Pressure effects in hollow and solid iron oxide nanoparticles

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ARTICLE INFO

Article history:
Received 29 November 2012
Received in revised form 17 January 2013
Available online 29 January 2013

ABSTRACT

We report a study on the pressure response of the anisotropy energy of hollow and solid maghemite nanoparticles. The differences between the maghemite samples are understood in terms of size, magnetic anisotropy and shape of the particles. In particular, the differences between hollow and solid samples are due to the different shape of the nanoparticles and by comparing both pressure responses it is possible to conclude that the shell has a larger pressure response when compared to the core.

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1. Introduction

Pressure is a thermodynamical parameter on which changes in structural and magnetic properties are commonly observed. In the case of nanoparticles (NPs), pressure modifies the transition temperature [1], the susceptibility and magnetization [2,3], the hysteresis cycles [2] and the effective anisotropy energy barrier [4]. The effect of pressure in the NPs core and surface is distinct, allowing disentanglement of core and shell magnetic properties. This is the case of the anisotropy energy barrier in spherical maghemite NPs; while at room pressure only an effective value can be obtained, with increasing pressure core and shell size have a different response and so does the effective anisotropy energy, such that core and shell components of the anisotropy energy can be extracted [4].

Core/shell models have been successfully used in the context of magnetic properties of maghemite NPs. These models often consider that the particles are constituted by a bulk-like core and a surface with distinct magnetic properties. In a seminal work, Coey described maghemite NPs as having a core with the bulk spin arrangement and a surface in which the spins are inclined at some angle [5]. The surface spins of maghemite NPs were lately shown to have spin-glass like properties [6]. In the case of magnetization (M) measurements, surface is often considered as constituted by single paramagnetic and/or aniferromagnetic ions, whose contribution to M is linear in field [7]. The origin of this surface magnetic behavior is associated with incomplete coordination of superficial ions and to the likely occurrence of structural defects at the surface, as shown by experimental techniques and computer simulations (see for instance Refs. [8–10]).

Since maghemite core and shell properties have a different pressure response, one can expect that maghemite particles with different geometry have a different behavior with pressure, allowing a better insight on the magnetic properties of core and shell. Hollow maghemite NPs are an exotic and interesting system where the relevance of surface is enhanced [11,12]. Accordingly, we investigate the effect of pressure in hollow maghemite NPs and we compare this effect with that observed in solid maghemite NPs obtained by polymeric-assisted synthesis and nonaqueous routes.

2. Experimental

Three different samples were synthesized and studied: a sample composed of hollow iron oxide NPs capped by oleylamine, a sample composed of solid iron oxide NPs capped by oleic acid and a sample composed of solid iron oxide NPs dispersed in a polymer and forming a composite.

Hollow iron oxide NPs were obtained by the nanoscale Kirkendall effect following a previously reported procedure [11]. Briefly, iron NPs were obtained by decomposition of iron pentacarbonyl in organic solvents containing amines. 10 ml of octadecene (C18H36) containing 0.67 mmol of oleylamine were heated inside a three-neck flask to 60 °C under vacuum for 30 min. While keeping the solution under argon, the temperature was raised to 200 °C. A precursor solution of 0.4 ml of Fe(CO)5 in 2 ml of octadecene was prepared separately under Ar. This was rapidly injected through a septum into the hot surfactant solution under vigorous stirring. The resulting solution was reacted for 20 min. Afterwards, to oxidize the formed iron NPs, 20 ml/min of a 20%
oxygen mixture in argon were flowed through the heated flask over 2 h.

Solid $\gamma$-Fe$_2$O$_3$ NPs were obtained by decomposing iron pentacarbonyl in octadecene in the presence of an excess of oleic acid. The presence of equivalent or excess amounts of oleic acid in the precursor solution initially results in the formation of iron oleate, which decomposes directly into iron oxide. In a typical synthesis, a mixture of 10 ml of octadecene and 2 ml of oleic acid were heated inside a three-neck flask to 60 $^{\circ}$C under vacuum for 30 min. While keeping the solution under argon, the temperature $T$ was estimated by the shift in the superconducting transition temperature of tin [18]. The ac magnetic response was measured using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) [16] and an isotropic model yielding an average apparent size. The average apparent size at room pressure is 3 nm crystal-crust, as shown in Fig. 1, top-left inset.

The size effects were treated with the integral breadth method using the Voigt model for both the instrumental and intrinsic broadening [16]. Despite the opposite trends of $H_C$ and $M_S$, $K_{eff}$ increases with pressure, anticipating a pressure dependence of the anisotropy energy transform of the SQUID voltage, which was measured after modification of the phase delay due to the eddy current of CuBe at each frequency.

3. Results and discussion

TEM micrographs of the hollow sample show the expected geometry of core/shell hollow/solid NPs with an average diameter of about 8 nm and a low size dispersion (Fig. 1). The iron oxide shell has about 3 nm, being polycrystalline, as seen in the HRTEM micrographs and corresponding Fourier transform (Fig. 1, right inset). Accordingly, the NP structure can be depicted as a tectonic crust, as shown in Fig. 1, top-left inset.

XRD patterns of the hollow sample show the existence of NPs with a spinel structure consistent with magnetite/maghemite (Fig. 2(a)). The patterns can be well reproduced by considering the $P4_3 32$ space group and a peak broadening due to finite size effects. Fits with similar quality are obtained when considering different Fe/O stoichiometry although the best fit is obtained with a stoichiometry closer to magnetite than to maghemite. This result should be taken carefully, since the background is ill-defined making difficult a proper determination of the relative intensity of the peaks. In fact, previous spectroscopy studies suggest that the iron oxide is maghemite rather than magnetite [11]. The contribution to the peak broadening due to strain is negligible compared to that of size. The average apparent size at room pressure is $\sim 2.2$ nm (Fig. 2(b)), in good agreement with the $\sim 3$ nm crystalline domains observed by HRTEM. The cell parameter decreases monotonically with pressure, whereas the average apparent size has no defined trend having values in the 2.1–2.4 nm range (which is probably close to its error bar).

At low temperature, magnetization shows hysteresis with field (Fig. 3(a)). The coercive field $H_C$ and the magnetization at the maximum field used in the experiment (denoted as $M_S$) are pressure dependent, increasing and decreasing with pressure, respectively (Fig. 3(b) and (c)). Taking into account these two dependencies it is possible to evaluate the pressure dependence of the effective anisotropy constant $K_{eff}$, since $K_{eff} \propto H_C M_S$. Despite the opposite trends of $H_C$ and $M_S$, $K_{eff}$ increases with pressure, anticipating a pressure dependence of the anisotropy energy barrier.

![Fig. 1. Typical TEM micrograph of the hollow maghemite NPs with 8 nm average size. Inset micrograph corresponds to a high resolution image of the same NPs and corresponding Fourier-transform. Top-left inset cartoon depicts the hollow polydomain structure of a NP.](image-url)
The pressure dependence of the ac susceptibility at room pressure of the hollow and solid samples shows the characteristic features of superparamagnetic NPs with a distribution of energy barriers undergoing an unblocking process as temperature increases from 20 to 100 K, showing a frequency-dependent maximum with temperature (blocking temperature $T_B$) at around $T_B=45$ K (Fig. 4). With the increase of pressure, $T_B$ at a fixed frequency increases to higher temperatures. At a given pressure, $T_B(f)$ follows a Néel–Arrhenius relation, $\tau_m = \tau_0 \exp(E/k_BT_B)$ as usually found in superparamagnetic NPs \cite{19,20}. Here $\tau_0$ is a microscopic characteristic time, $\tau_m$ is the characteristic measurement time equal to $1/(2\pi f)$ and $E$ is the anisotropy energy barrier, usually expressed as the product between $K_{eff}$ and the NPs average volume $V$. From the Néel–Arrhenius relation, the pressure dependence of $E$ can be estimated (Fig. 5). Qualitatively, the pressure dependence of $E$ is similar in the solid, hollow and polymer-grown maghemite NPs ($E_{solid}$, $E_{hollow}$ and $E_{polymer}$), increasing with pressure in the studied range. The increase of $E_{hollow}$ is in accordance with the increase of $K_{eff}$ determined from the magnetization results.

A better insight on the relation between $E$ obtained for the three studied samples is obtained by plotting two of them as a function of the third (Fig. 6). Since $E$ of the three samples was estimated at different pressure values, a simple interpolation procedure was applied. In the plot of Fig. 6, the similitude between the $E$ pressure dependence is apparent as a linear dependence between $E$ of the solid NPs and those of the hollow and polymer-grown NPs. Interestingly, while $E_{polymer}$ is simply proportional to $E_{solid}$, with the linear extrapolation crossing the $(0,0)$ point, $E_{hollow}$ is proportional to $E_{solid}$ with the linear extrapolation crossing the $x$-axis at a positive value, such that

$$E_{hollow} = E_{solid} - 627 \text{ K}$$

$$E_{polymer} = 0.176 E_{solid}$$

(1)

This means that the pressure dependence of the polymer-grown NPs and that of the solid maghemite NPs has the same physical origin, differing only by a constant term reflecting the different $E$ value of both samples at ambient pressure, associated with their different $V$ and $K_{eff}$. On the other hand, the slope of the $E_{hollow}$ vs. $E_{solid}$ dependence is quite close to 1 when $E_{hollow}$ extrapolates to zero, $E_{solid}$ has still a non-zero contribution of the order of 627 K. In a first approximation, this can be regarded as the $E_{solid}$ having two components; one component displaying a behavior similar to that of $E_{hollow}$ (the linear contribution) and a second component which is absent in $E_{hollow}$ (the non-zero contribution at $E_{hollow} = 0$). By geometrical arguments, the component common to both solid and hollow sample is the surface, while the second component present in the solid sample and absent in the hollow one is the core. This suggests that $E$ associated with the surface has the most relevant pressure dependence while $E$ associated with the core has
In summary, it was shown that the anisotropy energy of solid maghemite NPs prepared by different routes of synthesis has a similar pressure dependence, while the anisotropy energy of solid and hollow maghemite NPs shows different pressure dependence. This difference is due to the different geometry of the NPs and with the larger pressure response of the shell.

Acknowledgments

The Aveiro–Barcelona collaboration has been supported by the Integrated Spanish–Portuguese Action under the Grant no. AIB2010PT-00099. The Aveiro–Zaragoza collaboration has been supported by the Integrated Spanish–Portuguese Action PT2009-0131. The work in Zaragoza has been supported by the research Grants MAT2011-27233-C02-02, MAT2011-25991 and CONSOLIDER CSD2007-00010 from the Ministry of Education. The financial support of the CSIC and Spanish Ministerio de Ciencia e Innovación (PI201060E013) is also acknowledged. The work in Japan was supported by a Grant-in-Aid for Scientific Research (C) (No. 23550158) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. O.I. and A.L. acknowledge funding of the Spanish MICINN through Grant nos. MAT2009-08667 and CSD2006-00012, and Catalan DIUE through Project no. 2009SGR856. N.J.O.S. acknowledges FCT for Ciencia 2008 program.

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