Dynamic Magnetic Behaviour of Interacting γ-Fe_2O_3 Nanoparticles dispersed in Epoxy Resin

J. Mira, J. A. López-Pérez*, J. Rivas and M. A. López-Quintela*
Departamento de Física Aplicada and *Departamento de Química-Física
Universidade de Santiago, E-15706 Santiago de Compostela, Spain

R. Caciuffo and D. Rinaldi
Dept. di Scienze dei Materiali e della Terra, Università di Ancona
I-60131 Ancona, Italy

D. Fiorani
ICMAT-CNR, I-00016 Roma, Italy

Abstract—**The dynamical behaviour of γ-Fe_2O_3 particles synthesized by a microemulsion route, with an average diameter of 7 nm and dispersed in an epoxy-resin at different concentrations, has been investigated by a.c. magnetic susceptibility measurements ($8 < f\ (Hz) < 1000$). For the most diluted sample, the frequency dependence of the temperatures of the maximum of the in-phase susceptibility follow an Arrhenius law with physical τ_0 value (10^{-10} s). Unphysical, much lower values are found for samples consisting of interacting particles. The results are explained by accounting for the change of interparticle distance and number of particle neighbours.**

I. INTRODUCTION

In the framework of the renewed interest in magnetic nanoparticles, great attention has been devoted, from both theoretical and experimental point of view [1-4], to the effect of interparticle interactions on superparamagnetic relaxation. The modelling of interactions is a difficult task, because of the need to account for the complex microstructure of real systems. The effects of microstructure have been recently taken into account by Chantrell et al. [1], using Monte Carlo simulation, and by Dormann et al. [2,3,5], who proposed a model based on a statistical calculation of the interaction energy for a random assembly of particles, with size distribution and easy axes in random directions.

However, it is not straightforward to check the proposed models, because materials with controlled shape and size, with narrow size distribution are difficult to obtain. In particular, the control and homogeneity of interparticle distance represents the main difficulty.

In this context, the aim of this paper is to investigate the interparticle interaction effect by analyzing the dynamical behaviour of a series of samples consisting of γ-Fe_2O_3 particles of the same average size and distribution ($\langle\phi\rangle = 6.7 \pm 1.6$ nm) dispersed at different concentrations in epoxy resin.

Manuscript received January 31, 1997; revised received April 28, 1997
J. Mira, (34) 81 563100 ext. 14028, fax: (34) 81 520676, fajmirap@usc.es

II. EXPERIMENTAL DETAILS

A. Sample synthesis

The particles were prepared by the microemulsion method, which has the advantage of obtaining narrow size distribution, mixing two microemulsions at 65 °C. One microemulsion, with a volume ratio 90/7/3 in cyclohexylamine/Brij-97/acqueous solution of iron salts, was prepared. The molarities of the salts in the acqueous solution were 1 M in $FeSO_4 \cdot 7H_2O$, 0.5 M $FeCl_3 \cdot 6H_2O$ and 0.5 M in HCl. Acidic medium was used in order to avoid oxidation of Fe^{2+}. All chemicals were supplied by Aldrich and used without further purification. Another microemulsion, similar to the previous one, but without salts in the acqueous solution and with a 20% more in volume of cyclohexylamine was also prepared. Both were heated in a water bath until 65 °C was reached. At this temperature one single transparent phase of every microemulsion was formed. Then, the first was added to the second under mechanical stirring. After 15 min. of aging the mixture was cooled to room temperature.

The particles were washed with acetone and dispersed in ethanol. A portion of this solution was mixed in an epoxy-resin obtaining what we call C_0. Further dilutions at 1/3, 1/6, 1/12 and 1/30 of the original concentration were made (assuring therefore the same particles in all the cases), giving samples C/3, C/6, C/12 and C/30.

B. Characterization techniques

X-ray diffraction shows that the particles consist of single γ-Fe_2O_3 phase. TEM measurements, performed in a 200 kV- JEOL microscope, show for the C/30 sample quite spherical-shaped particles.

0018-9464/97$10.00 © 1997 IEEE

TABLE I

Sample	τ_0 (s)
C_O	$7 \cdot 10^{-17}$
C/3	$6 \cdot 10^{-15}$
C/6	$2 \cdot 10^{-11}$
C/12	$1 \cdot 10^{-10}$
C/30	$1 \cdot 10^{-10}$

Characteristic relaxation times, τ_0, extracted from fits to an Arrhenius law.

The diameter follow a log-normal distribution with $<\phi>$ = 6.7 nm and standard deviation σ= 0.2, highly dispersed in the resin. The interparticle distance decreases with increasing concentration until the most concentrated sample (C_0), which consists mainly of particle aggregates. With respect to γ-Fe_2O_3 particles in polyvinilic alcohol, recently investigated [2], higher dispersions were obtained in epoxy resin (in the most diluted sample the interparticle distance is higher than 10 times $<\phi>$) and samples with different concentrations were prepared.

III. RESULTS AND DISCUSSION

The real and imaginary parts, χ' and χ'', of the external complex ac susceptibility were measured at different frequencies (8 < f (Hz) < 1000) in the temperature range T= 13-300 K, with an amplitude H_{ac}= 300 A/m (3.75 Oe). D.C. susceptibility measurements were performed by using a commercial SQUID magnetometer following the usual zero-field-cooling (ZFC) and field-cooling (FC) procedures.

The χ' vs. T curve (Fig. 1) shows a maximum at a frequency dependent temperature (T_{max}), as usually observed for the blocking process of superparamagnetic particles. For a single particle of volume V, the relaxation time τ is expected to follow, in the high energy barrier limit ($E_B/k_BT > 2$), an Arrhenius law:

$$\tau = \tau_0 \exp\left(\frac{E_B}{k_B T}\right). \qquad (1)$$

For uniaxial symmetry, $E_B=K_a$ V (K_a is the anisotropy constant). The blocking temperature, T_B, is defined as the temperature for which τ = 1/f (measuring time) for a given particle volume V. Then, from the Arrhenius plot, ln(1/f) vs. 1/ T_B, the preexponential factor, τ_0, and the energy barrier, E_B, can be derived. For an assembly of independent particles with volume distribution the average blocking temperature is related to T_{max}, the exact relationship depending on the form of the particle size distribution. In a first approximation we can consider $T_{max}= <T_B>$ for a certain averaged volume [2,3,6].

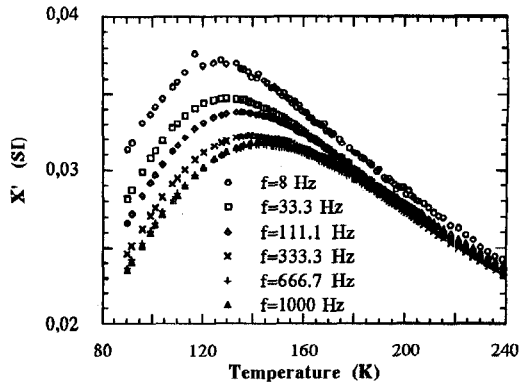

Fig. 1: a) Real part of the ac complex susceptibility (χ') versus temperature for the most concentrated sample, C_0. T_{max} is defined as the temperature at which the maximum in the signal takes place.

The data align in an Arrhenius plot for all the samples (see for example Fig. 2 for C/12, one of the most diluted samples). However, the extrapolated τ_0 value is physically meaningful (corresponding to the characteristic relaxation time of independent particles) only for the very diluted samples ($\tau_0 \approx 10^{-10}$ s for C/30 and C/12), where interparticle interactions can be neglected. Much lower, unphysical, values ($\tau_0 < 10^{-11}$ s) are obtained (Table I) for the concentrated samples (e. g. $\tau_0= 7 \cdot 10^{-17}$ s for C_0), indicating that the Arrhenius law cannot describe the frequency dependence of T_B due to the presence of interparticle interactions. In this case, deviations from linearity in the Arrhenius plot are expected when the measurements are performed in a larger time window. The τ_0 behaviour with concentration suggests that the particles remain basically almost independent with increasing contentration (moving from sample C/30 to C/12), while aggregation occurs for the sample C/3.

In the model proposed by Dormann et al. [2,3,5], the experimental τ_0 value (τ_{0exp}) has been related to the number of particle neighbours, n, decreasing with their number, independently on the interaction strength, which affects the anisotropy energy barrier.

$$\tau = \tau_0 \exp(-n_1) \exp\left(\frac{E_{B0} + n_1 M_{nr}{}^2 V a_1}{k_B T}\right) \qquad (2)$$

where E_{B0} is the energy barrier for isolated particles and $n_1 M_{nr}{}^2 V a_1$ is the dipolar interaction energy (M_{nr} is the non relaxing magnetization, $a_1=<V>/d^3$, where $<V>$ is the average volume and d is the interparticle distance), assuming strong interactions with first neighbour particles only.

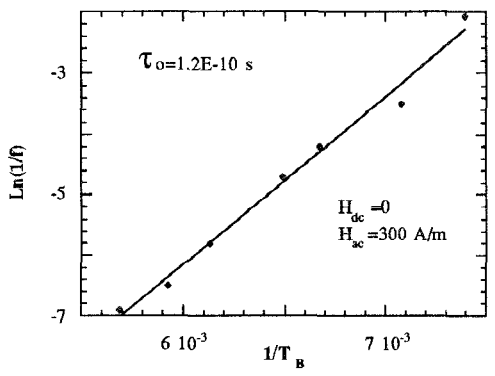

Fig. 2: Arrhenius plot of T_{max} for sample C/12. The solid line represents the fit to (1). The characteristic relaxation time, τ_0, is extracted from the extrapolation of the fit to the ln(1/f) axis.

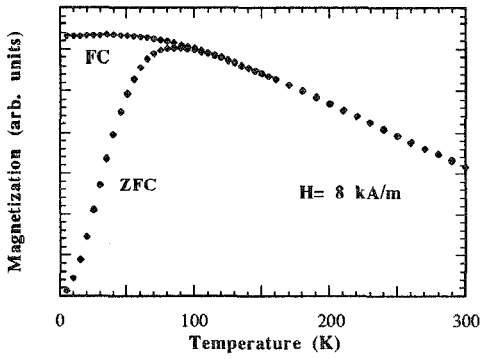

Fig. 3: D.C. magnetization versus temperature for the most concentrated sample, C_0, at a field of 8 kA/m. Both the maximum of the ZFC curve and the ZFC-FC splitting point remain almost at the same temperatures in all the series for this field.

This model allowed the authors [2,5] to give a satisfactory description of the dynamical behaviour of Fe particles dispersed in Al_2O_3 [5] and γ-Fe_2O_3 particles dispersed in polyvinilic alcohol [2], coherent with the variation of number of neighbours and interparticle distance within the investigated series, according to the concentration variation.

The τ_{0exp} variation we observed is coherent with the model (τ_{0exp} decreases with increasing concentration). As far as the total energy barrier and the dipolar interactions contribution to it are concerned, it is not possible to estimate them by fitting the data to (2), since d and M_{nr} are not yet determined. However, the increase of the slope with increasing interactions in the Arrhenius plot qualitatively reflects an increase of the total anisotropy energy barrier.

However, T_{max} decreases with increasing concentration (e. g. at 1000 Hz, T_{max}=183 K for C/30 and 145 K for C_0), unlike what observed in γ-Fe_2O_3 particles dispersed in polyvinilic alcohol. T_{max} is sensitive to the type of aggregation state and how it evolves with concentration. The different behaviour between the two systems should be due to the different type of arrangement of particles in the matrix, since the dipolar interactions are random, and to the different particles' aggregation state.

The decrease of T_B with increasing interactions has been proposed for weak interactions [5]. The model was applied to explain the observed concentration dependence of Mössbauer data on γ-Fe_2O_3 particles dispersed in polyvinilic alcohol, but it was not in agreement with the increase of T_{max} with increasing interactions [2].

The temperature of the maximum of the dc-ZFC susceptibiliy curve (Fig. 3) and the splitting temperature between ZFC and FC components do not change significantly with concentration. Both temperatures are much smaller than T_{max}, due to the longer measuring time and the effect of the much higher applied field, 8 kA/m (100 Oe), which modifies the energy barrier.

The interaction with the magnetic field masks the effect of interparticle interactions.

In conclusion, the investigation of the dynamical behaviour of γ-Fe_2O_3 particles dispersed in epoxy resin allowed to provide evidence of the development of interparticle interactions with concentration. The Arrhenius law is shown to be adequate to describe the temperature dependence of the relaxation time only in the high dilution limit, where interparticle interactions can be neglected.

ACKNOWLEDGMENT

The authors thank Senén Paz, from Gairesa (Ferrol-Spain) for providing us with the epoxy-resine (LAB-1258) used in this work.

REFERENCES

[1] R. W. Chantrell, G. N. Coverdale, M. El Hilo, and K. O'Grady, "Modelling of interaction effects in fine particle systems," J. Magn. Magn. Mat. vol. 157-158, pp. 250-255, 1996

[2] J. L. Dormann, F. D'Orazio, F. Lucari, E. Tronc, P. Prené, J. P. Jolivet, D. Fiorani, R. Cherkaoui, and M. Nogués, "Thermal variation of the relaxation time of the magnetic moment of nanoparticles with interparticle interactions of various strengths," Phys. Rev. B vol. 53, pp. 14291-14297, 1996

[3] J. L. Dormann, D. Fiorani, and E. Tronc, "Magnetic relaxation in fine particle systems," Adv. Chem. Phys. vol. 98, chap. 4, pp. 288-494, 1997

[4] S. Morup and E. Tronc, "Superparamagnetic relaxation of weakly interacting particles,", Phys. Rev. Lett., vol. 72, pp. 3278-3281, 1994

[5] J. L. Dormann, L. Bessais, and D. Fiorani, "A dynamical study of small interacting particles: superparamagnetic model and spin-glass law," J. Phys. C vol. 21, pp. 2015-2034, 1988

[6] K. O'Grady, M. El-Hilo and R. W. Chantrell, "The characterization of interactions effects in fine particle systems", IEEE Trans. Mag., vol. 29, pp. 2608-2613, 1993