Hyperfine Interactions **148/149:** 103–108, 2003.

Characterization of Nanosized Maghemite Particles Prepared by Microemulsion Using an Ionic Surfactant

M. J. TUEROS[1], L. A. BAUM[1], R. A. BORZI[1,*], S. J. STEWART[1], R. C. MERCADER[1], S. G. MARCHETTI[2], J. F. BENGOA[2] and L. V. MOGNI[2]
[1]*Departamento de Física, IFLP, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C.67, 1900 La Plata, Argentina*
[2]*Departamento de Química, Facultad de Ciencias Exactas, CINDECA (CONICET, CIC), 47 N° 257, 1900 La Plata, Argentina; e-mail: march@dalton.quimica.unlp.edu.ar*

Abstract. We have characterized a system of maghemite, γ-Fe_2O_3, nanosized particles prepared by a microemulsion method using an ionic surfactant. The Mössbauer spectra from 21 to 298 K evolve from a totally magnetically split signal at low temperatures to a single superparamagnetic (sp) doublet at 298 K with a blocking temperature of $\approx$150 K. The real component of the AC susceptibility ($5 \leqslant \nu \leqslant 10^4$ Hz) displays a behavior characteristic of a system of interacting particles. A broad distribution of the particle sizes is revealed by the much higher average energy barrier obtained by AC susceptibility than Mössbauer.

Key words: maghemite nanoparticles, preparation method, microemulsion, particle interactions.

1. Introduction

The control of the magnetic properties of nanosized ferrimagnetic systems is of great technological and basic importance. For this reason, there is a great effort towards the thorough understanding of their physics and chemistry. However, the ways in which different properties, like the blocking temperature and the interparticle interactions, depend on the history and preparation method are still not fully understood. In actual fine-particle systems, different factors such as the distribution of crystallite sizes, or the detailed geometrical arrangement and orientation of the easy axes, which play a central role in determining the strength of these interactions, are usually unknown [1].

Recently, the relaxation time τ of a system similar to the present one [2] has been modelled using the Néel–Brown equation valid for non-interacting particles:

$$\tau = \tau_0 \exp\left(\frac{\varepsilon_B}{kT}\right), \tag{1}$$

* Current address: School of Physics and Astronomy, University of St Andrews, Fife, KY16 9SS, Scotland.

where ε_B is the intrinsic anisotropy energy barrier, k is Boltzmann's constant and T is the temperature. However, because the assumptions leading to this expression are not too demanding, at least to a first approximation, Equation (1) is also valid for systems of interacting particles. Dormann *et al.* [1] modified the meaning of ε_B to take into account the existence of dipolar magnetic interactions between n_1 first magnetic neighbors:

$$\varepsilon_B = \varepsilon_{B0} - n_1 kT + n_1 a_1 M_{nr}^2(T)V, \tag{2}$$

where M_{nr} is the non-relaxing magnetization and V is the particle volume.

In this work we report the characterization by Mössbauer spectroscopy and AC susceptibility of the magnetic properties of a system of maghemite, γ-Fe_2O_3, nanosized particles prepared by a modified microemulsion method [3].

2. Experimental

The following three-phase system was selected for the synthesis of Fe_2O_3 nanoparticles [3]: $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution (0.053 M), hydrocarbon phase: 2-ethylhexanol and cetyl-trimethyl-ammonium-bromide (CTAB) as surfactant, with the following molar ratio: Fe : 2-ethylhexanol : CTAB = 1 : 14.34 : 3.58.

The micro-emulsified $Fe(NO_3)_3$, formed by mechanical stirring, was precipitated as $Fe(OH)_3$ by adding six drops of NH_3 (30%). The suspension was decanted and kept still overnight, and the solid recovered by centrifugation and washed three times with nanopure water. Then, the solid was dried overnight at 323 K and calcinated in air at 523 K during 15 minutes.

The sample was characterized by Mössbauer spectroscopy in a constant-acceleration spectrometer. AC susceptibility was measured in a LakeShore 7130 susceptometer at frequencies ν in the range $5 \leqslant \nu \leqslant 10^4$ Hz. Cu$K\alpha$ radiation was used to obtain the X-ray diffraction data in a Phillips PW-1710 diffractometer.

3. Results and discussion

Figure 1 shows the Mössbauer spectra of the solid taken at temperatures between 21 and 298 K. From 21 to 80 K a signal belonging to a sextet with slightly broadened external peaks and a background that curves progressively toward the higher temperatures can be seen coexisting. At temperatures between 100 and 298 K a new signal can be noticed, which increases in intensity and develops into a doublet, which comprises the larger part of the spectral area at 298 K. This behavior is typical of systems displaying superparamagnetic relaxation [4]. Accordingly, in different temperature ranges the spectra were fitted with a program that allows hyperfine field and quadrupole splitting distributions to one sextet, or to one sextet and one doublet simultaneously. The resulting hyperfine parameters at 21 and 298 K (Table I) are characteristic of γ-Fe_2O_3 [5] in agreement with the permanent

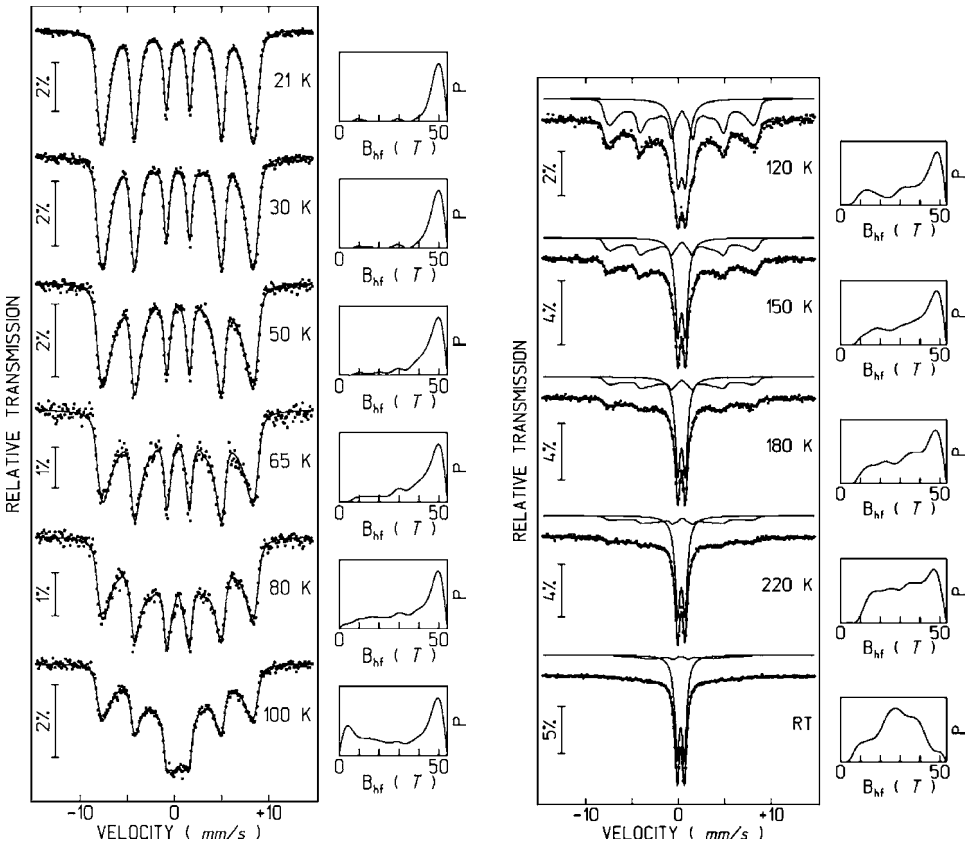

Figure 1. Mössbauer spectra taken at the temperatures indicated. The hyperfine fields distributions obtained as described in the text are displayed to the right of each spectrum.

magnetization of the sample (which is attracted by a hand magnet) and the X-ray diffraction pattern (Figure 2). Although the lines are very broad, the most intense peak of maghemite (indicated in the figure) can be clearly seen and no peak belonging to α-Fe_2O_3 – that may have similar Mössbauer parameters for small particles systems – is apparent.

The thermal dependence of the AC susceptibility results for different frequencies (Figure 3) display curves with maxima. These maxima shift to higher temperatures for higher frequencies. All curves merge into a single one when the temperature is increased. These results are characteristic of nanosized particles with superparamagnetic behavior, in agreement with the Mössbauer data. Also, it is worth noting that the temperature range in which both magnetic states (sp and blocked) are coexisting is very broad.

From these data it is possible to obtain the thermal dependence of the relaxation times. If the data are fitted assuming the Néel model, the value of τ_0 found is meaningless for a system of ferrimagnetic nanoparticles ($\tau_0 = 1.2 \times 10^{-30}$ s).

Table I. Mössbauer hyperfine parameters at 21 and 298 K. All isomer shifts are referred to α-Fe at 298 K. $\langle H \rangle$ is the average hyperfine field, σ the distribution standard deviation, $\langle \delta \rangle$ the average isomer shift, 2ε the average quadrupole shift, and $\langle \Delta \rangle$ is the average quadrupole splitting

	21 K	298 K
$\langle H \rangle \pm \sigma$ (T)	47 ± 7	29 ± 10
$\langle \delta \rangle$ (mm/s)	0.47 ± 0.01	0.45 ± 0.01
2ε (mm/s)	-0.03 ± 0.01	0.0
relative area (%)	100	20
$\langle \Delta \rangle$ (mm/s)	–	0.77 ± 0.01
$\langle \delta \rangle$ (mm/s)	–	0.34 ± 0.01
relative area (%)	–	80

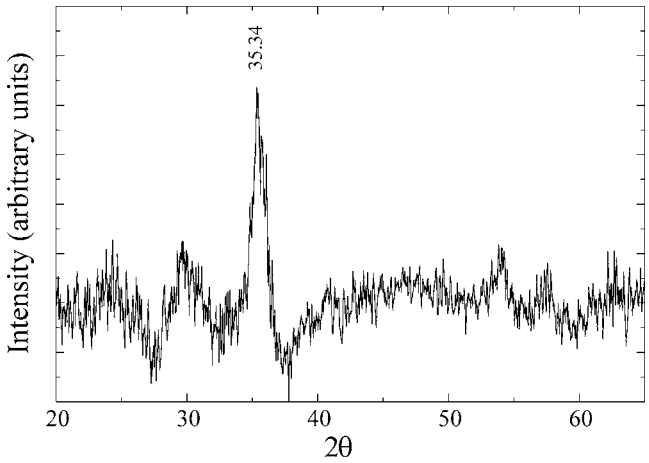

Figure 2. X-ray diffraction pattern of the maghemite sample. The position of the most intense peak of maghemite is indicated on its top.

Taking into account the existence of dipolar interactions between the first magnetic neighbors performing the fitting using the modified Néel–Brown model [1] and assuming M_{nr} to be:

(i) thermally independent: $M_{\mathrm{nr}}^2(T) =$ constant and taking $n_1 \leqslant 12$ ($n_1 = 12$ is the maximum possible number of first neighbors) again a meaningless value for τ_0 is found: $\tau_0 \leqslant 1.9 \times 10^{-25}$ s.

(ii) thermally dependent: $M_{\mathrm{nr}}^2(T) = M_{\mathrm{nr}}^2(0)(1 - 2a_{\mathrm{T}}T)$($a_{\mathrm{T}} =$ constant of the system) a good fit to the experimental data is obtained (Figure 3, inset) yielding the following parameters, which have physical meaning: $n_1 = 6$, $\tau_0 = 4 \times 10^{-10}$ s, $\varepsilon_{\mathrm{B0}} = 10^{-19}$ J.

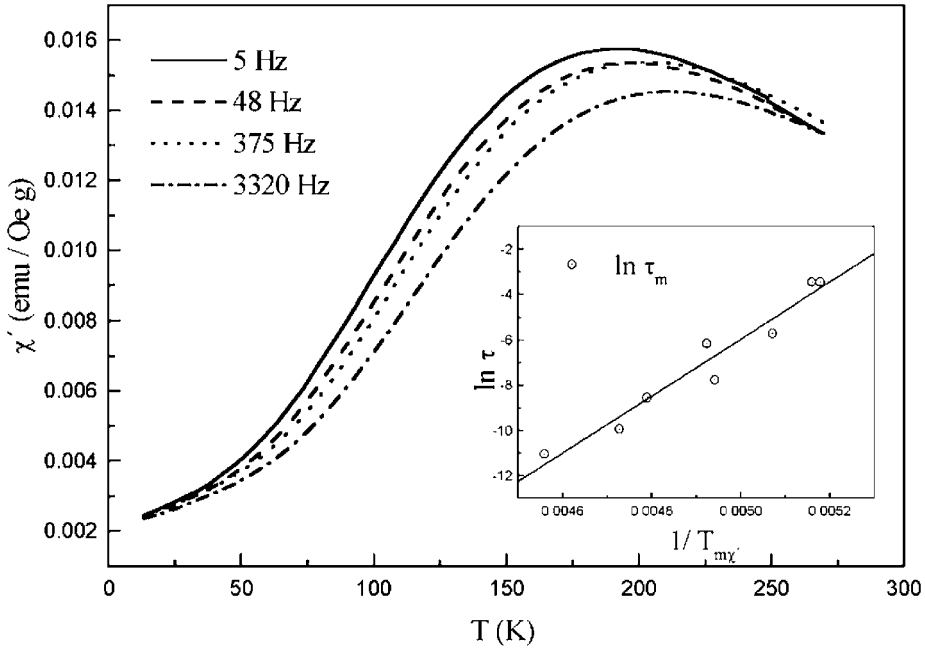

Figure 3. Thermal dependence of some AC susceptibility results. For clarity only four representative results are shown. Inset: the best least-squares fitting of all the experimental maxima as described in the text.

The application of these models shows that the system is made up of particles interacting probably through magnetic dipolar interactions.

The blocking temperature obtained by Mössbauer spectroscopy is about 150 K. The application of the Néel model [1], Equation (1), yields – using the $\tau_0 = 4 \times 10^{-10}$ s value obtained by fitting the AC susceptibility results – an average energy barrier ε_B of 7×10^{-21} J.

The parameters obtained in the best fitting of the AC suceptibility data allow to calculate, using Equation (2), an average energy barrier of $\varepsilon_B = 8 \times 10^{-20}$ J at 150 K. This value is an order of magnitude higher than those obtained from the Mössbauer results at the blocking temperature. Because the larger particles have a much greater weight in the magnetic response than the smaller ones, while the Mössbauer spectral area is a superposition of all particles irrespective of their hyperfine parameters [6] this situation is revealing a broad distribution of particle sizes. The behavior of the AC suceptibility curves as described above is also indicative of this broad size distribution.

4. Conclusions

We used a synthesis route that allowed us to obtain a system of γ-Fe_2O_3 nanoparticles displaying superparamagnetic relaxation. The best fitting of the AC sucep-

tibility data is obtained when a model with dipolar magnetic interactions between the particles and a packing lesser than compact ($n_1 = 6$) is considered. The estimated average energy barriers, calculated from the Mössbauer and AC suceptibility results, demonstrate the existence of a broad distribution of particle sizes.

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