

# Surface anisotropy in maghemite nanoparticles

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## Abstract

In this work we address the effect of surface anisotropy upon the magnetic structure of ferrimagnetic maghemite  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles in the limit of low temperatures. Our model is based on a three-dimensional classical Heisenberg–Hamiltonian involving  $\text{Fe}^{3+}$  nearest-neighbor interactions, surface and core anisotropies, and a Monte Carlo–Metropolis approach via simulated annealing for energy minimization. Results reveal a marked decrease of the Curie temperature of the considered nanoparticle with that obtained of a bulk maghemite, as well as severe variations with respect to a single domain phenomenology as surface anisotropy increases.

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PACS: 75.40.Mg; 75.50.Gg; 75.50.Tt

Keywords: Nanoparticles; Surface anisotropy; Maghemite; Monte Carlo

## 1. Introduction

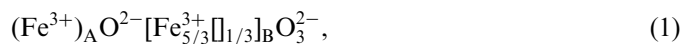
It is well established for nanoparticles that the average magnetic coordination number is strongly reduced as finite size effects become more pronounced [1–3], affecting therefore the magnetic properties. This fact arises as a boundary effect and can be enhanced by surface roughness as well as by vacancies, as it has been described elsewhere [3]. This feature has motivated us to consider a nanoparticle maghemite as a canonical example where the great amount of ions per unit cell can induce certain degree of roughness on the surface and where vacancies are distributed in octahedral sites. Maghemite is one of the currently iron oxides most studied, which exhibits ferrimagnetic behavior below around 1000 K. Such state arises from the competing character of the superexchange integrals present in the system. Maghemite is also found in corrosion products, in proteins, in medicine as drug delivery agent, in nuclear magnetic resonance imaging, and is widely used as magnetic storage medium.

In this work we stress on the magnetic properties of a bulk maghemite and a nanoparticle of about 3.3 nm of

diameter. This last value corresponds to four times the unit cell parameter of this cubic system. Magnetization versus temperature curves over a wide range of temperatures are presented and compared. Finally the effect of surface anisotropy upon the spin structure in the limit of low temperatures is also presented and discussed.

## 2. Model and simulation

Maghemite crystallizes in a spinel structure with 32  $\text{O}^{2-}$  ions, eight  $\text{Fe}^{3+}$  ions are located in tetrahedral sites (A-sites) and sixteen  $\text{Fe}^{3+}$  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  $\text{Fe}_A^{3+}$  and  $\text{Fe}_B^{3+}$  are represented by Heisenberg classical spins while oxygen ions are considered as nonmagnetic and they favor the superexchange interaction between Fe ions moments. The employed classical Heisenberg–Hamiltonian with cubic core magnetocrystalline anisotropy and single-ion site surface anisotropy describing

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our system reads as follows:

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

The first sum runs over nearest magnetic neighbors with the following coordination numbers depending on the crystallographic site:  $z_{AA} = 4$ ,  $z_{BB} = 6$ ,  $z_{AB} = 12$  and  $z_{BA} = 6$ . The magnitude of the spin is taken to be  $5/2$  according to the electronic configuration  $3d^5$  for  $\text{Fe}^{3+}$  ions. The second term accounts for the single-ion site surface anisotropy whereas the third term gives the core cubic magnetocrystalline anisotropy for which  $K_V$  ( $= 8.13 \times 10^{-3} \text{ K}$ ) is the bulk anisotropy constant. Concerning the interactions  $\text{Fe}_A^{3+} - \text{Fe}_A^{3+}$ ,  $\text{Fe}_A^{3+} - \text{Fe}_B^{3+}$ , and  $\text{Fe}_B^{3+} - \text{Fe}_B^{3+}$ , the respective superexchange integrals were taken to be  $J_{AA} = -1.3 \text{ K}$ ,  $J_{AB} = -33.9 \text{ K}$  and  $J_{BB} = +7.3 \text{ K}$  [4]. In our simulation we have employed a single-spin movement Metropolis Monte Carlo algorithm to study three dimensional lattices with symmetry  $Fd3m$ . For the bulk system, periodic boundary conditions and several linear system sizes  $L$  ranging from 2 up to 10 with a total number of magnetic ions  $N = 24 \times L^3$  were considered. Additionally a closely spherical nanoparticle with free boundary conditions having 1362  $\text{Fe}^{3+}$  ions and a diameter of about 3.3 nm was considered. Simulated annealing procedure starts from a random spin configuration at a temperature far above Curie temperature  $T_C$ , then cools slowly down to 2 K, for which the obtained spin configurations are assumed to be similar to that one at the ground state. In computing equilibrium averages, an average of  $5 \times 10^3$  Monte Carlo steps per spin were considered after equilibration. The computed basic thermodynamic quantities were the total energy and the magnetization per spin. Magnetic contributions to the total magnetization per magnetic site arising from A and B sites were also analyzed separately. This fact constitutes one of the enormous advantages of the Monte Carlo simulation compared to experimental bulk magnetic measurements. Dipolar interactions can be neglected at this level [3] and the unit vector on the surface at each  $i$ -th position with vector  $\mathbf{P}_i$ , is computed according to [1]

$$\hat{n}_i = \Sigma(\mathbf{P}_i - \mathbf{P}_j) / |\Sigma(\mathbf{P}_i - \mathbf{P}_j)|, \quad (3)$$

where the sum runs over nearest magnetic neighbors  $A$  and  $B$ . Finally, the ratio  $K_S/K_V$  was taken to range between  $10^0$  and  $10^7$ .

### 3. Results and discussion

Regarding a bulk maghemite, Fig. 1 shows the temperature dependence of the modulus of the magnetization per spin, including the A and B contributions. The obtained total magnetization, lying below these contributions, reveals effectively the onset of ferrimagnetic order.

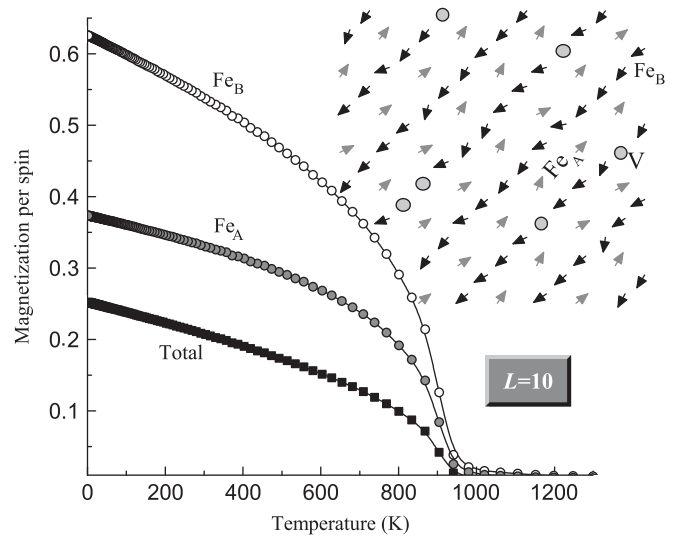


Fig. 1. Temperature dependence of the magnetization for a bulk maghemite. Inset shows the spin configuration at 2 K revealing the occurrence of ferrimagnetic order.

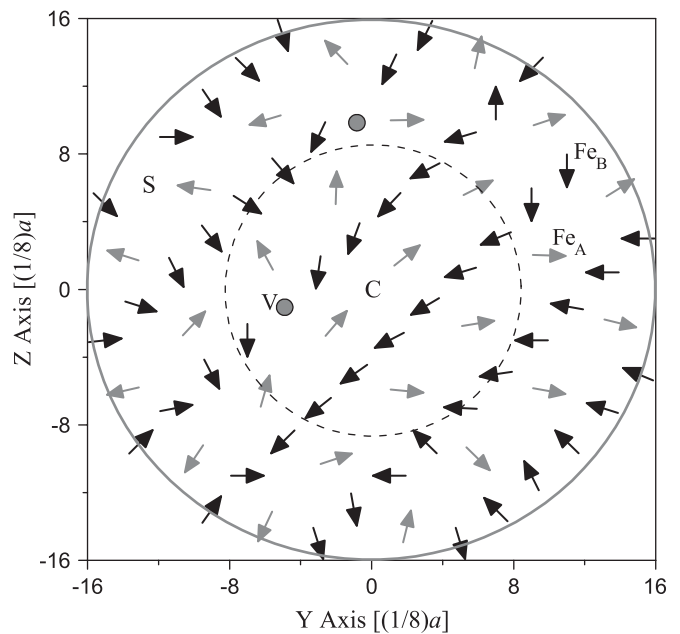


Fig. 2. Spin configuration at 2 K for  $K_S/K_V = 10^7$ . Labels S, C and V stand for surface, core and vacancies respectively. Dark and gray arrows represent  $\text{Fe}_B$  and  $\text{Fe}_A$  spins, respectively.

As concerns for the nanoparticle, the temperature dependence of the magnetization is qualitatively similar to that shown in Fig. 1, but quantitatively three differences respect to the bulk maghemite are evidenced. Firstly,  $T_C$  in the nanoparticle is around 200 K smaller, consistent with the smaller average magnetic coordination number. Secondly, a smoother tail at around  $T_C$  is the typical signature of a finite size effect. Finally, magnetizations at 2 K (the smallest simulated temperature), compared to those obtained in Fig. 1, exhibit a strong reduction which

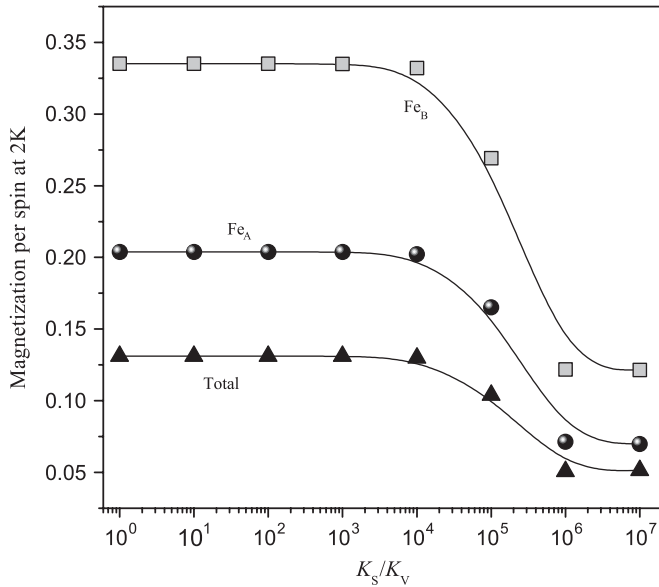


Fig. 3. Dependence of the magnetization with  $K_S/K_V$ .

becomes greater as  $K_S/K_V$  increases. Fig. 2 shows how it looks like a cross view of the spin structure at 2 K when  $K_S/K_V = 10^7$ .

The reduction of the magnetization is ascribed to surface spin disorder as a consequence of the angular distribution of unit vectors. This fact contradicts the assumption of radial surface anisotropy which has been adopted by several authors. Such phenomenology resembles a spin-glass-like surface behavior with a tendency of the moments to be randomly oriented. This behavior propagates through the core via superexchange coupling as  $K_S/K_V$  increases. At the core, the A–B antiferromagnetic coupling, responsible for ferrimagnetism, is still evidenced. In this

regime, typical of a throttled state, deviations from a single domain phenomenology are observed. Finally, Fig. 3 shows two regimes for the dependence of the magnetization with  $K_S/K_V$ .

Below  $K_S/K_V = 10^4$  the spin structure can be considered single domain with ferrimagnetic order, whereas above this value a throttled state with a smaller magnetization is observed.

#### 4. Conclusions

From our results, a remarkable reduction of  $T_C$  for the nanoparticle respect to the bulk case is concluded, attributable to the breaking of symmetry at the surface and consequently to a lower density of magnetic bonds. Finally for low  $K_S/K_V$  ratios, the nanoparticle exhibits a close single-domain state. In contrast, as  $K_S/K_V$  increases, a throttled state becomes evidenced.

#### Acknowledgements

This work was supported by Univ. de Antioquia, Project SIU24-1-28, and by COLCIENCIAS Grant CENM043-2005. Simulations were performed on the Hercules cluster <http://urania.udea.edu.co/facom/index.php>.

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