

**MAGNETIC PROPERTIES OF MAGHEMITE NANOPARTICLES:
A HEISENBERG – MONTE CARLO STUDY**

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RESUMEN

En este trabajo se investigan las propiedades magnéticas de nanopartículas de maghemita $\gamma\text{-Fe}_2\text{O}_3$ utilizando el método de Monte Carlo-Metropolis sobre la base de un modelo de Heisenberg clásico tridimensional con anisotropía magnetocristalina. La estructura espinela ha sido simulada en forma realista con condiciones de frontera libres para tener en cuenta el efecto de la superficie en una nanopartícula de diámetro 3.34 nm. También se han tenido en cuenta las diferentes interacciones de superintercambio competitivas entre iones de Fe^{3+} incluyendo sitios tetraédricos y octaédricos. Los resultados revelan una marcada disminución de la temperatura de Curie de la nanopartícula considerada respecto a aquella de una maghemita en bulk, como consecuencia del menor número de coordinación promedio. Finalmente se presenta y discute el efecto de la anisotropía de superficie sobre la configuración magnética de los espines en el límite cuando la temperatura tiende a cero.

Palabras claves: Monte Carlo, Heisenberg, nanopartículas, maghemite

ABSTRACT

In this work, the magnetic properties of maghemite $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles by using the Monte Carlo-Metropolis method on the basis of a three-dimensional classical Heisenberg model with magnetocrystalline anisotropy are investigated. The spinel structure has been simulated in realistic way with free boundary conditions in order to take into account the surface effect on a nanoparticle of diameter 3.34 nm. The different competing superexchange interactions between Fe^{3+} ions involving tetrahedral and octahedral crystallographic sites have been also taken into account. Results reveal a marked decrease of the Curie temperature of the considered nanoparticle with that obtained for a bulk maghemite, as a consequence of the smaller coordination number. Finally the effect of surface anisotropy upon the magnetic spin configuration in the limit when the temperature goes to zero is presented and discussed.

Key Words: Monte Carlo, Heisenberg, nanoparticles, maghemite

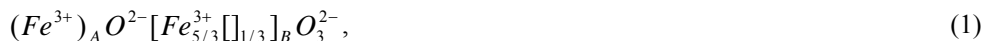
1. Introduction

It is well established for nanoparticles that the average magnetic coordination number is reduced as finite size effects become pronounced [1-4], affecting magnetic properties. This fact arises from boundaries and can be enhanced by surface roughness as well as by vacancies [5]. This feature has motivated us to consider a nanoparticle of maghemite as a canonical example where the 56 ions per unit cell can induce certain degree of roughness on the surface and where vacancies are distributed in octahedral sites. Maghemite is also one of the currently iron oxides

most studied, which exhibits ferrimagnetic behavior below 1000 K due to the superexchange integrals competition between tetrahedral and octahedral sites. It is also found in corrosion products, proteins, in medicine as drug delivery agent, in nuclear magnetic resonance, and is widely used as magnetic storage medium. In this work we consider a maghemite nanoparticle of 3.34 nm of diameter, corresponding to four times the unit cell parameter. The magnetization versus temperature curves for both the nanoparticle and a bulk maghemite are presented and compared, stressing on the differences between the Curie temperatures. Finally the effect of surface anisotropy in the range $10^3 \leq K_S/K_V \leq 10^6$ on the spin structure at 2 K is also discussed.

2. Model and Simulation

Maghemite crystallizes in a spinel structure with 32 O^{2-} ions, eight Fe^{3+} ions are located in tetrahedral sites (A-sites) and sixteen Fe^{3+} ions belong to octahedral sites (B-sites) per unit cell. The chemical formula can be written as:



where the symbol \square stands for vacancies. In our model magnetic ions Fe^{3+}_A and Fe^{3+}_B are represented by Heisenberg classical spins while oxygen is consider as non magnetic. The employed classical Heisenberg Hamiltonian with cubic core magnetocrystalline anisotropy and single-ion site surface anisotropy describing our system reads as follows:

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

The first sum runs over nearest magnetic neighbors with the following coordination numbers: $z_{AA}=4$, $z_{BB}=6$, $z_{AB}=12$ and $z_{BA}=6$. The magnitude of the spin is $|\vec{S}| = 5/2$ according to the electronic configuration $3d^5$ for Fe^{3+} . The second term gives the core cubic magnetocrystalline anisotropy where K_V ($=8.13 \times 10^{-3}$ K) is the bulk anisotropy constant, whereas the third term corresponds to the single-ion site surface anisotropy [1,5]. Concerning the interactions $Fe^{3+}_A - Fe^{3+}_A$, $Fe^{3+}_A - Fe^{3+}_B$, and $Fe^{3+}_B - Fe^{3+}_B$, the respective superexchange integrals values where taken to be $J_{AA}=-1.3K$, $J_{AB}=-33.9K$ and $J_{BB}=+7.3K$ [6]. In our simulation we have employed a single-spin movement Metropolis Monte Carlo algorithm with periodic boundary conditions for the bulk case and linear system sizes L between 2 and 10 with a total number of $N=24 \times L^3$ magnetic ions. Additionally, a closely spherical nanoparticle with free boundary conditions and a diameter of 3.34 nm was also simulated. Figure 1 shows how it looks like the nanoparticle containing 1362 Fe^{3+} ions. Simulated annealing from an infinite temperature spin configuration down to 2 K, for which the obtained spin configurations we assume similar to that of the ground state, was carried out. In computing averages, 5×10^3 Monte Carlo steps per spin were considered after equilibration. The basic thermodynamic quantities are the total energy and the magnetization per spin. Magnetic contributions to the total magnetization per magnetic site arising from tetrahedral and octahedral sites were also analyzed separately.

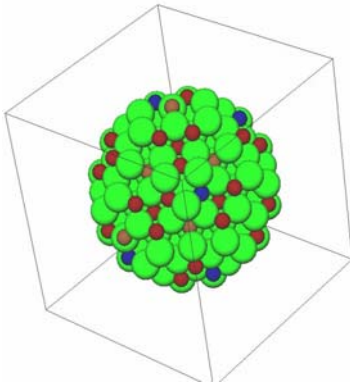


Fig. 1. Schematic representation of the simulated nanoparticle of 3.34 nm of diameter. Different colors stand for O^{2-} , Fe^{3+}_A , Fe^{3+}_B and vacancies. Real ionic radii have been considered.

3. Results and discussion

In the case of a bulk maghemite with periodic boundary conditions, figure 2 shows the temperature dependence of the modulus of the magnetization per spin, including the *A* and *B* sites contributions in a differentiated way. The obtained total magnetization, lying below the *A* and *B*-sites magnetization curves, reveals the occurrence of ferrimagnetic order, as can be also evidenced in the spin configuration at 2K in figure 3. On the other hand, for the nanoparticle, figure 4 shows the corresponding curves for the temperature dependence of the magnetization per spin when K_S/K_V is 10^3 . From this figure, three remarkable differences respect to the bulk maghemite can be observed. Firstly, the Curie temperature becomes around 200 K smaller at around 800 K. This behavior, due to symmetry breaking, is consistent with a smaller average coordination number.

Secondly, the smooth tail at around 800 K is the signature of a finite size effect. Additionally, the magnetizations at the smallest temperature achievable in this simulation, compared to those obtained in figure 2 reveal a strong reduction of the magnetization per spin. As is observed in figure 5, this behavior can be ascribed to the surface disorder arising from the angular distribution of the unit vectors for surface anisotropy, contrary to the assumption of radial surface anisotropy. Such phenomenology resembles a spin-glass-like behavior for which the tendency of the moments to be randomly oriented can be the responsible for the observed decrease of the magnetization as K_S/K_V increases. Figure 5 showing a cross view of spin structure of the nanoparticle at 2 K, reveals the antiferromagnetic coupling between *A* and *B* sublattices, responsible for ferrimagnetism.

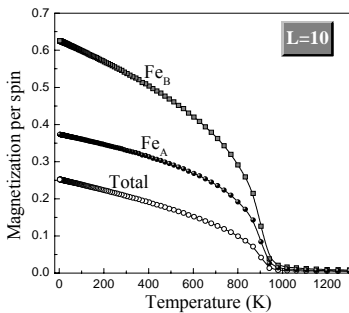


Fig. 2. Temperature dependence of the magnetization for a bulk maghemite.

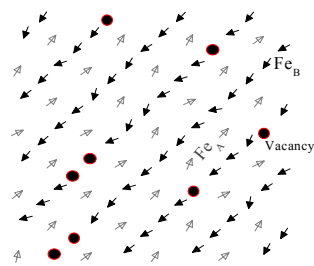


Fig. 3. Spin configuration at 2 K for two adjacent planes involving Fe^{3+}_A (open arrows) and Fe^{3+}_B (dark arrows).

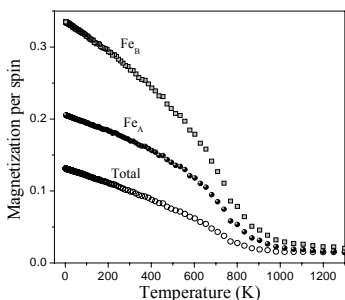


Fig. 4. Temperature dependence of the magnetization per spin for the nanoparticle. A reduction of around 200 K in T_C respect to the bulk is observed.

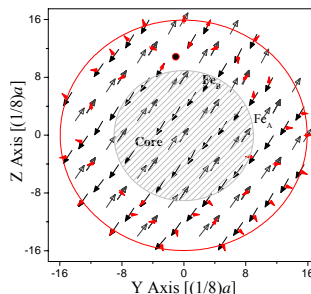


Fig. 5. Spin configuration at 2 K for three adjacent planes involving Fe^{3+}_A (open arrows) and Fe^{3+}_B (dark arrows). Small arrows correspond to surface anisotropy vectors.

As K_S/K_V increases, surface spin disorder increases and this tendency propagates through the core via superexchange coupling, implying reduction of magnetization (Figs. 6 and 7). Configuration shown in Fig. 6 is better known as a throttled state.

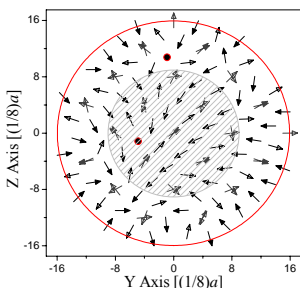


Fig. 6. Spin configuration at 2 K for three adjacent planes involving Fe^{3+}_A (open arrows) and Fe^{3+}_B (dark arrows). Vacancies are also observed as dark circles.

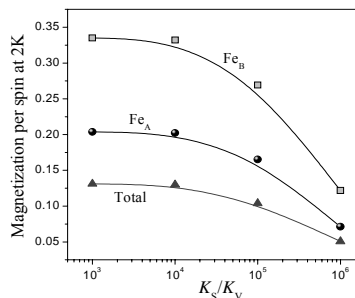


Fig. 7. Dependence of the magnetization per spin at 2K for the nanoparticle, as a function of surface anisotropy in a range of four decades.

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