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Magnetism of Nanosized Oxide Systems Investigated by Mössbauer Spectroscopy

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Abstract. The Mössbauer characterization of nanosized iron oxides is based on the dependence of the magnetic relaxation time on several parameters. Because the contributions of the magnetic anisotropy and of the particle volume cannot be separated, the knowledge of properties other than hyperfine by the use of several techniques is needed to achieve a full understanding of the studied system. In this work, after a brief review of the difference between bulk and nanostuctured magnetism, we show how Mössbauer spectroscopy, complemented by other techniques, applied to nanosized systems of maghemite and hematite, yields a good characterization of the solids and of the interparticle interactions. In the case of hematite we also show that more work is needed to identify in depth the parameters that determine the Morin transition.

Key words: magnetism of nanosized iron oxides, Mössbauer spectroscopy, superparamagnetism, nanoparticle size determination.

1. Introduction

In the synthesis of systems of iron oxides for different purposes, some parameters, like the average particle size or certain magnetic transitions, are of great importance. Because X-ray diffraction or electron microscopy sometimes are impossible or very difficult to apply, Mössbauer spectroscopy has proved to be a very useful tool to monitor the process. With relative ease, the magnetic hyperfine response of the system yields information on the size and interactions of the particles making up the sample and its magnetic transitions. There are situations in which nothing else is needed and a quick characterization of the system is obtained by measuring the temperatures at which the magnetic regimes change. However, because the relaxation time depends both on the particle's volume and the magnetic anisotropy energy, on many occasions it is not possible to know one if the other is not known. Since, in particular for nanosized particles, the anisotropy is a function of their diameter [1], the knowledge of the contribution of each term may prove impossible.

Many efforts have been carried out to measure the contribution of the different terms to the anisotropy, but the spin structure and surface anisotropy are hard to

assess and in a real sample with non-uniform particle volumes it is usually impossible to separate the different contributions. Recently, some authors have complemented the experimental difficulties with computer simulations [2].

In this paper, after a brief introduction to indicate the difference between bulk and nanoparticle magnetism, we give two examples of the application of Mössbauer spectroscopy to the understanding of maghemite and hematite nanostructured systems.

2. Magnetic ordering

The temperature T_{cr} of the transition from an ordered magnetic state to a disordered one reflects the intensity of the interaction responsible for the ordering. By equating the energy at which the order is destroyed by the thermal agitation, the Boltzmann distribution allows to estimate T_{cr} from the relation $kT_{cr} = E_m$, where E_m is the intensity of the magnetic interaction and k is the Boltzmann constant.

Any magnetic energy that orders or orients the magnetic moments can be described by an effective magnetic field $\mathbf{H}_{eff}$. As the magnetic moment of the electrons is of the order of the Bohr magneton, μ_B, the effective magnetic field is defined through the equation:

$$\mathbf{H}_{eff} = \frac{E_m}{\mu_B} = \frac{kT_{cr}}{\mu_B}.$$

$\mathbf{H}_{eff}$ is indeed an effective field of electronic (and not magnetic) origin. For example, for metallic iron at room temperature, $\mathbf{H}_{eff}$ would have the unrealistic value of $\approx$1000 T, which denotes its true quantum (exchange) nature. In weak magnetic materials, the almost thermally independent magnetic ordering interactions are competing with thermal disorder at room temperature, but the strong magnetic materials – ferri and ferromagnetic – are already ordered microscopically by the electrostatic interaction in magnetic domains. These are exchange-ordered regions of about 10^7 interatomic distances separated by Bloch walls, which minimize the magnetostatic energy. The minimized energy is the total one, which includes the exchange, anisotropy and domain wall contributions. The final balance determines the structure and shape of the domains.

When the size of the crystal decreases, the competence between the magnetostatic energy and the cost to create a wall causes that below a certain limit in the crystal size, a single-domain structure exists. For typical magnetic materials the single-domain limit is in the range of $\approx$20 to 800 nm.

The anisotropy energy K in a single-domain particle in a first approximation is proportional to the volume V. For uniaxial anisotropy, the energy barrier separating easy magnetization directions is $E_B = KV$, and for a certain grain size it may be comparable to or lower than the thermal energy kT. Thus, the energy barrier for magnetization reversal may be overcome, and then the total magnetic moment can

fluctuate thermally leading to a region of magnetic disorder, which is not unlike the behavior of a paramagnetic material. The observed magnetic behavior depends on the value of the measuring time of the experimental technique, τ_m, with respect to the relaxation time, τ, that is the time that the system takes to overcome the energy barriers. Although the theory was developed initially for ferro- or ferrimagnetism, the idea of exchange-coupled regions can be extended to antiferromagnetic materials without loose of generality.

3. Magnetic relaxation

The Néel–Brown model [3] describes the dependence of the relaxation time on temperature and the anisotropy barrier for non-interacting particles with uniaxial anisotropy and expresses the relaxation time τ as:

$$\tau = \tau_0 \exp(E_B/kT).$$

As mentioned above, if there is an anisotropy barrier of height $E_B = KV$, the total magnetic anisotropy is given by $E(\theta) = E_B \sin^2(\theta)$, where θ is the angle between the magnetization direction and the easy direction axis. There is a particle size for which $E_B \leqslant kT$ and then the energy barrier can be overcome by magnetization reversal and the total magnetic moment (of several hundreds or thousands of Bohr magnetons) can fluctuate thermally, like a single spin in a bulk paramagnetic material. Because the statistics involves two levels, the population still is described by the Boltzmann's distribution, and the equation expressing the phenomenon is similar to the bulk equation, except that now the entire spin system of the particle can rotate coherently. This type of behavior is called superparamagnetism.

Over the years, the same simplified expression for τ has been used, but the meanings of K, V and τ_0 have been modified to account for all the complexity of the relaxation process. For example, there are several contributions to K, like magnetocrystalline, shape, stress, dipolar interaction, exchange, surface, and induced magnetic anisotropies. Excellent reviews are found in the literature, which describe these terms in detail [3, 4].

For $KV/kT \geqslant \approx 2.5$ the expression is still valid although τ_0 will depend on several parameters and on the symmetry of the relaxation barriers. The assumptions of the model (coherent rotation of all the particle spins and one uniaxial energy) are not too exacting, and hence, to a first order approximation, the expressions for τ remain valid even when the anisotropy energy has more secondary minima than the two main ones. The validity of the approximation has been experimentally verified for several systems [5].

As mentioned earlier, the relaxation times obtained in an experiment depend on the type of technique used. Typically, DC magnetization measurements sense the system for a time $\tau_m \approx 100$ s [6]. For AC susceptibility measurements the

frequencies used for the exciting field vary from ≈1 Hz to ≈10 kHz ($\tau_m = 1$ to 10^{-4} s). Mössbauer spectroscopy of ^{57}Fe is limited by the mean lifetime, 98 ns, of the 14.4 keV level.

Accordingly, a system that shows superparamagnetic behavior for one technique can display a split static hyperfine magnetic signal for another. In this way, the superparamagnetic blocking temperature, T_B, defined as the temperature at which τ is slow compared to τ_m, varies from one technique to the other.

A real system made up of interacting particles, which generally displays volume distribution and random easy axes orientations, is a complex problem to tackle [7]. Because of the changing character of the magnetic dipole–dipole interactions, which are antiferromagnetic or ferromagnetic according to the relative orientations of their spins, the system can exhibit spin-glass-like behavior. Depending on the strength of the interparticle interactions, additional energy minima can modify the anisotropy energy barriers of the different particles and render the barriers interdependent [8]. The competition of the anisotropy and interaction energies will determine the final behavior.

When the interactions are weak, superparamagnetism still holds within the Néel–Brown model to first order, and within the frame of the Dormann–Bessais–Fiorani model when interparticle interactions are taken into account [9, 10].

When the interparticle interactions are strong, the above-mentioned models no longer hold, the particles do not show distinct energy barriers and only the energy of the whole system has meaning. Spin-glass-like collective states are attained, which have complex properties and are currently intensely studied [11].

4. Hyperfine field reduction caused by magnetic excitations

In Mössbauer spectroscopy T_B is defined as the temperature at which the spectral area of the superparamagnetic signal amounts to half the total spectral area. Although below T_B the hyperfine field splits the nuclear levels, there is a non-zero probability that the hyperfine field $\langle \mathbf{H} \rangle$ fluctuates close to the direction of easy magnetization. These fluctuations are described by the collective magnetic excitations model [12]. For non-interacting particles and $kT/KV \leqslant 0.05$, the following approximation can be used:

$$\langle \mathbf{H} \rangle = \mathbf{H}_0 \left(\frac{1 - kT}{2KV} \right),$$

where $\mathbf{H}_0$ is the saturation value for the investigated system.

Therefore, from the slope of the $\mathbf{H}(T)$ curve, the value of KV can be estimated from a different relation than T_B. In many cases, the application of this method has given excellent estimates of the average particle size when K is known [12].

In the case when the particle interactions are not negligible, the approximation is no longer valid and more effort has to be developed to understand the system's magnetic behavior.

5. Maghemite

Because maghemite (γ-Fe_2O_3) has a ferrimagnetic behavior, in a system made up of nanoparticles, the magnetic dipolar interactions between neighboring particles may be present. These interactions prevent to ascertain only through Mössbauer measurements the different structural properties of the solids, like the average particle size. The situation is even more complex if the sample has a broad size distribution. Although in other cases AC susceptibility is a good complement for Mössbauer spectroscopy, when the particle sizes are very different, because the size effect is reflected differently by both techniques, they yield widely different average crystallite diameters.

In the following paragraphs we describe how Mössbauer results may help determine in a simple way the average particle size of two different γ-Fe_2O_3 systems. One is a system of silicagel-supported γ-Fe_2O_3 nanoparticles prepared by dry impregnation from an aqueous iron nitrate solution [13]. The other is a sample of nanostructured γ-Fe_2O_3 prepared by a microemulsion method [14].

For both solids, X-ray diffraction is of limited value as a characterization technique to determine the average particle size, since the supported maghemite pattern does not display any identifiable peak, and the second system is a poorly crystalline solid.

One possible approach to estimate the average particle size is to use the model of collective magnetic excitations in the following way:

- measure the Mössbauer spectra at different temperatures between 298 K and the lowest attainable temperature of the cryogenic system,
- represent $\langle \mathbf{H} \rangle$ *versus* T and determine the temperature range in which the model is obeyed,
- use a reported correlation between K and the average particle size, $K(\overline{D})$ for a very similar system [15],
- iterate self-consistently between $K(\overline{D})$ and $\langle H(\overline{D}, T) \rangle$ equations, and obtain an average diameter $\overline{D}$ of the iron oxide nanoparticles.

Figure 1 shows that the sample of supported γ-Fe_2O_3 follows the behavior described by the collective magnetic excitations model with and an average diameter value of 25 nm. However, when applied to the sample prepared by microemulsion, the model does not reproduce its thermal dependence. The discrepancy is very likely due to the presence of interparticle dipolar and/or contact magnetic interactions.

For the second case, it is apparent that Mössbauer spectroscopy alone it is not sufficient to achieve a reasonable characterization of this extremely complex sample. In many laboratories there are not external magnetic in-field measurements to obtain an independent measurement of the size. However, crossing Mössbauer and AC susceptibility measurements new evidence for the average particle size may be obtained.

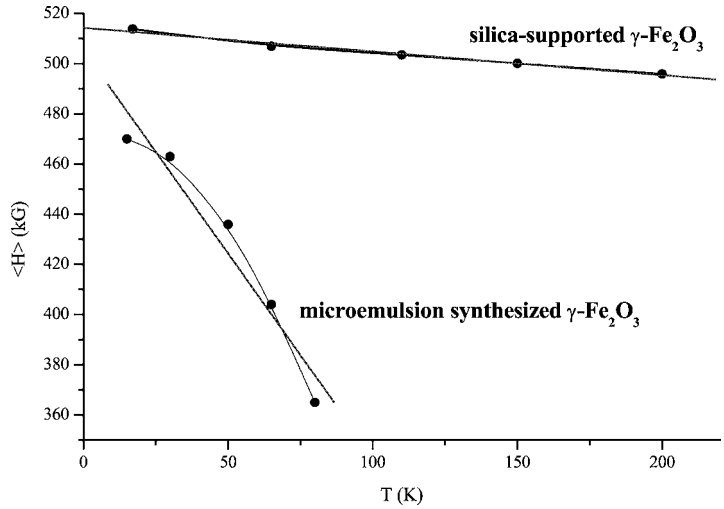

Figure 1. Average hyperfine fields obtained after static distribution fittings of Mössbauer spectra obtained at different temperatures for supported and unsupported samples of maghemite. The straight lines are linear regressions using collective magnetic excitations model. The curved line for the unsupported sample is a guide for the eye.

Using the model developed by Dormann–Bessais–Fiorani – valid for weak dipolar magnetic interactions – with physically meaningful parameters, a good fit to the experimental data is obtained yielding the following values: $n_1 = 6$, $\tau_0 = 4 \times 10^{-10}$ s, $\varepsilon_{B0} = 10^{-19}$ J [14]. The goodness of the fit indicates that the γ-Fe_2O_3 nanoparticles are non-independent and consequently it is not possible to determine its diameter from the Mössbauer spectroscopy measurements alone.

We are forced to conclude that in systems of medium or strongly interacting particles, the only reliable method to estimate the diameter is electron microscopy, which is not a quick characterization technique; it rather requires a great effort to achieve a representative value.

6. Hematite

Bulk hematite (α-Fe_2O_3) has a Néel temperature of 950 K and is a weak ferromagnet at room temperature. At a temperature T_M the spins undergo a spin–flip transition (the Morin transition), which brings them along the c-axis into a pure AF state. In the bulk material $T_M \approx 260$ K, but it changes from sample to sample and depends on the lattice order and notoriously with the particle size and shape for reasons still under discussion [16].

It is generally accepted [17] that the Morin transition occurs because of the competition of two anisotropy energy terms, the long-range dipolar one and the fine-structure local one, which have different thermal dependencies. The Morin transition can be altered or even suppressed by different means: applying pressure,

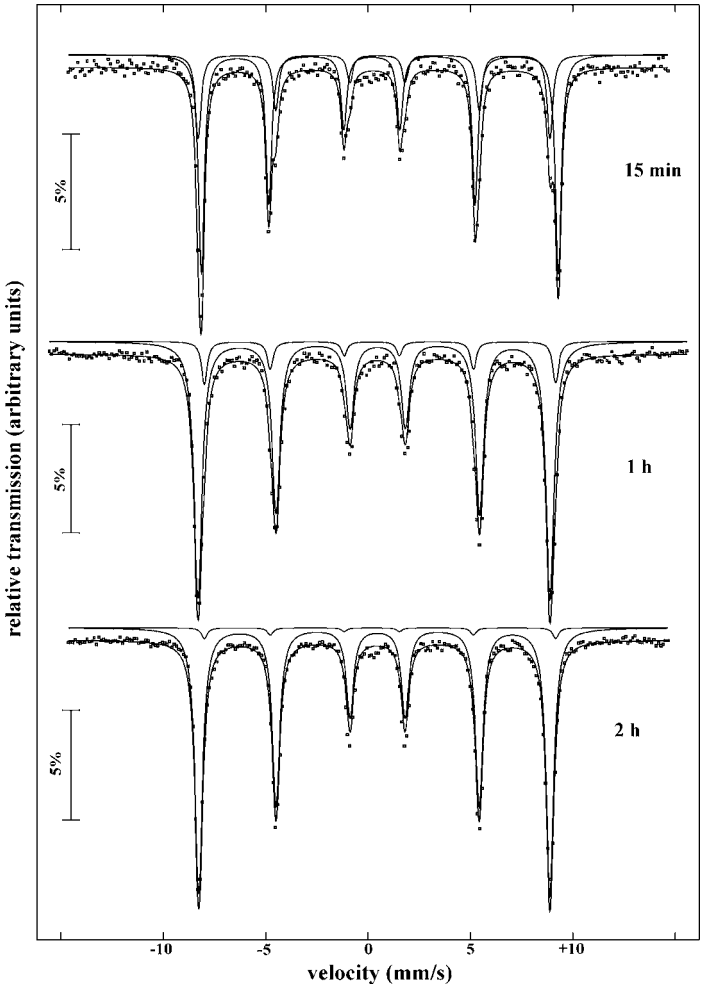

Figure 2. Mössbauer spectra at 21 K of pure hematite milled for the times shown on the right. The thin solid lines are the contributions of the antiferromagnetic and weak ferromagnetic signals.

doping with impurity ions, incorporating OH groups or water into the structure, reducing the grain size, or changing the morphology of the particles [18].

Mössbauer spectroscopy is very sensitive to the Morin transition; the quadrupole shift is $2\varepsilon = \Delta(3\cos^2\theta - 1)/2$, where Δ is the quadrupole splitting and θ is the angle between the principal component of the electric field gradient and the magnetic hyperfine field. In a bulk material, as the temperature is raised through the Morin transition (from an antiferromagnetic ordering, $\theta = 0°$, to a weak ferromagnetic one, $\theta = 90°$) 2ε changes from $+0.4$ mm/s to -0.2 mm/s. The local nature of Mössbauer spectroscopy allows measuring the fraction of the sample that has experienced the transition.

The Mössbauer spectra at 21 K of anhydrous hematite ball-milled for different times are shown in Figure 2. The fraction of the sample that undergoes the Morin

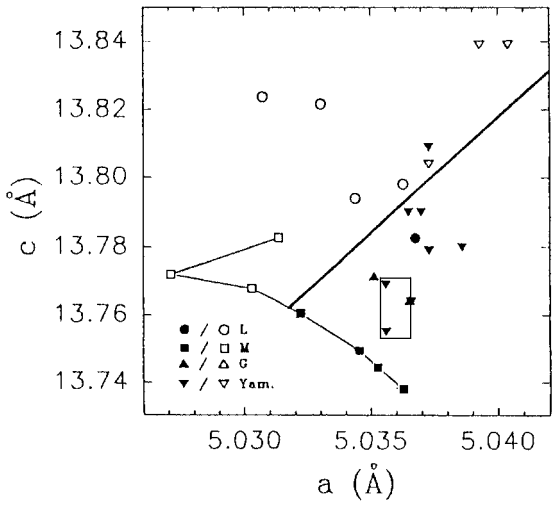

Figure 3. *c versus a* plot for hematite samples prepared by different methods (from [16]). The open symbols are samples which do not undergo a Morin transition. The rectangle comprises all the *c* and *a* values obtained for anhydrous milled samples (from [19]) where, down to 21 K, only the 15 min milled sample undergoes the Morin transition.

transition can be clearly resolved; at 21 K after a milling for 15 min, 73 ± 2% of the sample undergoes the transition, 16 ± 3% for 1 h, and after 2 h the transition is suppressed for 97 ± 2% of the sample.

Investigating how the disorder introduced by the grinding of hematite affects its magnetic response, we found by Rietveld analysis of X-ray diffraction data that hematite grains attain nanometric size after 30 min of milling [14]. For longer milling times, the crystals decrease in size and suffer anisotropic lattice dilation, which is more pronounced as the grain size decreases. Although AC susceptibility allows determining when the sample is undergoing the Morin transition, only by Mössbauer spectroscopy it is possible to assess the amount of sample that undergoes transition. In other words, the microscopic character of Mössbauer spectroscopy allows determining the changes in the Morin transition temperature better than macroscopic magnetic techniques. Through its application, it is found that the milling process, even for the shortest milling time of 15 min, alters T_M.

Carefully performed Rietveld analysis of X-ray diffraction data demonstrate that the modification of the effective T_M is related to the anisotropic expansion of lattice parameters of the α-Fe_2O_3 crystals. This anisotropic dilation strongly affects the balance between the anisotropy energies, shifts the temperature and the temperature interval that takes the transformation. In contrast to chemically prepared α-Fe_2O_3 nanoparticles, the modification of the Morin transition in our nanostructured hematite is not only restricted to surface or grain boundary regions but involves the whole volume of the grains.

In the graph of *c versus a* shown in Figure 3, obtained from [16], Dang *et al.* propose a line that divides the plane into regions where the Morin transition is

observed and others where it is suppressed. In the same figure, inside the rectangle we display the results of our milled samples, where only for the 15 min case the Morin transition is observed, in spite that the rest of the points lie in the region where the transition is supposed to occur. This state of facts calls for more studies to achieve a better knowledge of the factors that are responsible for this spin–flip transition.

7. Conclusions

In many examples where the necessary characterization of synthesized nanostructured iron oxide systems is sometimes impossible or difficult to achieve by techniques like X-ray diffraction or electron microscopy, Mössbauer spectroscopy can be a quick and convenient way to assess the average size distribution in systems of non-interacting particles. However, not to obtain incorrect values of the average volume, care must be exercised when interparticle interactions or a broad distribution of particle sizes exist in the system.

We have shown that in the case of hematite particles, the Morin transition is followed with better accuracy by Mössbauer spectroscopy, although more work is needed to estimate the true parameters that are determining the samples which undergo from those which do not undergo the transition.

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