Magnetic Behavior and Stoichiometry on Magnetite Nanoparticles

Comportamiento Magnético y Estequiometria en Nanoparticulas Magnéticas

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Resumen

En este trabajo investigamos las propiedades magnéticas de nanopartículas de magnetita usando simulación Monte Carlo en el marco de un modelo *"core-shell"*. Los cálculos se realizan con base en un Hamiltoniano Heisenberg clásico tridimensional con interacción a primeros vecinos y la dinámica de Metropolis. El Hamiltoniano incluye interacciones de superintercambio entre iones de Hierro, un término de anisotropía de Néel para átomos de superficie y anisotropía cúbica magnetocristalina para los átomos del interior. Se implementaron condiciones de frontera libres y se simularon nanopartículas de diferentes diámetros con el fin de estudiar el efecto del cambio en la estequiometría y del tamaño sobre el comportamiento magnético. Para el sistema en '*bulk*' se implementaron condiciones de frontera periódicas, y los resultados se comparan con los correspondientes a las nanopartículas con el objetivo de notar el comportamiento de la temperatura crítica al cambiar el tamaño del sistema, y el rol que juega la superficie sobre las propiedades magnéticas.

Palabras claves: nanopartículas, magnetita, efectos de tamaño y superficie

Abstract

In this study we investigate the magnetic properties of magnetite fine particles by means of Monte Carlo simulation in the framework of a core-shell model. Calculations are performed on the basis of a three-dimensional classical Heisenberg Hamiltonian, with nearest magnetic neighbor interactions, and the Metropolis dynamics. The Hamiltonian includes interactions between Fe ions through the superexchange integrals for the different crystallographic sites, a Néel's surface anisotropy term applied to surface ions, and a cubic magnetocrystalline anisotropy term for those ions belonging to the core. Free boundary conditions were implemented and nanoparticles of different diameters were simulated in order to study the effect of the change in the stoichiometry and particle size on the magnetic behavior. Periodic boundary conditions were used to simulate a large enough bulk system and results were used to compare with those of nanoparticles in order to evidence the behavior of the critical temperature with the system size and the role played by the surface on the magnetic properties.

Key Words: nanoparticles, magnetite, finite size and surface effects.

1. Introducción

It is well known that magnetic properties exhibited by nanoparticles of several oxides are different from those found under bulk conditions, and they are strongly dependent upon finite size effects [1-4]. Such effects include changes in the coordination number, and the presence of uncompensated spins due to the breaking of symmetry at the boundary of the sample. Other features like roughness, structural disorder on the surface and deviations from ideal stoichi-ometry increase the complexity [2-4]. The aim of this work is to investigate the magnetic properties of single Fe_3O_4 magnetite spherical-shaped nanoparticles of different sizes.

2. Model and simulation details

Magnetite is a widely used ferrimagnetic inverse spinel compound having Fe^{3+} and Fe^{2+} ions distributed in two sublattices with different O^{2-} coordination [5]. Its structure (space group *Fd3m* with 32 oxygen and 24 iron ions per
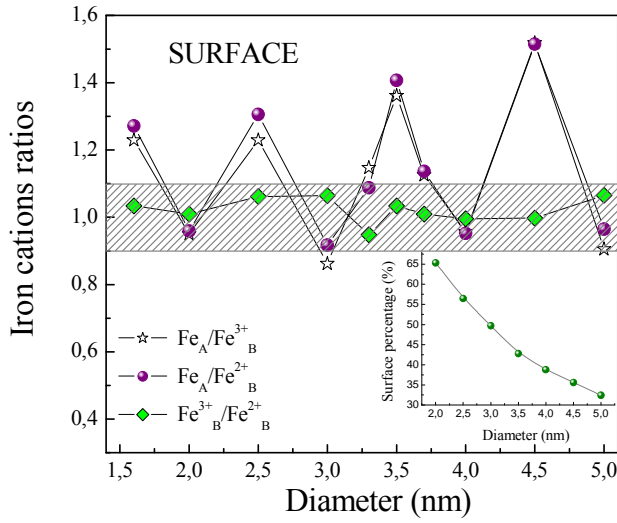
Fig. 1. Diameter dependence of the different iron cations ratios for the core of the particles. Inset shows the percentage of surface Fe-cations as a function of the nanoparticle diameter.
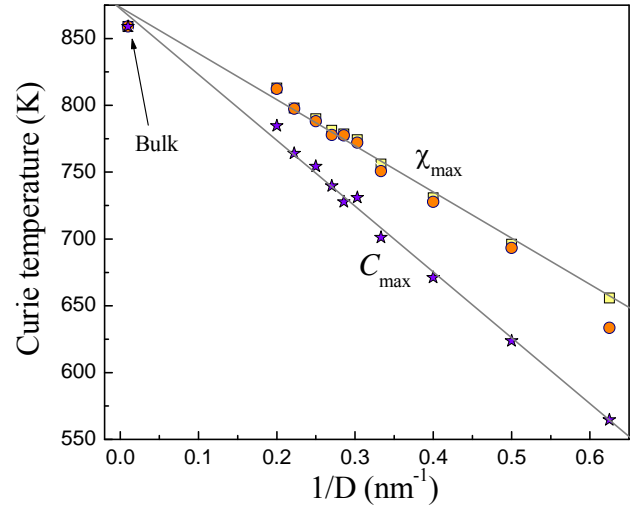

Fig. 2. Curie temperature as a function of the inverse of the diameter. Data taken from the positions at which the maxima of the susceptibility (*A* and *B* sites) and heat capacity take place.

unit cell) consists on 8 tetrahedral positions (*A*-sublattice) occupied by Fe^{3+} ions and 16 octahedral sites (*B*-sublattice) having 8 Fe^{2+} and 8 Fe^{3+} ions. Nanoparticles were simulated by implementing free boundary conditions. The system sizes ranged between 1.6 and 5.0 nm in diameter. Our Hamiltonian can be written as:

$$H = -2 \sum_{<i,j>} J_{ij} \vec{S}_i \cdot \vec{S}_j - K_S \sum_k (\vec{S}_k \cdot \hat{n}_k)^2$$
$$- K_V \sum_i (S_{x,i}^2 S_{y,i}^2 + S_{y,i}^2 S_{z,i}^2 + S_{x,i}^2 S_{z,i}^2). \qquad (1)$$

The first sum runs over nearest magnetic neighbors with the following coordination numbers depending on the crystallographic sites: $z_{AA}=4$, $z_{BB}=6$, $z_{AB}=12$ and $z_{BA}=6$. Surface was defined as formed by those ions having coordination numbers smaller than the nominal numbers for bulk conditions. Magnetic ions Fe^{3+}_A, Fe^{3+}_B, and Fe^{2+}_B are represented by classical Heisenberg spins ($S=5/2$ for Fe^{3+} and $S=2$ for Fe^{2+}). Oxygen ions were considered as non magnetic. The second term accounts for the single-ion site Neel`s surface anisotropy and the unit vector on the surface at each $\vec{P}_i$ position was computed using the relationship [6]:

$$\hat{n}_i = \sum (\vec{P}_i - \vec{P}_j) \Big/ \Big| \sum (\vec{P}_i - \vec{P}_j) \Big| , \qquad (2)$$

Here the sum runs over nearest magnetic neighbors surrounding the ith ion. The third term in Eqn. (1) gives the core cubic magnetocrystalline anisotropy, with constant $K_V=1.35\times10^4$ J/m^3 [7]. Numerical values of the integrals employed were $J_{AA} = -0.11$ meV, $J_{AB} = J_{BA} = -2.92$ meV

and $J_{BB} = +0.63$ meV [8]. A single-spin movement Metropolis Monte Carlo algorithm for computing equilibrium thermodynamic properties was employed. For the bulk system, periodic boundary conditions and a linear system size $L=10$, with a total number of magnetic ions $N = 24\times L^3$, were considered. Up to three different configurations and around 7×10^5 Monte Carlo steps per spin (mcs) were considered to compute equilibrium averages. The first 5×10^5 configurations were discarded for equilibration. The thermodynamic quantities computed were total energy, magnetization per spin, magnetic susceptibility and heat capacity. Contributions to the total magnetization per magnetic site (and to magnetic susceptibility) arising from surface, core, *A* and *B* sites were also obtained. Finally, a value of K_S/K_V =10 was assigned to the anisotropy constant ratio [9].

3. Results and discussion

Figure 1 shows the behavior of the ratios between the different combinations of Fe cations as functions of the diameter for the surface of the nanoparticles considered. Such ratios give information on the stoichiometry of the system. Under bulk conditions all of them should be equal to one. However, as can be evidenced from this figure, deviations from an ideal stoichiometric magnetite are mainly due to surface and strongly dependent on the system size. For the core case, fluctuations on stoichiometry (not shown) are not so big above around 3 nm, and most of them fit onto the shadow region which involves a relative deviation of 10 %. For 1.6 and 2 nm the Fe^{3+}_A/Fe^{2+}_B and Fe^{3+}_A/Fe^{3+}_B ratios take on values 0.33 and 1.50 respectively. It must be stressed that the system size at around 3 nm coincides with that at which the percentage of cations on the surface corresponds to one half the total number of cations (see inset in Fig. 1).
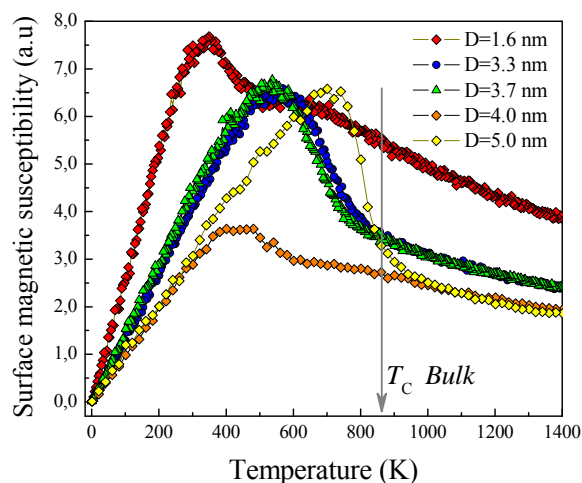
Fig. 3. Temperature dependence of the surface magnetic suscepti-
bility for some selected nanoparticle diameters

Thus, for small system sizes, magnetic properties become
mainly dominated by the surface.

Despite the observed fluctuations in stoichiometry, depen-
dence of the Curie temperature, which is displayed as a
function of the inverse of the diameter in Figure 2, follows a
linear behavior. Such a behavior differs from that found in
maghemite Ising nanoparticles where a power law behavior
characterized by a ν exponent equals to 0.49(3) was ob-
tained [10]. Contrary to this, in our case such an exponent
seems to be equal to one. The best estimate for the intercept
was 871 ± 4 K which is quite similar to that found in our
simulation under bulk conditions by using periodic boun-
dary conditions (859 ± 4 K). Finally, concerning the mag-
netic behavior on the surface, Figure 3 shows the tempera-
ture dependence of magnetic susceptibility computed from
the fluctuations on the magnetization contribution arising
exclusively from those cations belonging to the surface (i.e.
those having a magnetic coordination smaller than the no-
minal coordination number under bulk conditions). Hence
the oscillatory behavior in the maxima positions agrees to
that observed on stoichiometry.

Conclusions

As concluding remarks our results allow inferring: *i*) Criti-
cal temperatures are smaller than that of bulk magnetite.
This finite size effect is due to the symmetry breaking and
the presence of dangling bonds on the surface and *ii*) the
well-behaved T_C vs. D^{-1} dependence is characterized by an
exponent ≈ 1.0

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