MAGNETIC PROPERTIES OF MAGHEMITE: A HEISENBERG-MONTE CARLO APPROACH

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RESUMEN

En el presente trabajo se estudian las propiedades magnéticas de maghemite en *bulk* por medio del método de Monte Carlo en el marco de un modelo de Heisenberg clásico tridimensional con anisotropía cristalina cúbica. La estructura cristalina ha sido simulada en la forma más realista y se han considerado diferentes conjuntos de integrales de intercambio tomadas de la literatura con el fin de analizar su influencia sobre las propiedades magnéticas. De aquí, se obtuvieron diferentes curvas de magnetización en función de la temperatura consistentes con un orden ferrimagnético por debajo de la temperatura de Curie. Finalmente se presenta y discute el efecto de las vacancias, las cuales fueron introducidas en la simulación en la forma de huecos magnéticos diluidores.

Palabras clave: Maghemita, Monte Carlo, Propiedades magnéticas.

ABSTRACT

Magnetic properties of bulk maghemite are addressed by means of the Monte Carlo method in the framework of a three dimensional classical Heisenberg model with cubic crystalline anisotropy. The crystalline structure has been simulated in the most realistic way and different sets of exchange integrals have been taken from literature in order to check their influence upon the magnetic properties. Hence, different curves of magnetization as a function of temperature consistent with ferrimagnetic order below the Curie temperature were obtained. Finally, the effect of vacancies, which are introduced in the simulation as magnetic dilutor holes, is also presented and discussed.

Key words: Maghemite, Monte Carlo, Magnetic properties.

INTRODUCTION

Maghemite is one of the currently iron oxides most studied. Most of the reported work deals with γ-Fe_2O_3 nanoparticles and the surface effects upon the magnetic properties of this system [1-2]. However is still controversial the magnitudes and signs of the involved exchange integrals that rule out the interactions in this system and other similar iron oxides like magnetite as well as the effect of vacancies in octahedral sites upon the magnetic properties of this system [3]. These features have motivated us to consider the present system. In this work we consider the exchange integrals J_{AA}, J_{BB} and J_{AB} reported by several authors, where labels A and B refer to tetrahedral and octahedral sites, for which we analyze the effect upon the magnetization versus temperature curves. Additionally, we consider two cases with and without vacancies for comparison purposes.

MODEL

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:

$$(Fe^{3+})_A O^{2-}[Fe^{3+}_{5/3}[]_{1/3}]_B O^{2-}_3, \qquad (1)$$

where the symbol [] stands for vacancies. In our model magnetic ions $Fe^{3+}{}_A$ and $Fe^{3+}{}_B$ are represented by Heisenberg spins while oxygen ions are consider as non magnetic. The employed classical Heisenberg Hamiltonian with cubic magnetocrystalline anisotropy describing our system reads as follows:

$$H = -\sum_{<i,j>} J_{ij}\vec{S}_i.\vec{S}_j - K_V \sum_i (S^2_{x,i}S^2_{y,i} + S^2_{y,i}S^2_{z,i} + S^2_{x,i}S^2_{z,i}). \qquad (2)$$

The first sum runs over nearest magnetic neighbors with the following coordination numbers according to 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 $|\vec{S}| = 5/2$ according to the electronic configuration $3d^5$ for Fe^{3+} ions. The second term gives the cubic magnetocrystalline anisotropy and K_V (=8.13x10^{-3} K) is the bulk anisotropy constant. Concerning the interactions $Fe^{3+}{}_A$-$Fe^{3+}{}_A$, $Fe^{3+}{}_A$-$Fe^{3+}{}_B$, and $Fe^{3+}{}_B$-$Fe^{3+}{}_B$, several situations were considered according to what we find in literature as is shown in table 1.

Table 1. Different reported values for the superexchange integrals found in the literature.

Authors/Integrals	J_{AA} **(K)**	J_{BB} **(K)**	J_{AB} **(K)**
Kodama & Berkowitz [1]	-21.0	-8.6	-28.1
Uhl & Siberchicot [3]	-2.1	+9.6	-33.4
Uhl & Siberchicot *nn* approx. [3]	-1.3	+7.3	-33.9
Néel [4]	-17.4	+0.5	-23.2
Glasser & Milford [5]	0	+2.8	-27.8
Möglestue [3]	-17.6	+3.6	-28.1
E. de Grave [6]	-11.0	+3.0	-22.0
Gr. Diff. In. Neutrons [7]	-18.1	+3.0	-27.6

For our simulation we have employed a single-spin movement Metropolis Monte Carlo algorithm [9,10] to study L^3 *Fd3m* lattices with periodic boundary conditions and several linear system sizes L ranging from 2 up to 10 with a total number of magnetic ions N=24×L^3 . Figure 1 shows the relaxed positions of the involved ions in maghemite.

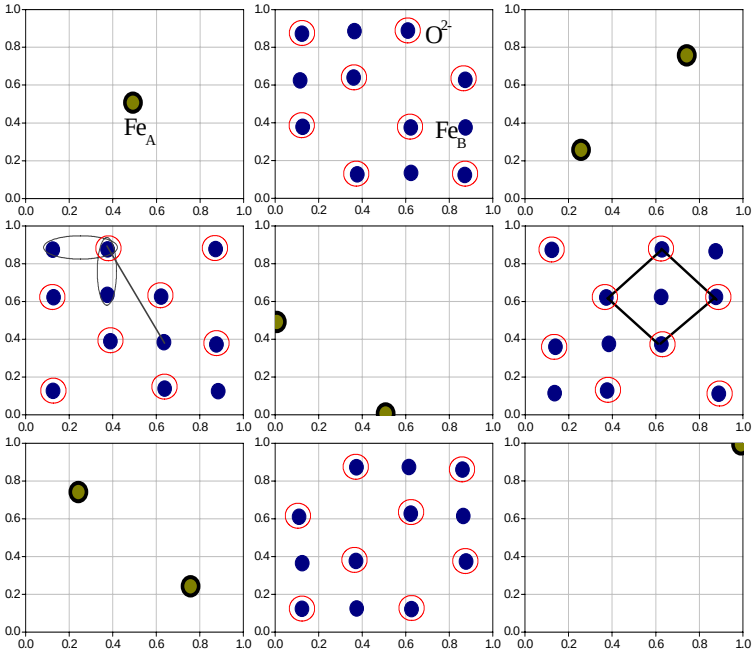

Figure 1. Relaxed positions per unit cell of the involved ions in maghemite.

Simulated annealing from well above the Curie temperature down to 2 K was carried out by starting from a random spin configuration corresponding to infinite temperature. In computing equilibrium averages, an average of 5×10^3 Monte Carlo steps per spin (mcs) were considered after equilibration. The basic thermodynamic quantities of interest are the total energy E computed from Eqn. (2), and the magnetization per spin. Magnetic contributions to the total magnetization per magnetic site arising from tetrahedral and octahedral sites were also analyzed separately. This fact constitutes one of the enormous advantages of the Monte Carlo method compared to bulk magnetic measurements.

RESULTS AND DISCUSSION

Figure 2 shows the employed simulated annealing curve of the form $T=T_0\alpha^t$ with T_0=1300 K and α=0.98. This kind of path through the phase space allows reaching the low temperature regime in a very gradual way for which the obtained spin configuration at 2 K is supposed to be similar to what should be expected in the ground state. Figure 3 shows the temperature dependence of the magnetization per spin for the system size with L=10 where the employed superexchange integrals are those provided by Uhl and Siberchicot in the nearest neighbor approximation without considering vacancies [3].

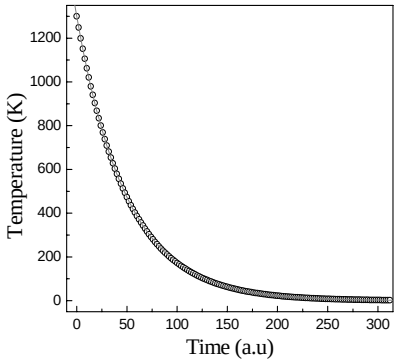

Figure 2. Simulated annealing curve.

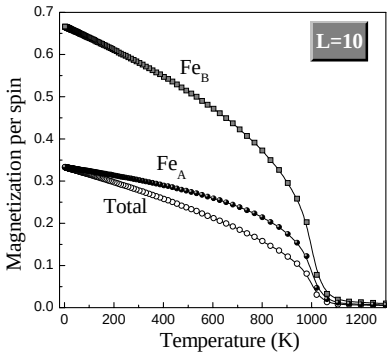

Figure 3. Temperature dependence of the magnetization per spin for L=10 without considering vacancies.

As can be observed from the saturation values in Fig. 3, both the total magnetization as well as the contribution of thetrahedral sites, collapse to 1/3 as the temperature tends to zero. This value implies a ferrimagnetic ordering for which the contribution of the octahedral sublattice is antiparallel to that of the tetrahedral one. The 1/3 value is a direct consequence of the number of ions per unit cell, namely $N(Fe_B)$=16, $N(Fe_A)$=8 and N_{total}=24, from which we get $[N(Fe_B)-N(Fe_A)]/ N_{total}$=1/3 accordingly with a ferrimagnetic state. The obtained Curie temperature in this case is around of 1000 K. Table 2 shows the obtained estimates of the critical temperature when considering the superexchange integrals listed in table 1.

Finally, Figures 4 and 5 show the temperature dependence of the magnetization per spin when considering vacancies (see Eqn. 1) and the respective spin configuration at 2 K for two adjacent planes in the spinel structure. In this case the ferrimagnetic order is also obtained but now the saturation values are different as a consequence of a smaller number of Fe^{3+} ions in octahedral sites.

Table 2. Estimates of the T_C obtained in this work for the superexchange integrals listed in table 1.

References	T_C (K)±50 K
Kodama & Berkowitz [1]	520
Uhl & Siberchicot [3]	1000
Uhl & Siberchicot *nn* approx. [3]	1000
Néel [4]	500
Glasser & Milford [5]	800
Möglestue [3]	700
E. de Grave [6]	600
Gr. Diff. In. Neutrons [7]	650

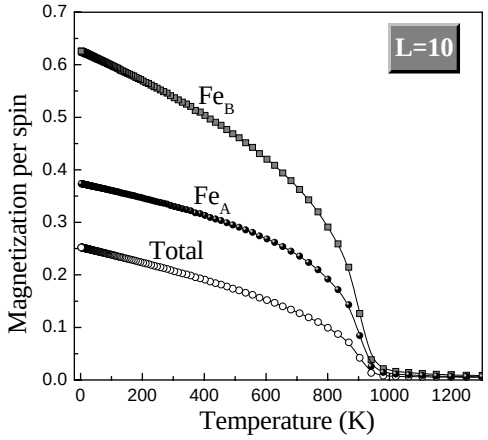

Figure 4. Temperature dependence of the mag-netization per spin when considering vacancies and using the same integrals employed in Fig.3.

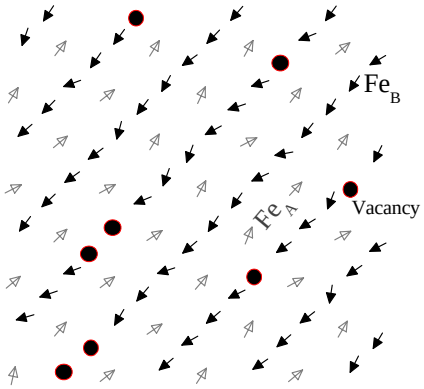

Figure 5. Spin configuration at 2 K for two adjacent planes involving Fe^{3+} ions in tetrahedral sites (gray arrows) and Fe^{3+} ions in octahedral sites (black arrows).

CONCLUSIONS

Different magnetization versus temperature curves and their respective tetrahedral and octahedral contributions were computed from Monte Carlo simulation. Results reveal the occurrence of ferrimagnetic order with different saturation values in the low temperature regime depending on weather vacancies are considered or not. Finally, by comparing figures 3 and 4 the Curie temperature becomes shifted to lower values when considering vacancies due to a lower density of magnetic bonds involving Fe^{3+} octahedral ions.

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