

## MAGNETIC PROPERTIES OF $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NANOPARTICLES

D. Predoi<sup>a\*</sup>, V. Kuncser<sup>a</sup>, G. Filoti, G. Schinteie

National Institute of Materials Physics, RO-76900 Bucharest-Magurele, Romania

<sup>a</sup>LMOV, CNRS-Universite de Versailles, 78035 Versailles-Cedex, France

The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with different surface states are investigated by X-ray Diffraction, Electron Microscopy, Differential Thermal Analysis and magnetic measurements in low applied field. The influence of the adsorbed species (H<sub>2</sub>O and sulphate complexes) on the inter-particle magnetic interactions is analysed in relation to both the magnetic states of the surface and the inter-particle distance.

(Received July 22, 2002; accepted after revision March 12, 2003)

*Keywords:* Nanostructures, Surfaces and interfaces, Chemical synthesis

### 1. Introduction

Fine magnetic particles present an interesting area for magnetic study [1-3] and for application in magnetic recording [4]. Magnetic properties of nanoscale  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles are different from the corresponding bulk material, due to the small size effects and particle interactions. Below a certain dimension, each particle behaves as a magnetic monodomain, with the magnetic anisotropy energy proportional to the particle volume. For an enough small volume, the thermal energy can approach the anisotropy energy, for temperatures lower than the Curie temperature of the bulk material. Under these circumstances, the magnetic moment of the particle no longer remains blocked along the direction of weak magnetization and can fluctuate or even change the sense along this direction [5]. Moreover, the small particle dimension induces a high surface to volume ratio. The surface effects become of increasing importance as the dimension decreases [6]. The lattice interruption generates additionally high surface magnetocrystalline anisotropy and the surface atoms behave different from the bulk atoms. Therefore, the surface effects depend on the chemical state of the surface and influence the inter-particle magnetic interactions. These interactions, of dipolar type or between atoms of neighbouring particles, can play a significant role, especially if the particles are very close to each other or dispersed in to a matrix of particular properties. If the interactions are sufficiently weak, the dynamic properties remain to be governed by the superparamagnetic relaxation, excepting for very low temperatures. If the interactions are sufficiently strong, a collective behaviour is expected. In the present work we report on the preparation and characterisation of different systems of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> spherical nanoparticles with a mean size of only 4.1(4) nm. The inter-particle magnetic interactions controlled by different induced surface states and/or inter-particle distances were studied via the evolution of the blocking temperature.

---

\* Corresponding author: [predoi@cat.mec.pub.ro](mailto:predoi@cat.mec.pub.ro)

## 2. Experimental

### 2.2. Sample preparation

The materials have been prepared according to [7], by the oxidation of the colloidal magnetite. Sol fractions of 30 ml have been obtained by two ways: (1) neutralizing the surface electrostatic charge (pH ~ 8) and, (2) by rapidly adding 100–150 ml of H<sub>2</sub>SO<sub>4</sub> 1 M. The precipitates were separated after centrifugation and dried at room temperature, producing thus samples 4N (way 1) and 4S (way 2). Samples N were heated at 150° and 200 °C for 2 h, resulting samples 4N150 and 4N200. A fourth reference sample with very weak inter-particle magnetic interaction was obtained by dispersing the particles in polyvinilic alcohol PVA ([- CH<sub>2</sub>CH(OH) -]<sub>n</sub>), considering 1 % volume ratio, as previously detailed in [8]. Standard chemical analyses have been used to determine Fe and S concentrations.

### 2.2. Sample characterization

The materials were characterized by X-Ray Diffraction (XRD) using CuK $\alpha$  radiation, and Transmission Electronic Microscopy (TEM). Thermal analyses were done over a temperature interval of 20-100 °C with a temperature increment of 5 °C/min. Magnetic measurements (M<sub>FC</sub> and M<sub>ZFC</sub>) were performed using a SQUID magnetometer, in a field of 15 Oe, parallel to the sample plane.

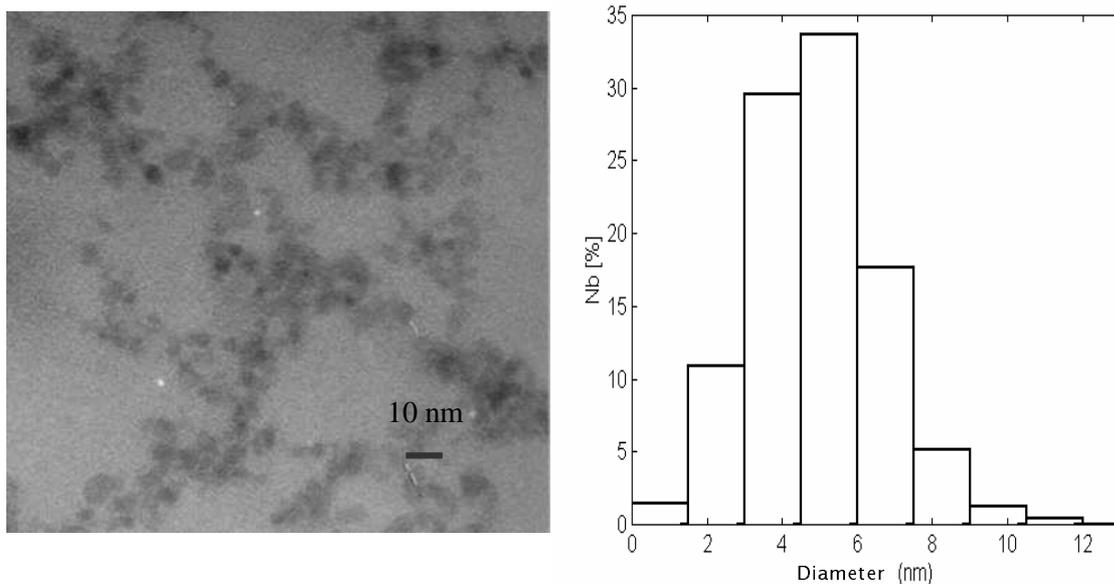


Fig. 1. (a) Micrograph of a sample 4N (b) Size distribution obtained from the TEM micrograph of the sample. A mean particle diameter of 4.1 (4) nm was derived from this distribution.

## 3. Experimental results and discussion

The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> grains present a lattice parameter  $a = 0.834$  nm and a mean size of ~ 4.1(4) nm, as determined from TEM micrographs (Fig. 1). The size distribution, determined by counting ~ 400 particles (Fig. 1(a)), shows a lognormal type dependence (Fig. 1(b)) with a width at half maximum approaching 70% of the mean size.

The mean crystallite size was deduced from the full width at half maximum (FWHM) of six lines in the X-ray diffraction pattern (Fig. 2) following Scherrer's relation. FWHM of the CuK $\alpha$  peaks were determined from profile fit analysis done with Philips PC-APD software and assuming Gaussian

profiles. A value of 3.6(4) nm was obtained for the coherent crystallite size, lower than the mean size of the particles derived from TEM. The result infers highly disordered boundaries of the nanoparticles, as expected for this chemical way of preparation.

The particles hydration obtained by thermal analysis, neglecting residual perchlorate, is given in Table 1. From these results it can be considered that for sample 4N, the surface Fe atoms, Fe<sub>surf</sub>, are contained in an outer layer of about 0.3 nm thick and in average one H<sub>2</sub>O molecule corresponds to a surface Fe atom. For samples 4S, the S content deduced by chemical and thermal analysis are in very good agreement. The analytical data (Table 1) suggest adsorbed species with composition SO<sub>2</sub>, 2H<sub>2</sub>O, and stoichiometry S/Fe<sub>surf</sub> = 1.

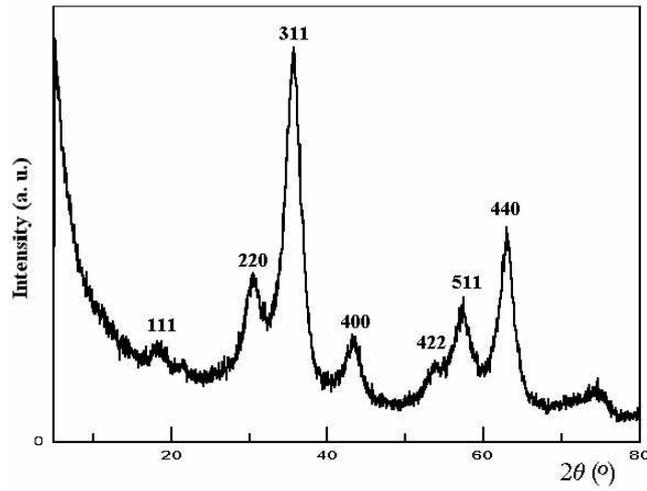


Fig. 2. X-ray diffraction pattern of the 4N sample (Cu K $\alpha$ ). A mean coherence length of 3.6(4) nm was derived by using Scherer's formula.

Table 1. Some characteristics of the analysed samples.

Sample	D(nm)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	H <sub>2</sub> O/Fe (mol/mol)	A/Fe (mol/mol)	Fe <sub>surf</sub> /Fe
4N	4.1	92.2	0.38	-	0.30
4S	4.1	72.2	0.59	0.32	0.30

Note: A stands for SO<sub>2</sub> in samples S

Magnetic measurements in low applied field provide the average blocking temperature T<sub>B</sub>, and emphasize magnetic irreversible phenomena (separations of ZFC and FC curves).

If a random assembly of particles is cooled down under an applied field, the magnetic moment vectors tend to become frozen at low temperature, parallel to the field. If the temperature is re-increased and magnetisation is measured in the same field (field cooled magnetisation M<sub>FC</sub>), the magnetisation will decrease continuously due to the magnetic relaxation. On the other hand, if the particle assembly is cooled down in zero applied field, at equilibrium, the magnetic moments become frozen, with random orientation. If the magnetisation is measured vs. an increased temperature in a small static applied field, the magnetic moments will tend to align along the field and the magnetisation will increase as long as the relaxation phenomena are insignificant. Nevertheless, at higher temperatures, the relaxation becomes more and more activated. The consequence is that above a certain temperature, the zero field cooled magnetisation (M<sub>ZFC</sub>) decreases and finally equals the M<sub>FC</sub> magnetisation, when all particles are in the superparamagnetic state (Fig. 3). The temperature T<sub>max</sub>, corresponding to the maximum of the variation M<sub>ZFC</sub> versus T, is a blocking temperature related to an averaged volume of the nanoparticle.

The temperature  $T_{\max}$  and the temperature at which the  $M_{ZFC}$  equals the  $M_{FC}$  magnetisation, denoted in the following by branchement temperature ( $T_{bra}$ ), are both rising with increasing interparticle magnetic interactions and are lower for samples 4S than for samples 4N (Table 2).

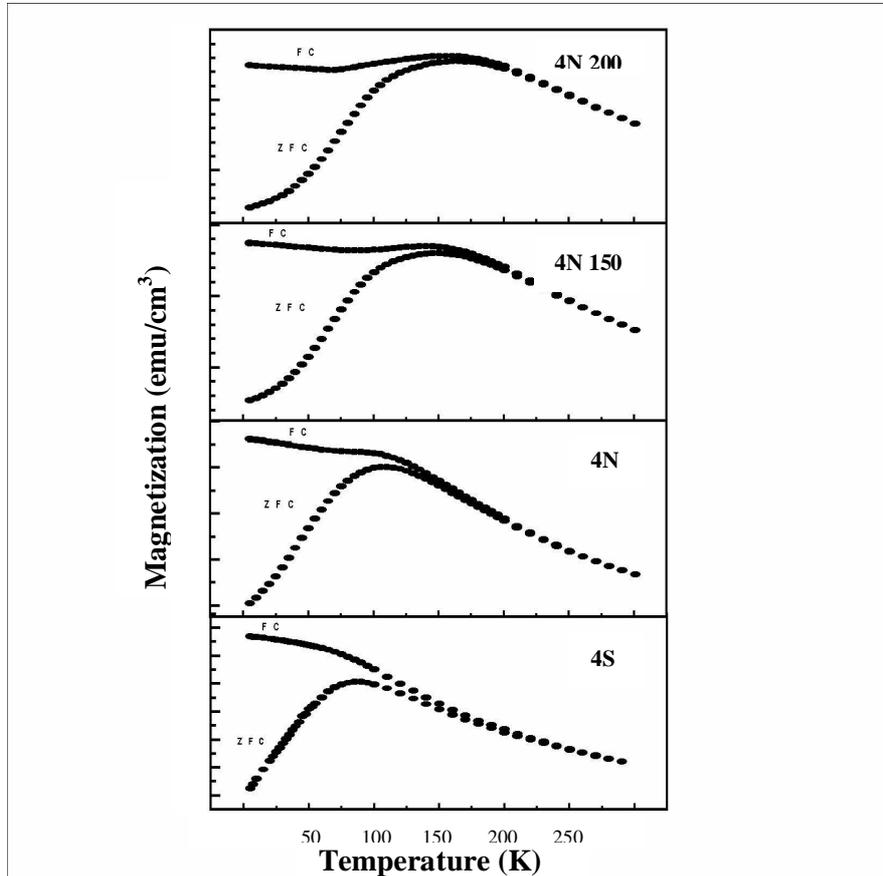


Fig. 3. Thermal variations of zero field cooled and field cooled magnetisation for  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles with different interparticle magnetic interactions.

Table 2. Magnetic characteristics of hydrated and sulphated samples.

Sample	D(nm)	$T_{\max}$ (K)	$T_{bra}$ (K)	$T_{bra}/T_{\max}$	$(M_{ZFC})_{\max}$ (uem/cm <sup>3</sup> )
4S	4.1	89	140	1.57	5.064
4N	4.1	108	148	1.37	4.016
4N150	4.1	146	185	1.26	2.603
4N200	4.1	160	191	1.19	2.554

This variation is due to interactions effect [9-11], which is much stronger in samples 4N than in samples 4S. Stronger interactions are produced either by a diminishing solvation layer (water, sulphate) and, consequently, a smaller interparticle distance, or by an increasing aggregation. Fig. 4 shows the thermal variation of  $M_{ZFC}$  for the 4S, 4N, 4N150 and 4N200 samples as well as for the reference sample of nanoparticles diluted in PVA. The broadness of the peak and his position,  $T_{\max}$ , increases from 40 K (4PVA) to 89 K (4S), 108 K (4N), 146 K (4N150) and 160 K (4N200). This is due to increasing interparticle interactions, mainly as a result of the decreasing interparticle distance. The differences between 4N150 and 4N200 samples are consistent with the different degree of hydration (Table 2) proving many hydroxyl groups at the surface of 4N150, decreasing thus the interparticle interactions. According to our previous studies [12-14], the particles exhibit pure Néel-

Brown superparamagnetic relaxation (4PVA), superparamagnetic relaxation modified by the interactions (4S, 4N), and collective interactions (4N150, 4N200).

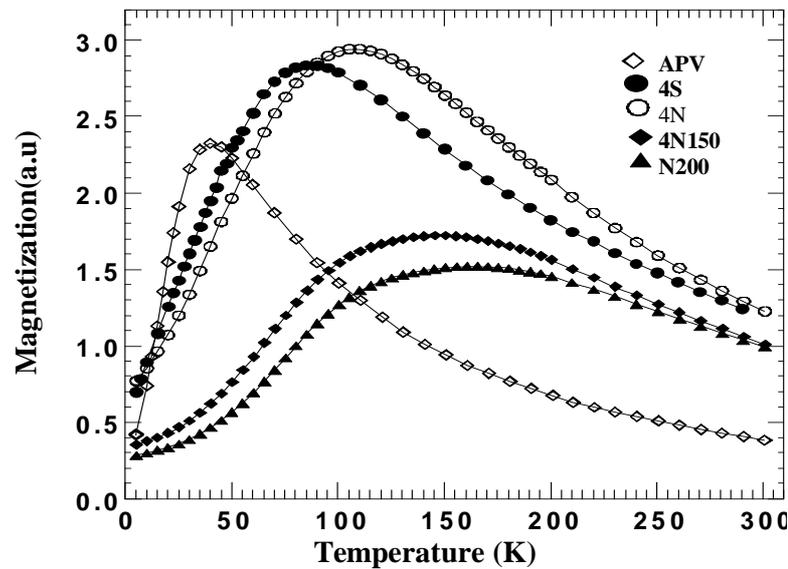


Fig. 4. Zero field cooled magnetisation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles, sulphate-coated (S); uncoated (N), dried at RT and after heating at 150°C or 200°C; diluted in a polymer (APV).

#### 4. Conclusions

Spherical nanoparticles of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with 4.1(4) nm mean size, were prepared by sol-gel method as powder and characterized by magnetic measurements.

The ZFC and FC magnetisation curves rise up the possibility for the evaluation of both blocking and branching temperatures for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with different surface chemical states. The value of  $T_B$  and  $T_{bra}$  decrease with the number of surface states, whereas their ratio  $T_{bra}/T_B$  is decreasing. The behavior is analogous with the one of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles dispersed in a polymer matrix, with the strength of the inter-particle interactions controlled via different dispersions [15-16]. Direct proofs that the inter-particle magnetic interactions can be controlled via different surface states induced by the preparation conditions are obtained.

The above presented preparation method is suitable for the designated purpose. It provides a variety of surface chemical states resulting in the adjustment of the interparticle distance and controlling thus the nature and strength of the magnetic interparticle interactions.

#### References

- [1] N. H. Gangas, A. Simopoulos, A. Kostikas, N. J. Yassoglou, S. Filippakis, *Clays Clay Miner.* **21**, 151 (1973).
- [2] J. M. D. Coey, *Proceed. of 6<sup>th</sup> Intern. Conf. on Mössbauer Spectroscopy*, A. Z. Hryniewicz and J. A. Sawicki Eds. **2**, 133 (1975).
- [3] J. M. D. Coey, *At. Energy Rev.* **18**, 73 (1980).
- [4] T. Shinjo, H. D. Pfannes, U. Gonser, *Proceed. of 6<sup>th</sup> Intern. Conf. on Mössbauer Spectroscopy*, A. Z. Hryniewicz and J. A. Sawicki Eds. **2**, p 465.

- 
- [5] J. L. Dormann, D. Fiorani, E. Tronc, *Advances in Chemical Physics* **98**, 283 (1997).
- [6] R. H. Kodoma, A. E. Berkowitz, S. Foner, *Phys. Rev. Lett.* **77**, 394, (1996), *J. Appl. Phys.* **81**, 5552 (1997).
- [7] J. L. Dorman, D. Fiorani, E. Tronc, *Adv. Chem. Phys.* **98**, 283 (1997).
- [8] E. Tronc, J. P. Jolivet, *Hyperfine Interact.* **28**, 525, (1986).
- [9] D. Prodan, C. Chanéac, E. Tronc, J. P. Jolivet, M. Noguès, J. L. Dormann, *J. Magn. Magn. Mater.* **203**, 63 (1999).
- [10] C. Cannas, G. Concas, D. Gatteschi, A. Musinu, C. Sangregorio, G. Piccaluga, *J. Mater. Chem.* **11**, 3180 (2002).
- [11] C. Cannas, C. Concas, A. Falqui, D. Gatteschi, A. Musinu, G. Piccaluga, C. Sangregorio, G. Spao, *Phys. Chem. Chem. Phys.* **3**, 832 (2001).
- [12] J. L. Dormann, R. Cherkaoui, L. Spanu, M. Noguès, E. Tronc, J. P. Jolivet, *J. Magn. Magn. Mater.* **187**, L139 (1998).
- [13] J. L. Dormann, F. D’Orazio, R. Lucari, E. Tronc, P. Prené, J. P. Jolivet, D. Fiorani, R. Cherkaoui, M. Noguès, *Phys. Rev. B* **53**, 14291 (1996).
- [14] S. P. Gubin, *Colloid and Surfaces A: Physico-chemical and Engineering Aspects* **202**, 155-163 (2002).
- [15] J. L. Dormann, F. D’Orazio, F. Lucari, E. Tronc, P. Prené, J. P. Jolivet, D. Fiorani, R. Cherkaoui, M. Noguès, *Phys. Rev. B* **53**, 14291 (1996).
- [16] E. Tronc, J. P. Jolivet, in “Magnetic Properties of Fine Particles”, Eds., J. L. Dormann, D. Fiorani, North-Holland, Amsterdam (1997).