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Interaction effects in magnetic oxide nanoparticle systems

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Abstract. The interaction effects in magnetic nanoparticle system were studied through a Monte Carlo simulation. The results of simulations were compared with two different magnetic systems, namely, iron oxide polymer nanocomposites prepared by polymerization over core and nanocrystalline cobalt ferrite thin films prepared by sol–gel process. The size of the particles in the nanocomposites were estimated to be ∼15 nm with very little agglomeration. The low values of the coercivity obtained from the hysteresis measurements performed confirm that the system is superparamagnetic. SEM studies showed the cobalt ferrite films to have a nanocrystalline character, with particle sizes in the nanometer range. Hysteresis measurements performed on the thin films coated on silicon do not give evidence of the superparamagnetic transition up to room temperature and the coercivity is found to increase with decreasing film thickness. Comparison with simulations indicate that the nanocomposites behave like a strongly interacting array where exchange interactions lead to high blocking temperatures, whereas the films are representative of a semi-infinite array of magnetic clusters with weak interactions and thickness-dependent magnetic properties.

Keywords. Superparamagnetism; Monte Carlo; sol–gel; anisotropy; nanocomposites.

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1. Introduction

Magnetic nanoparticle systems are important because they have applications in magnetic memory devices, refrigeration and sensors [1,2]. The coercivity, retentivity, superparamagnetism and saturation magnetization are seen to be very sensitive to the grain size, cluster size and interactions [3–5]. Experimentally, these properties can be investigated by measuring the hysteresis, zero-field-cooled–field-cooled magnetization and by studying the response of the susceptibility to temperature. To gain an insight into the role of interactions we investigate two different systems through simulations as well as experiments and compare our results.

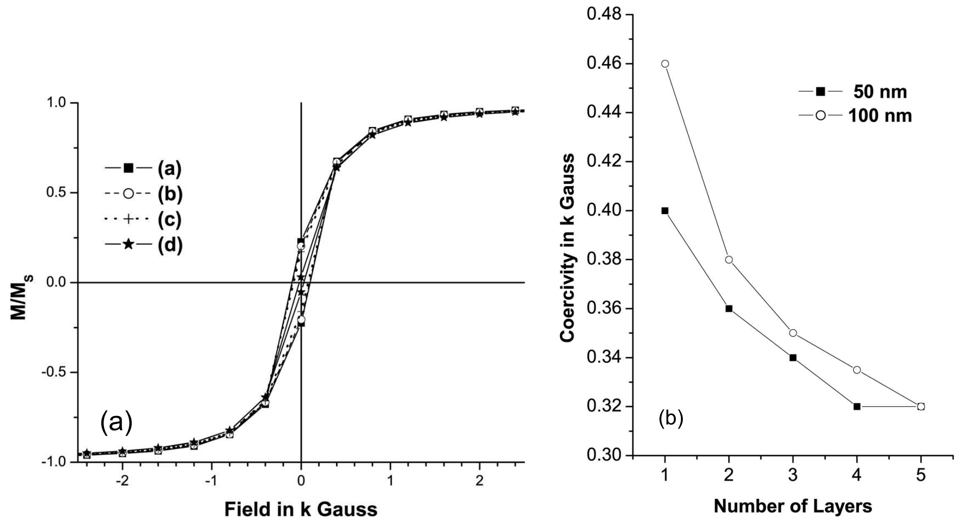

Figure 1. (**a**) Room temperature hysteresis for a strongly interacting array of magnetic particles with decreasing interactions (concentrations) (from a–d) and (**b**) coercivity variation with a number of layers for thin films of two different thicknesses.

2. Model and simulation

The Monte Carlo simulation [4,6,7] for the hysteresis of an array of interacting magnetic clusters is performed with the following Hamiltonian [6]:

$$H = -K\sum_i V_i\left(\frac{\vec{\mu}_i\cdot\vec{n}_i}{|\vec{\mu}_i|}\right)^2 - \sum_{\langle i\neq j\rangle} J\vec{\mu}_i\cdot\vec{\mu}_j - \mu_0\sum_i \vec{H}\cdot\vec{\mu}_i$$
$$-\mu_0\sum_{\langle i\neq j\rangle}\frac{3(\vec{\mu}_i\cdot\vec{e_{ij}})(\vec{\mu}_j\cdot\vec{e_{ij}})-\vec{\mu}_i\cdot\vec{\mu}_j}{r_{ij}^3}, \qquad (1)$$

where the symbols have the usual meaning [6]. The room temperature anisotropy parameters for the simulation are 0.1×10^5 J/m^3 for the nanocomposites and 0.6×10^5 J/m^3 for the films. The average cluster sizes are 15 nm for the nanocomposites and 10 nm for the films. The simulation system for the nanocomposite consists of a cube with 64 single domain particles arranged randomly, with periodic boundary conditions along each direction, while for the film it consists of layers comprising of 36 clusters in each layer with periodic boundary conditions along the x- and y-axes and different numbers of layers in the z-direction with a finite layer thickness of (a) 50 nm or (b) 100 nm. The long-range dipolar interaction energy in both systems is calculated using the Lekner summation method [8]. Thin films of various thicknesses are studied by changing the number of layers each of thickness 50 nm or 100 nm. The results of the simulation for the room temperature hysteresis of nanocomposite systems with decreasing concentrations (and hence interactions) are shown in figure 1a, curves a–d. With decreasing particle concentration, both

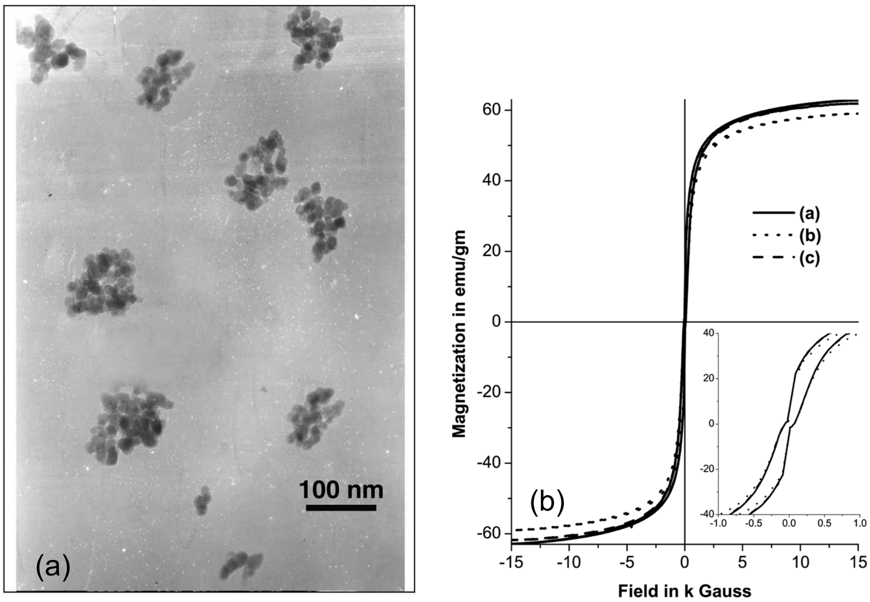

Figure 2. (**a**) TEM for γ-Fe_2O_3–PPy nanocomposite prepared by polymerization over core for the concentration ratio 1 : 1.6 and (**b**) room temperature hysteresis for the γ-Fe_2O_3 : PPy concentration ratios (a) 1 : 0.6, (b) 1 : 1.2 and (c) 1 : 1.6.

the exchange and dipolar interactions are weakened and the system shows progressively lower coercivity and magnetization. This also indicates that the blocking temperature of the system is decreasing with decreasing interactions. The blocking temperatures for all the simulated systems are well above room temperature and it is expected that the most dilute system has the lowest blocking temperature since its coercivity is $\sim$0. In figure 1b, we plot the variation of the film coercivity with increasing number of layers for two different thicknesses. We find that the coerviv-ity for both the film thicknesses studied reduces as we increase the number of layers in the simulation system. The initial sharp change in the coercivity is followed by a slower change to an almost constant value on increasing the number of layers. This possibly indicates an increasing contribution from exchange interactions due to enhanced cluster sizes. Since the effect of increasing number of layers is also found to decrease with the number of layers, the system might be showing a transition from a quasi-two-dimensional $(2d + h)$ to bulk $(3d)$ behaviour.

The powders of maghemite nanoparticles prepared by the sol–gel method were used as core particles for the polymerization of pyrrole [5,9]. PVA was added as a binding agent and has no effect on the polymerization. This method was followed for different γ-Fe_2O_3 : PPy concentration ratios of 1 : 0.2, 1 : 1.2 and 1 : 1.6. The presence of pyrrole was confirmed by FTIR. This process is found to yield single phase magnetic iron oxide particles for all concentrations studied as confirmed from X-ray measurements [5]. Figure 2a shows the TEM picture for one composition of the nanocomposite, which shows particles with an average size of

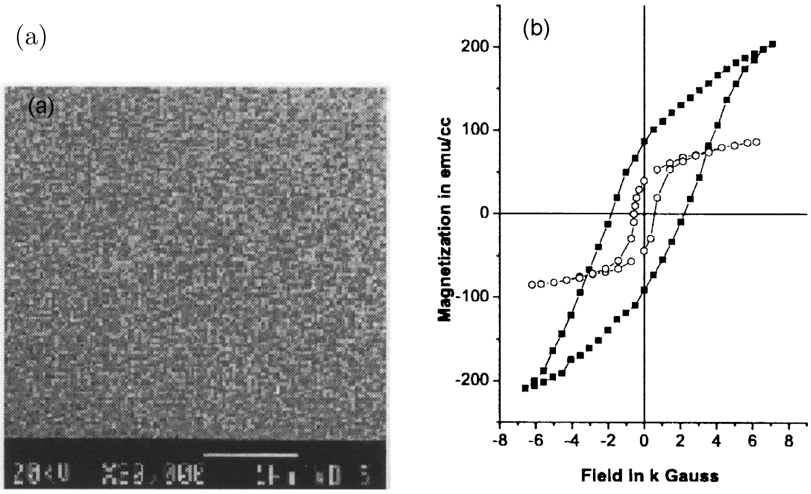

Figure 3. (**a**) SEM for $CoFe_2O_4$ thin films of thickness 100 nm and (**b**) RT hysteresis loops for thin films of thicknesses 100 nm and 500 nm.

15 nm and less agglomeration. In figure 2b we show the room temperature hysteresis for the three concentrations. Coercivity is found to be small and is almost the same for the different pyrrole concentrations and a very slight decrease in the saturation magnetization is seen with increasing monomer concentrations, which is expected because the amount of polymerization is very small (confirmed by TGA). The low value of the coercivity indicates the approach to the superparamagnetic limit.

Weighed quantities of ferric nitrate and cobalt nitrate were dissolved in 2-methoxy ethanol to get the solutions containing iron and cobalt nitrates separately. The two solutions having Co : Fe cation ratio 1 : 1.5 was prepared which was filtered to remove suspended particles. The solution was used to spin cast films on single crystal silicon wafers grown along (111) direction. The thickness was controlled by coating multilayers. The thickness was measured using a DEKTEK profilometer. The composition was confirmed from the ESCA studies to be $CoFe_2O_4$. The films were annealed at 700°C. The XRD shows the formation of a single spinel structure. In figure 3a we show the SEM of the film of thickness ∼100 nm. The SEM photograph shows a uniform structure without any cracks. Further, the nanocrystalline nature of the films was seen with the thinner films exhibiting a smaller grain size. In figure 3b the hysteresis loops recorded for two different film thicknesses are shown. It is observed that the thin film shows both higher magnetization and coercivity compared to the thicker film. The system anisotropy is estimated from the weakly interacting model to be 0.6×10^5 J/m^3.

3. Conclusions

The results of simulations performed on a random anisotropy interacting model compare well with the two magnetic systems investigated. The nanocomposites behave like a strongly interacting array of single domain particles, with high blocking temperatures. The thin films are a prototype of a weakly interacting semi-infinite system with thickness-dependent magnetic properties. A further systematic investigation of the thin film systems coupled with the simulations would help us tailor-make systems with required properties for various applications.

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References

[1] J L Dormann, D Fiorani and E Tronc, *Adv. Chem. Phys.* **XCVIII**, 283 (1997)
[2] J F Bobo, L Gabillet and M Bibes, *J. Phys.: Condens. Matter* **16**, S471 (2004)
[3] R Sharma, S Lamba, S Annapoorni, P Sharma and Akihisa Inoue, *J. Appl. Phys.* **97**, 014311 (2005)
[4] L Wang, J Ding, H Z Kong, Y Li and Y P Feng, *Phys. Rev.* **B64**, 214410 (2001)
[5] R Sharma, S Lamba and S Annapoorni, cond-mat/0410760 (2004); *J. Phys.* **D38**, 3354 (2005)
[6] S Lamba and S Annapoorni, *Euro. Phys.* **B39**, 19 (2004)
[7] K Binder and D W Heerman, Monte Carlo simulation in statistical physics, in: *Springer series in solid state science* (Springer, New York, 1988) Vol. 80
[8] S Lamba, *Phys. Status Solidi* **B340**, (2004)
[9] K Suri, S Annapoorni, R P Tandon and N C Mehra, *Synth. Metals* **126**, 137 (2002)