CRITICAL BEHAVIOR OF MAGNETITE: A MÖSSBAUER AND MONTE CARLO STUDY

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RESUMEN

Por medio de la espectrometría Mössbauer se estudió una muestra de magnetita en el rango de temperaturas de 170 a 900 K. Los resultados revelan un colapso de los espectros Mössbauer a una única línea de absorción a una temperatura crítica T_C alrededor de los 870 K caracterizado por un exponente crítico β=0.28(2) para el campo magnético hiperfino. Para describir la dependencia del campo hiperfino con la temperatura, se llevó a cabo una simulación Monte Carlo-Metropolis de una magnetita estequiométrica con base en un modelo de Ising. Finalmente se presenta una discusión sobre el comportamiento crítico de la magnetita y una comparación entre el campo hiperfino obtenido por la técnica Mössbauer y la magnetización calculada a partir de la simulación computacional.

Palabras clave: Magnetita, Monte Carlo, Mössbauer, Exponentes críticos.

ABSTRACT

Powder magnetite was analyzed via Mössbauer with temperatures ranging from 170 K up to 900 K. Results reveal a collapse of the Mössbauer spectra onto a single absorption line at a critical temperature T_C of around 870 K characterized by a critical exponent β=0.28(2) for the hyperfine field. In order to describe such temperature dependence of the hyperfine field, a Monte Carlo-Metropolis simulation based on a stoichiometric magnetite and an Ising model was carried out. A discussion about the critical behavior of magnetite and a comparison between the hyperfine field obtained via Mössbauer and the magnetization obtained via Monte Carlo is finally presented.

Key words: Magnetite, Monte Carlo, Mössbauer, Critical exponents.

INTRODUCTION

Magnetite has been one of the most studied iron oxides mainly from the experimental point of view [1], and some few simulational works have been published, most of them dealing with micromagnetic calculations in nanoparticulate magnetite [2-4]. Nevertheless, to the best of our knowledge, critical exponents of bulk magnetite have not been reported. Additionally, the influence of having different exchange integrals upon the critical behavior remains a subject of much interest [5]. These features have motivated us to consider the Mössbauer and Monte Carlo approaches to elucidate the critical magnetic behavior associated to the ferrimagnetic to paramagnetic transition in magnetite.

EXPERIMENTAL

Pure magnetite was synthesized by means of a hydrothermal method similar to that described by Cornell & Schwertmann [1]. Zero-field ^{57}Fe Mössbauer spectra were recorded in standard transmission geometry using a ^{57}Co source in a Rh matrix. Low temperature measurements were performed by cooling the sample in a closed-cycle helium cryostat with temperatures ranging from 290 K down to 170 K every 20 K. High temperature measurements from 300 K up to 900 K every 50 K where in turn carried out in a Mössbauer furnace at a relative pressure of 10^{-3} Torr. All Mössbauer spectra were fitted by using the *Normos Distri* program with two sextets ascribed to the tetrahedral and octahedral sites of magnetite. X-ray pattern was also taken to starting sample.

MODEL

As is well established, stoichiometric magnetite crystallizes in an inverse spinel structure with *Fd3m* symmetry having eight Fe^{3+} ions located in tetrahedral sites (A), and eight Fe^{2+} with eight Fe^{3+} ions distributed in octahedral sites (B) per unit cell. Moreover, Mössbauer results on magnetite exhibit a component of mixed valence (2.5+) for octahedral sites attributed to the electron hopping between $Fe^{3+}{}_{B}$ and $Fe^{2+}{}_{B}$ ions [1]. In the Monte Carlo simulation this fact has been taken into account by means of a flat random distribution of Fe^{3+} and Fe^{2+} ions at B-sites. Magnetic ions $Fe^{3+}{}_{A}$, $Fe^{3+}{}_{B}$, and $Fe^{2+}{}_{B}$ are represented by Ising spins and their interactions are described by the Hamiltonian:

$$H = -\sum_{<i,j>} J_{ij}\varepsilon_i \varepsilon_j \sigma_i \sigma_j \qquad (1)$$

The sum runs over nearest magnetic neighbors (next nearest ionic neighbors) where oxygen ions are considered as non magnetic. σ_i takes on the values ±1 and the ε_i's are uncorrelated quenched parameters chosen to be 5/2 for Fe^{3+} ions and 2 for Fe^{2+} ions accordingly with the electronic configurations of these ions. Considering spins $Fe^{3+}{}_{A}$- $Fe^{3+}{}_{A}$, $Fe^{3+}{}_{A}$-$Fe^{3+}{}_{B}$, $Fe^{3+}{}_{A}$-$Fe^{2+}{}_{B}$ interact via antiferromagnetic superexchange interactions whereas $Fe^{3+}{}_{B}$-$Fe^{3+}{}_{B}$, $Fe^{3+}{}_{B}$-$Fe^{2+}{}_{B}$, $Fe^{2+}{}_{B}$-$Fe^{2+}{}_{B}$ are ferromagnetic interaction couplings [6]. Such a scenario makes the exchange integral J_{ij} a distributed function of the form:

$$P(J_{ij}) = \sum_{km} x_{km}\delta(J_{ij} - J_{km}) \qquad (2)$$

where x_{km} (k,m=1,2) is the bond density involving a k-m coupling with k,m=1 for Fe ions at A-sites, and k,m=2 for Fe ions at B-sites, where in addition Σx_{km}=1 and $\int P(J_{ij})dJ_{ij}$=1. These values were fitted in order to reproduce the T_C value of pure magnetite [6] and the integrals ratio was preserved accordingly with the first principles study of superexchange integrals in magnetite by Uhl and Siberchicot [6] in the nearest neighbor approximation. In the simulation we employ a single-spin flip Metropolis dynamics [7], periodic boundary conditions and several linear system sizes L ranging from 3 up to 15 with a total number of magnetic ions N=24$\times L^3$.

RESULTS AND DISCUSSION

Figure 1 shows the Rietveld refinement of the x-rays diffractogram of the initial sample. Clearly the fit agrees with Mössbauer results in showing just magnetite phase. Figure 2 shows the Mössbauer spectra for some selected temperatures. As is observed, spectra evolve with temperature from a well-defined sextet pattern toward a single absorption line as the Curie temperature at around 870 K is approached.

Such behavior, as is expected for a thermally-driven magnetic phase transition, reveals a temperature dependence of the hyperfine fields as that shown in Fig. 3, characterized by a sharp drop as the critical temperature T_C is reached.
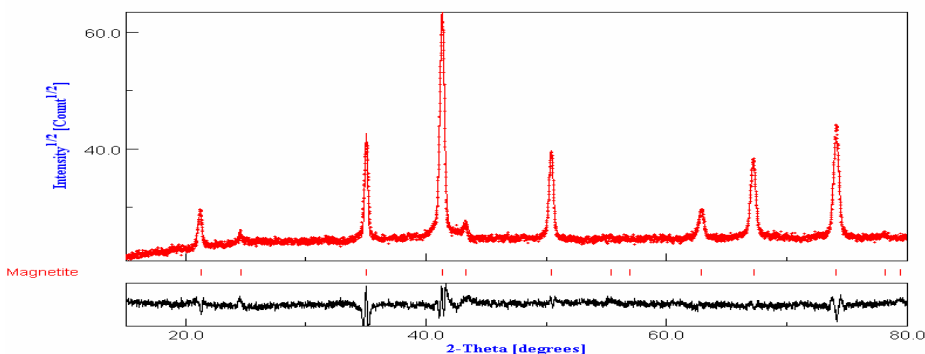

Fig. 1. X-rays diffractogram for the starting sample.

Experimental data close and below T_C were fitted according to the following expression:

$$B_{hf} = \hat{B}_0 \left(1 - \frac{T}{T_C} \right)^{\beta} \tag{3}$$

Additionally, by assuming an occupancy of vacancies equally probable in both sites, we obtain an oxida-tion parameter $x=0.06$ lea-ding to the formula $Fe_{2.94}O_4$.

Concerning Monte Carlo results, Figure 4 shows the temperature dependence of the total magnetization and their contributions per site for $L=15$. As is shown in this figure the critical temperature takes place at around 860 K. The occu-rrence of ferrimagnetic order below T_C is also evidenced by the different magnitudes of the contri-butions $m_{Fe_A^{3+}}$ and m_{Fe_B} relative to the total magne-tization.
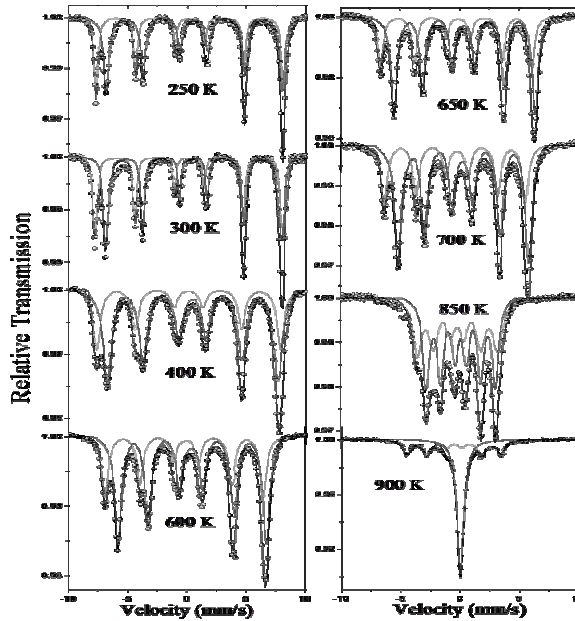
Fig. 2. Mössbauer spectra for some temperatures.

Such ferrimagnetic order is characterized by an antiparallel alignment between spins on different sublattices with different magnetization values. The best estimate of the Curie temperature is $T_C(\infty) = 860 \pm 3\,K$ relatively close to the experimental value.
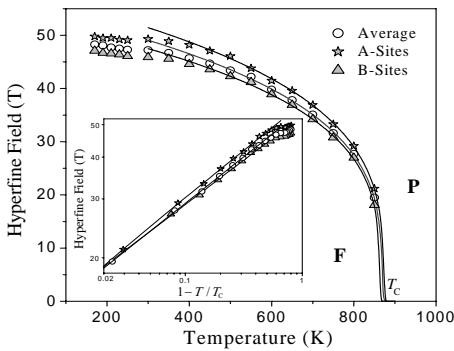

Fig. 3. Temperature dependence of the hyperfine field obtained via Mössbauer. Inset shows the same dependence in a semilog plot as a function of $1 - (T/T_C)$.
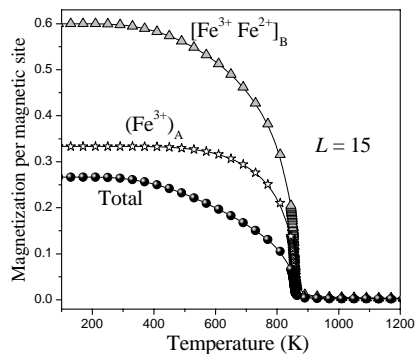

Fig. 4. Temperature dependence of the magnetization per magnetic site. A and B contributions are shown.

According to finite size scaling theory [7,8,9] we have:

$$\left\langle \left| m\left(T_C\left(\infty\right)\right) \right| \right\rangle \propto L^{-\beta/\nu} , \tag{4}$$

and we obtain the estimate for β as 0.35(1). This exponent differs slightly from that of the pure Ising model $\beta=0.3258(4)$ [8]. This fact can presumably be ascribed to the distributed character of the superexchange integrals (Eq. 2), since as is well established, the critical Behavior is rule out by the degree of scattering of the exchange integrals [5].
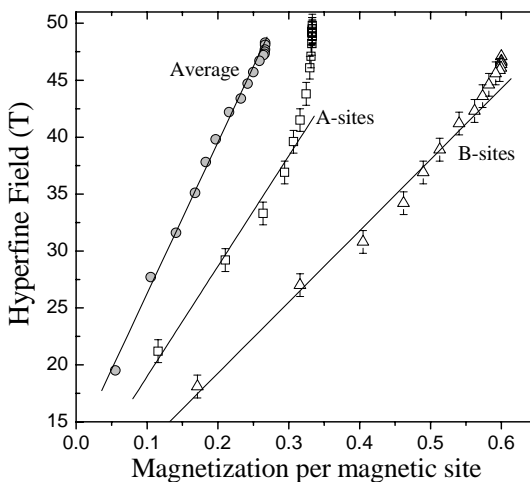

Fig. 5. Correlation between de hyperfine field and the magnetization per magnetic site.

Finally from Figures 3 and 4, a correlation between the magnetization per magnetic site, including the contributions from Fe_A^{3+} and (Fe_B^{2+}, Fe_B^{3+}) ions, and the respective hyperfine fields was carried out (Fig.5). Results reveal a closely linear relationship between the hyperfine field and the magnetization. On the other hand, the observed linear behavior can be understood in terms of the dipolar contribution to the hyperfine field acting on the Mössbauer nucleus. So, an increase on the magnetization will give rise to a greater magnetic dipolar field and consequently a greater hyperfine field.

CONCLUSIONS

Firstly, the difference between the β exponent in our Monte Carlo computation and that of the pure Ising model can presumably be ascribed to the distributed character of the superexchange integrals. Although the β exponent for the critical behavior of B_{hf} (0.28) and that for the magnetization via Monte Carlo (0.35) should be similar according to the proportionality on these

quantities, the observed difference could be mainly attributed to: i) It is necessary to obtain more experimental points in the critical region to be conclusive. ii) the non-stoichiometric character of the real magnetite sample and the real magnetocrystalline anisotropy different from that of the employed Ising model and iii) the fact of considering interactions only within the first magnetic coordination shell. Finally, a predominant and closely linear dependence between the magnetization and the hyperfine field was observed.

REFERENCES

[1] R. Cornell and U. Schwertmann, in: The Iron Oxides, Weinheim, Germany, 1996.

[2] A. R. Muxworthy and W. Williams, J. Geophys. Res. 104 (1999), 29203.

[3] W. Williams and T. M. Wright, J. Geophys. Res. 103 (1998), 30537.

[4] Michael Winklhofer, Karl Fabian and Franz Heider, J. Geophys. Res. 102 (1997), 22695.

[5] R. J. Birgeneau, R. A. Cowley, G. Shirane, H. Yoshizawa, D. P. Belanger, A. R. King, and V. Jaccarino, Phys. Rev. B 27 (1983), 6747.

[6] M. Uhl and B. Siberchicot, J. Phys.: Condens. Matter 7 (1995), 4227.

[7] D. P. Landau and K. Binder, in: A Guide to Monte Carlo Simulations in Statistical Physics (Cambridge University Press, Cambridge, 2000), p.71.

[8] Alan M. Ferrenberg and D. P. Landau, Phys. Rev. B 44, 5081 (1991).

[9] Michael E. Fisher and Michael N. Barber, Phys. Rev. Lett. 28, 1516 (1972).