FINITE SIZE EFFECTS IN SMALL PARTICLE SYSTEMS

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Abstract. We present the results of Monte Carlo simulations of a model of a γ-Fe₂O₃ (maghemite) single particle of spherical shape. The magnetic Fe³⁺ ions are represented by Ising spins on a spinel lattice that consists on two sublattices with octahedral and tetrahedral coordination with exchange interactions among them and with an external magnetic field. By varying the particle diameter, we have studied the influence of the finite size of the particle on the equilibrium properties, field cooling magnetization and hysteresis loops. The simulations allow to distinguish the different roles played by the surface and the core spins of the particle on its magnetic properties. We show that for small particle sizes the core is uncoupled from the surface, that behaves as a quasi-independent layer, whereas for bigger particles the surface and the core are coupled and follow the behaviour of the bulk.

1. INTRODUCTION

Recent experimental studies in small particle systems of nanometric size have brought renewed interest in these kind of systems because of their anomalous magnetic properties at low temperatures. Among the static properties, experiments have shown that in these systems the hysteresis loops display high closure fields and do not saturate even at fields of the order of 50 Tesla \[1, 2, 3\] which indicates that the anisotropy fields cannot be the only responsible mechanism for the magnetization reversal. Low magnetization as compared to bulk, shifted loops after field cooling and irreversibilities between the field cooling and zero field cooling processes even at high fields are also observed \[2, 3\]. On the other hand, the time-dependence of the magnetization, in particular the existence of aging phenomena \[4\], indicates that there must be some kind of freezing preventing the system to evolve towards equilibrium.

Whether these phenomena can be ascribed to intrinsic properties of the particle itself (surface disorder which creates an exchange field on the core of the particle), or they are due to a collective effect induced by interparticle interactions \[5, 6, 7\] has been the object of controversy in recent years and up to the moment there is no model giving a clear-cut explanation of this phenomenology although simulation results for general small particle systems \[8, 9, 10\] and in particular for maghemite \[11, 12\] have been recently published. In order to elucidate this controversy we present the results of a Monte Carlo simulation of a single spherical particle which aims to clarify what
is the specific role of the finite size and the surface on the magnetic properties of the particle, disregarding the interparticle interactions effects.

2. MODEL

$\gamma$-Fe$_2$O$_3$, maghemite, is one of the most commonly studied nanoparticle compounds [12] presenting the above mentioned phenomenology. Maghemite is a ferrimagnetic spinel in which the magnetic Fe$^{3+}$ ions with spin 5/2 are disposed in two sublattices with different coordination with the O$^{2-}$ ions. Each unit cell has 8 tetrahedric (T) and 16 octahedric (O) sites and in the real material one sixth of the O sites has randomly distributed vacancies. Thus, the spins in the T sublattice have $N_{TT} = 4$ nearest neighbours in T and $N_{TO} = 12$ in O and the spins in the O sublattice have $N_{OO} = 6$ nearest neighbours in O and $N_{OT} = 6$ in T. In our model the Fe$^{3+}$ magnetic ions are represented by Ising spins $S_i^\alpha$ distributed in two sublattices $\alpha = T, O$ of linear size $N$ unit cells, thus the total number of spins is $(24N^3)$. The choice of Ising spins allows to reproduce a case with strong uniaxial anisotropy while keeping computational efforts within reasonable limits.

The spins interact via antiferromagnetic exchange interactions with the nearest neighbours on both lattices and with an external magnetic field $H$, and the corresponding Hamiltonian of the model is

$$\mathcal{H}/k_B = - \sum_{\alpha,\beta = T, O} \sum_{i=1}^{N_{\alpha}} \sum_{n=1}^{N_{\alpha\beta}} J_{\alpha\beta} S_i^\alpha S_{i+n}^\beta - h \sum_{\alpha = T, O} \sum_{i=1}^{N_{\alpha}} S_i^\alpha .$$

The reduced magnetic field $h = \mu H/k_B$ is in temperature units. The values of the nearest neighbour exchange constants for maghemite are [12] $J_{TT} = -21 \text{ K}$, $J_{OO} = -8.6 \text{ K}$, $J_{TO} = -28.1 \text{ K}$. We have used periodic boundary conditions to simulate the bulk properties and free boundaries for a spherically shaped particle with $D$ unit cells in diameter when studying finite size effects. In the latter case two different regions are distinguished in the particle: the surface formed by the
3. RESULTS and DISCUSSION

In Fig. 1 we present the thermal dependence of the total equilibrium magnetization for a system with periodic boundaries and two different particle sizes. First of all we note that the transition temperature does not depend significantly on the system size and has roughly the experimental value of the bulk \( T_c \approx 900 \text{ K} \), taking into account that in the simulations the value of the spin has been set to 1 instead of 5/2. On the contrary, the ordering temperature for the spherical particle with free boundaries decreases with decreasing particle size. For the D=3 particle the total magnetization is dominated by the contribution of the surface, and the core, which includes only few spins, is almost uncoupled from the surface and follows the bulk behaviour. For D=6, the core and the surface are more coupled and the total magnetization is an average of surface and core contributions. In agreement with experimental observations, \( M_{\text{Total}} \) increases with decreasing particle size at a finite \( T \), tending to the bulk value.

To see what is the effect of a magnetic field on the magnetic order we have studied the field cooled (FC) magnetization at different cooling fields. The simulation procedure has been started from a disordered state at a temperature well above \( T_c \), which is progressively reduced at a constant rate. The results for periodic boundaries show that at high enough fields there is a maximum in the outermost unit cells and an internal core of diameter \( D_{\text{Core}} \) unit cells. The size of the studied particles ranges from \( D = 3 \) to 6 corresponding to real particle diameters from 30 to 50 Å.
FC curve slightly below $T_c$ that is due to the competition between the ferromagnetic order induced by the field and the spontaneous ferrimagnetic order below $T_c$ (see Fig. 2a). This feature is also observed for the spherical particles but progressively disappears as the particle size is decreased (see Figs. 2b and 2c). This fact is much more pronounced in the core than in the surface due to the frustration induced by broken links at the particle boundary. As the particle size is decreased, the total magnetization becomes dominated by the contribution of the surface spins independently of the magnetic field (note that the continuous and dot-dashed lines in Fig. 2c superimpose for the $D=3$ particle). Independently of the particle size and the cooling field, the core magnetization tends to the bulk value at low $T$ because below $T_c$ the core tends to order ferrimagnetically. The shape of the FC curves for the core resemble the one for periodic boundaries even for the smallest particle, where the total magnetization is completely dominated by the surface and the core contains only 5% of the total number of spins. However, this phenomenon is not observed in the surface contribution due to the fact that the FC strongly depends on the magnetic field even at temperatures below $T_c$. The ferrimagnetic order is less perfect in the surface and the magnetic field induces ferromagnetic ordering at much lower field values.

Finally, we have simulated hysteresis loops for two particle sizes at a temperature $T = 20K$ well below $T_c$ (see Fig. 3). First of all, let us note that the saturation field and the high field susceptibility increase as the particle size is reduced (compare the continuous lines of Fig. 2a and Fig. 2b) reducing the squareness of the loops, an effect that is due to the increasing importance of the surface contribution in the smallest particles. The hysteresis loop of the core is squared for both particle sizes: the core suddenly reverses as a whole, coherently rotating at the coercive field. In contrast, the surface hysteresis loop has a shape similar to the total magnetization loop, closing at the same field than the core but with coercive fields lower than the closure field as the particle size decreases. This indicates that the surface gradually reverses its magnetization and that the surface spins rotation is not coherent as in the core.

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References

1. R. H. Kodama, S. A. Makhlof, and A. E. Berkowitz (1997), Finite Size Effects in Antiferromagnetic NiO Nanoparticles, *Phys. Rev. Lett.*, **79**, 1393.
2. M. García del Muro, X. Batlle, and A. Labarta (1999), Erasing the glassy state in magnetic fine particles, *Phys. Rev. B*, **59**, 13584.
3. B. Martínez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty (1998), Low Temperature Surface Spin-Glass Transition in $\gamma$-Fe$_2$O$_3$ Nanoparticles, *Phys. Rev. Lett.*, **80**, 181.
4. T. Jonsson, J. Mattisson, C. Djurberg, F. A. Khan, P. Nordblad, and P. Svedlindh (1995), Aging in a magnetic particle system, *Phys. Rev. B*, **75**, 4138.
5. X. Batlle, M. García del Muro, and A. Labarta (1997), Interaction effects and energy barrier distribution on the magnetic relaxation of nanocrystalline hexagonal ferrites, *Phys. Rev. B*, **55**, 6440.
6. J.L. Dormann, R. Cherkaoui, L. Spinu, M. Nogus, F. Lucari, F. D’Orazio, D. Fiorani, A. Garcia, E. Tronc, and J.P. Jolivet (1998), From pure superparamagnetic regime to glass collective state of magnetic moments in $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies, *J. Magn. Magn. Mat.*, **187**, L139.
7. S. Morup and E. Tronc (1994), Superparamagnetic Relaxation of Weakly Interacting Particles, *Phys. Rev. Lett.*, **72**, 3278.
8. K. N. Trohidou and J. A. Blackman (1990), Monte Carlo calculations on antiferromagnetic Ising particles, *Phys. Rev. B*, **41**, 9345.
9. D. A. Dimitrov and G. M. Wysin (1994), Effects of surface anisotropy on hysteresis in fine magnetic particles, *Phys. Rev. B*, **50**, 3077.
10. D. A. Dimitrov and G. M. Wysin (1995), Magnetic properties of spherical fcc clusters with radial surface anisotropy, *Phys. Rev. B*, **51**, 11947.
11. H. Kachkachi, A. Ezzir, M. Nogués, and E. Tronc (2000), Surface effects in nanoparticles: application to maghemite $\gamma$-Fe$_2$O$_3$, *Eur. Phys. J. B.*, **14**, 681; H. Kachkachi, M. Nogués, E. Tronc, and D. A. Garanin (1999), Surface effects in nanoparticles, *Cond.-Mat./9910393*.
12. R. H. Kodama and A. E. Berkowitz (1999), Atomic-scale magnetic modeling of oxide nanoparticles, *Phys. Rev. B*, **59**, 6321.