \langle\mu\rangle/2$. It is argued that the above two approaches yield consistent and physically meaningful results as long as the width parameter, s, of the log-normal distribution is less than 0.83.

1. Introduction

Magnetic properties of nanoparticles (NPs) depend not only on their size, size distribution and morphology but also on several other factors such as interparticle interactions, interactions between the surface spins and ligands, the presence of defects, and the degree of ordering in the surface and core spins and interactions between them. Understanding these different effects requires detailed investigations of the magnetic properties as a function of temperature, magnetic fields, and measuring frequencies on structurally well-characterized samples of different sizes, which are often synthesized by different methods. The interesting physics emanating from such investigations and diverse applications of magnetic NPs in catalysis, ferro-fluids, high-density magnetic storage and biomedicine have continued to attract the interest of researchers worldwide [1–6].

Nanoparticles of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), the two stable oxides of iron with ferrimagnetic ordering, have potential applications in ferrofluids and in biomedicine (targeted drug delivery, and magnetic hyperthermia) [1,4–6]. Bulk Fe_3O_4 (γ-Fe_2O_3) has a spinel structure with lattice constant $a = 0.839$ nm (0.835 nm), ferrimagnetic Néel temperature $T_{FN} \simeq 948$ K (600 K) and 8 (32/3) formula units per cell with the following cationic arrangements on the A and B sites: 8 $Fe_3O_4 = 8\ [Fe^{3+}]_A\ [Fe^{3+} \cdot Fe^{2+}]_B\ O_4$ and (32/3) γ-$Fe_2O_3 = [8\ Fe^{3+}]_A\ [(40/3)\ Fe^{3+} \cdot (8/3)\ V]\ O_{32}$ where V represents a vacancy. For Fe_3O_4, the ferrimagnetic moment results from Fe^{2+} ions, leading to calculated saturated magnetization $M_S = 106$ emu/g using $\mu(Fe^{2+}) = 4.4\ \mu_B$ in the limit of $T \to 0$ K. A similar calculation for γ-Fe_2O_3, in which ferrimagnetism results from unequal numbers of Fe^{3+} ions on the A and B sites, yields $M_S = 87$ emu/g using $\mu(Fe^{3+}) = 5\ \mu_B$. Because of the high magnitudes of T_{FN}, the measured magnitudes of M_S at room temperature are expected to be only slightly lower than the above values. These high magnetization values for Fe_3O_4 and γ-Fe_2O_3, combined with their resistance to oxidation and biocompatibility, make them highly suitable for biomedical applications [1,4–6]. The often-observed decrease of room temperature super-paramagnetic magnetization with decrease in particle size, D, in both Fe_3O_4 [7] and γ-Fe_2O_3 [8], has been interpreted in terms of a core–shell structure with a magnetically dead shell of about 1 nm not contributing to M_S. However, in γ-Fe_2O_3 NPs with inherent presence of cationic vacancies, spin disorder in the core

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http://dx.doi.org/10.1016/j.jmmm.2015.02.038
0304-8853/

spins has also been concluded from the observations of large coercivity H_C and large high-field susceptibility [9,10]. Thus, in addition to size, the method of preparation of the γ-Fe_2O_3 NPs may also determine their magnetic properties. The recent studies by Vaishnava et al. [11] on several different size NPs of γ-Fe_2O_3 dispersed in a polystyrene resin matrix have addressed the issue of the size distribution on the measured dc magnetic properties.

In this paper, we report results of our investigations of the dc and ac magnetic properties of γ-Fe_2O_3 NPs of size $D \simeq 7$ nm, covering the temperature range from 2 K to 350 K in dc magnetic fields H up to 90 kOe and in ac measuring frequencies f_m from 10 Hz to 10 kHz. Measurements of the ac susceptibilities as a function of f_m are essential for determining the relaxation rate needed for magnetic hyperthermia applications and for determining the strength of any interparticle interactions [12,13]. In our previous studies of γ-Fe_2O_3 NPs [14] and those of Vaishnava et al. [11], the ac susceptibility studies were not carried out. In this paper, analysis of the magnetic data on the 7 nm γ-Fe_2O_3 NPs prepared by the method of Hyeon et al. [15] and structurally characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermo-gravimetric analysis (TGA) and diffuse reflectance spectroscopy (DRS) is reported with the following important results: (i) The blocking temperature $T_B \simeq 35$ K is determined from dc magnetization measurements carried out under the zero-field-cooled (ZFC) and field-cooled (FC) conditions. (ii) From the analysis of change in T_B with measuring frequency f_m, negligible interparticle interaction is inferred for these oleic acid (OA)-coated particles with the relaxation attempt frequency $f_o \simeq 2.6 \times 10^{10}$ Hz of the Néel–Brown relaxation [16,17]. (iii) For $T > T_B$, the fit of the M vs. H data to the modified Langevin function yields the magnetic moment per particle $\mu_p \simeq 7300\ \mu_B$. (iv) Measurements by TEM yield a log-normal size distribution of NPs with average diameter $D = 7.04$ nm and standard deviation $\sigma = 0.78$ nm. (v) The effects of the log-normal particle size distribution on the particle moment distribution are analyzed and correlated with the results obtained from the modified Langevin variation fit. (vi) For $T < T_B$, the negligible measured coercivity $H_C \approx 15$ Oe, suggests coherent rotation of the spins under applied H and well-ordered spins in the nanoparticles. Details of the experimental procedures, experimental results, and their analysis and discussion are presented below.

2. Theoretical considerations

Here we briefly summarize the basic equations in NP magnetism which are used later for the interpretation and discussion of the experimental results. For non-interacting NPs with volume V and anisotropy K_a, the frequency f for the reversal of its magnetic moment μ_p is given by the Neel–Brown relaxation [16,17]:

$$f = f_o \exp(-T_a/T) \tag{1}$$

here $T_a = K_a V/k_B$ where k_B is the Boltzmann constant and f_o is the attempt frequency. The blocking temperature T_B defined by $f = f_m$ (measuring frequency) is then given by

$$T_B = T_a/\ln(f_o/f_m). \tag{2}$$

In the presence of interparticle interactions (IPI), Eq. (2) is replaced by the Vogel–Fulcher relaxation equation [18,19] leading to

$$T_B = T_o + \left[T_a/\ln(f_o/f_m)\right] \tag{3}$$

where T_o is a measure of the strength of the IPI. For uncoated, strongly interacting NiO NPs, $T_o = 70$ K was determined with $f_o = 9.2 \times 10^{11}$ Hz [20]. According to Eq. (3), IPI effectively increase the energy barrier of the system, a conclusion also reached by the theoretical/computational studies of Chantrell et al. [21]. The presence of IPI in NPs can also be determined from the measured variation of T_B with change in f_m by calculating the quantity Φ given by [22]

$$\Phi = \Delta T_B/T_B \Delta \log_{10} f_m \tag{4}$$

It is known [22] that $\Phi \geq 0.13$ for non-interacting particles and Φ is very small (0.005–0.05) for spin glasses. The intermediate values of Φ ($0.05 \leq \Phi \leq 0.13$) signify the presence of IPI with decreasing effect for increasing values of Φ. The magnitude of Φ can be determined from the change in T_B measured using ac susceptibilities χ' and χ'' as a function of temperature at a frequency f_m, since χ'' peaks at T_B and $\chi'' = C\partial(T\chi')/\partial T$ [12,23].

For $T > T_B$, the NPs are in the super-paramagnetic state and M vs. H data are expected to obey the modified Langevin function [24,25]:

$$M = M_o \mathcal{L}\left(\mu_p H/k_B T\right) + \chi_a H \tag{5}$$

Here $\mathcal{L}(x) = \coth(x) - (1/x)$ is the Langevin function, M_o is the temperature dependent saturation magnetization, μ_p is the average magnetic moment per particle, and χ_a is the linear component of the susceptibility usually estimated from the high-field data. In the case of a size distribution of particles, Eq. (5) has to be modified to include a corresponding distribution of the magnetic moments μ_p of the particle [11,26]. This issue is discussed later in the paper.

3. Synthesis and structural characterization

To synthesize the γ-Fe_2O_3 NPs, the procedure described by Hyeon et al. [15] was employed since this method is known to produce highly crystalline NPs [14,15]. Briefly, 0.2 mL of $Fe(CO)_5$ was added to a mixture of octyl ether (10 mL) and oleic acid (1.28 g) at 100 °C and refluxed for one hour resulting in a change of color of the solution from orange to black. The solution was then allowed to cool to room temperature, 0.34 g of dehydrated trimethylamine N-oxide $(CH_3)_3NO$ was added and the solution was heated to 130 °C and held at that temperature for 2 h. The temperature was then raised slowly until reflux, and held for one hour. The solution was then allowed to cool to room temperature, and ethanol was added until a black precipitate formed. A strong magnet was used to hold the precipitate in place as the excess liquid was poured off. The NPs were re-suspended in a small amount of toluene and ethanol was again used to precipitate the NPs. This washing process was repeated three times before the particles were stored in toluene until used.

A transmission electron micrograph (TEM) of the sample obtained using a JEOL JEM-2100 transmission electron microscope is shown in the inset of Fig. 1. Using 'imageJ' software, dimensions and areas of the NPs were measured. The aspect ratio of 87% of the NPs was found to be less than 1.3 indicating nearly spherical shape. The particle diameters were calculated from the areas assuming spherical shapes; a histogram of this distribution is shown in Fig. 1. The size distribution is fit to the log-normal distribution:

$$f(D) = \frac{1}{2\pi\lambda_D D} \exp\left\{\frac{-[\ln(D/D_o)]^2}{2\lambda_D^2}\right\} \tag{6}$$

with D_o = median particle diameter and λ_D = width of the distribution with average particle diameter $\langle D \rangle = D_o \exp\left(\lambda_D^2/2\right)$ and the standard deviation $\sigma = \langle D \rangle \left[\exp\left(\lambda_D^2\right) - 1\right]^{1/2}$. The fit shown by the solid line in Fig. 1 yields $\lambda_D = 0.11$, $D_o = 7.0$ nm, $< D > = 7.04$ nm and $\sigma = 0.78$ nm.