MODIFIED THEORY FOR MÖSSBAUER SPECTRA OF SUPERPARAMAGNETIC PARTICLES : APPLICATION TO Fe_3O_4

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Résumé. — L'article présente un modèle modifié pour relaxation superparamagnétique. Ce modèle associe le superparamagnétisme conventionnel avec l'effet, dernièrement décrit, des excitations collectives de l'aimantation autour d'une direction facile. Il y a aussi une discussion des effets prononcés de granulométrie. Le modèle explique la valeur réduite des domaines hyperfins observés, ainsi que les formes de raies asymétriques de spectres Mössbauer de petites particules de composés arrangés selon leur magnétisme. L'adsorption chimique de molécules différentes sur particules de Fe_3O_4 indique que l'énergie anisotropique est sensible aux effets de surface.

Abstract. — A modified model for superparamagnetic relaxation is presented. This model combines the conventional superparamagnetism with the recently described effect of collective excitations of the magnetization around an easy direction. The marked effects of particle size are also discussed. The model explains the reduced value of the observed hyperfine fields and the asymmetric line shapes of Mössbauer spectra of small particles of magnetically ordered compounds. Chemisorption of different molecules on Fe_3O_4 particles shows that the anisotropy energy is sensitive to surface effects.

1. **Introduction.** — Mössbauer spectroscopy has given a great number of different types of information about surfaces and small particle systems [1]. For example superparamagnetic relaxation is conveniently studied by this method. The superparamagnetic relaxation time τ depends strongly on temperature and particle size. For a given particle size the Mössbauer spectrum is Zeeman split well below a certain temperature, the blocking temperature. Considerably above the blocking temperature a paramagnetic spectrum with one or two lines is found. Near the blocking temperature the value of τ is close to the nuclear Larmor precession time and spectra with broadened lines are found.

For a particle with volume V and with uniaxial symmetry the anisotropy energy may be written in the form :

$$E(\theta) = - KV \cos^2 \theta \qquad (1)$$

where K is the anisotropy energy constant and θ is the angle between the magnetization vector and the easy direction.

The superparamagnetic relaxation process has been described in terms of transitions between the two orientations of the magnetization given by $\theta = 0$ and $\theta = \pi$.

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Such a two-level model reproduces most of the features of the experimental spectra [2]. However, the model fails to explain the small reduction in the hyperfine field and the asymmetric line broadening which are often found below the blocking temperature.

In a recent publication [3] it was shown that the diminished value of the hyperfine field in small particles below the superparamagnetic blocking temperature can be explained by fluctuations of the magnetization direction around an energy minimum corresponding to an easy direction of magnetization. For convenience we will denote this phenomenon collective magnetic excitations. The average magnetization at temperature T is then given by [3]

$$M(V, T) = M(V = \infty, T) < \cos \theta >_T ,$$

where

$$< \cos \theta >_T = \frac{\int_0^{\pi/2} \exp \{ - E(\theta)/kT \} \cos \theta \sin \theta \, d\theta}{\int_0^{\pi/2} \exp \{ - E(\theta)/kT \} \sin \theta \, d\theta} . \qquad (2)$$

For large values of KV/kT (i. e. well below the superparamagnetic blocking temperature) it was found that $< \cos \theta >_T \simeq 1 - kT/2\,KV$. As the fluctuations of the magnetization around the energy minimum are fast compared to the nuclear Larmor precession time the magnetic hyperfine splitting of the Mössbauer spectrum is proportional to $< \cos \theta >_T$.

In this paper we extend the relaxation model to include both the above-mentioned effect of collective magnetic excitations and conventional superparamagnetism. This extension leads not only to a better fit of the data but gives access to a better understanding of the magnetic properties of small particles.

The theoretical results are compared to Mössbauer spectra of 60 Å and 100 Å Fe_3O_4 particles.

2. **Theoretical model.** — A superparamagnetic crystallite may be considered as a particle with spin S. Typically, S is of the order of 10^4. Such a particle may be found in one of $2S + 1 \simeq 2 \times 10^4$ states.

For calculation of the Mössbauer spectrum, transitions between any two states have to be considered. This involves the inversion of a matrix of the order of 2×10^4. However, as the transition rate is high for transitions among states which are not separated by an energy barrier (states close to the same energy minimum) we may simplify the calculations considerably by limiting ourselves to consider only two states and the transitions between them, namely the *thermally averaged states* (defined as thermal averages of the states near the two minima at $\theta = 0$ and $\theta = \pi$) with hyperfine fields given by :

$$H(V, T) = H(V = \infty, T) < \cos\theta >_T ; \qquad (3)$$

where $< \cos\theta >_T$ is given by eq. (2).

The dependence of the superparamagnetic relaxation time τ on KV/kT has been calculated by Brown [4] and Aharoni [5]. For $KV/kT > 1.0$, τ is to a good approximation given by

$$\tau = \frac{M_S \pi^{1/2}}{2 K \gamma_0} \left(\frac{KV}{kT}\right)^{-1/2} \exp\left(\frac{KV}{kT}\right) ; \qquad (4)$$

where M_S is the magnetization and γ_0 is the gyromagnetic ratio. For a particle with uniaxial symmetry, Mössbauer spectra can then be calculated by using the hyperfine field given by eq. (3) and the analytical expression for the line shape in the presence of relaxation given by Wickman [6]. In practice, the sample will always contain particles with different volumes. Therefore, one has to sum theoretical spectra with different values of KV/kT weighted with the particle size distribution of the sample.

3. **Experimental.** — The preparation and characterization of the Fe_3O_4 crystallites is described elsewhere [7]. The particle size distributions were determined by use of electron microscopy. The average particle size was also determined by use of x-ray diffraction methods [7]. It was controlled that no irreversible changes such as oxidation or sintering took place in the samples during the Mössbauer measurements.

The Mössbauer spectra were obtained using a conventional constant acceleration spectrometer with a source of ^{57}Co in Pd giving a line width of about 0.23 mm/s with a thin absorber of metallic iron.

4. **Results.** — In figures 1 and 2 Mössbauer spectra of 60 Å and 100 Å particles of Fe_3O_4 are shown together with theoretical spectra. The latter were computed by use of the theoretical model described in sec. 2. It was found that the theoretical Mössbauer line shape depends critically on the particle size distribution. The particle size distributions (with 200 different particle sizes) on the basis of which the theoretical spectra were computed, were chosen to give good agreement with the experimental spectra. Figure 3 shows the experimentally found particle size distribution determined by electron microscopy together with the distribution used to produce the theoretical Mössbauer spectra shown in figure 1.

The conventional superparamagnetic relaxation is the most important factor determining the temperature dependence of the spectra for the 60 Å particles (Fig. 1). The relaxation time appears to be in accordance with eq. (4). For this sample the effect of collective magnetic excitations shows up as shifts and broadenings of the magnetically split lines.

In the spectra of the 100 Å particles (Fig. 2) no central absorption line was found. The theoretical spectra were therefore computed assuming an infinite relaxation time and only effects of collective magnetic

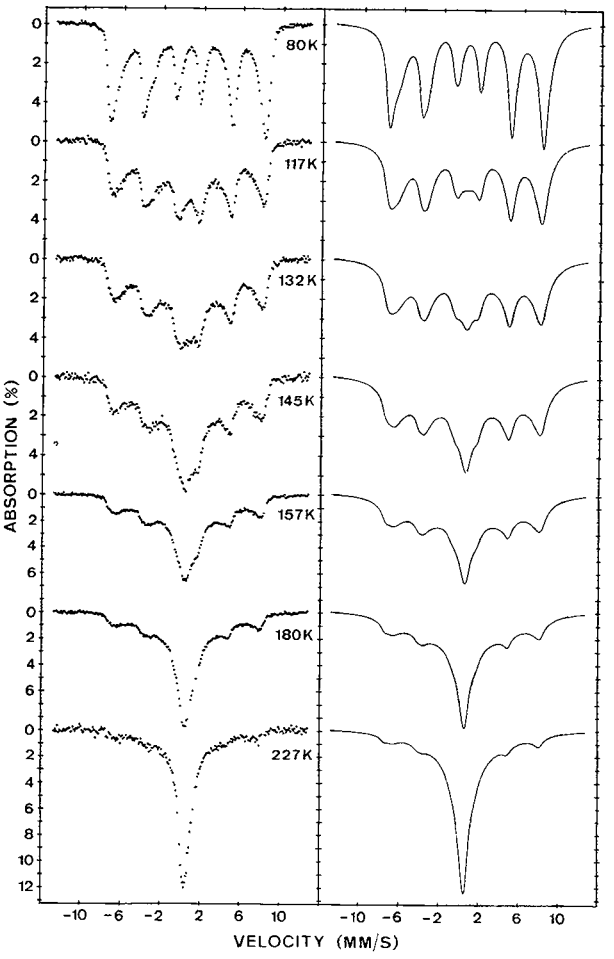

FIG. 1. — Experimental and theoretical Mössbauer spectra of 60 Å Fe_3O_4 particles at various temperatures.

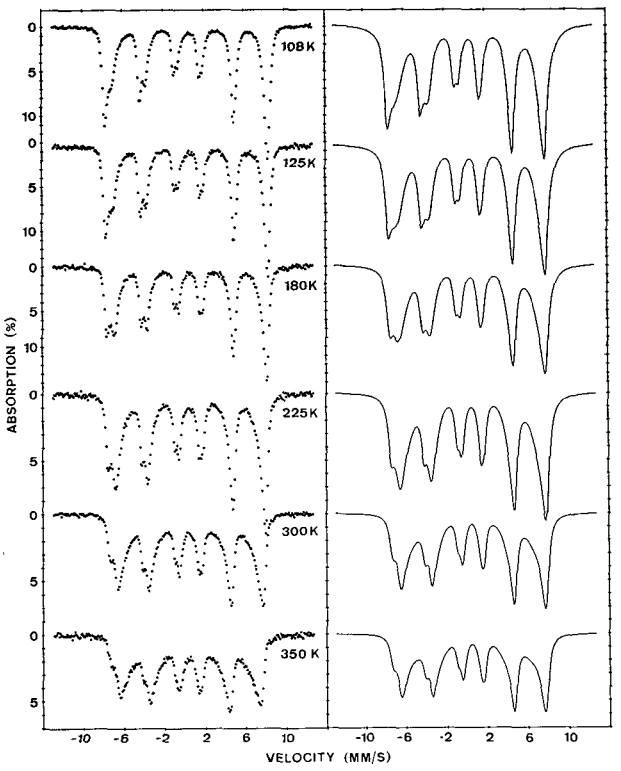

FIG. 2. — Experimental and theoretical Mössbauer spectra of 100 Å Fe_3O_4 particles at various temperatures.

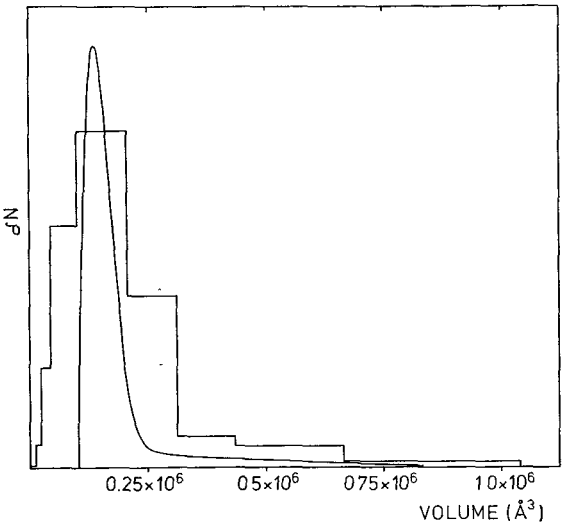

FIG. 3. — Experimental (stepped curve) and theoretical (smooth line) particle size distribution for 60 Å particles of Fe_3O_4.

excitations for different particle sizes are taken into account. The experimental spectra show an apparent temperature dependence of the ratio of the areas of the A and B spectra. However, the theoretical spectra show that this effect as well as the line shifts and the line broadenings are explained by the model of collective magnetic excitations together with the particle size distribution. Since no superparamagnetic relaxation is present a fit not including the model of collective magnetic excitations will give the typical well resolved spectra of large crystals of magnetite. The Mössbauer parameters used in the simulated spectra of each particle size are similar to those of large crystals of Fe_3O_4, but the line widths of the B-spectra were allowed to increase more with decreasing temperature than they do in macroscopic crystals [8, 9].

The anisotropy energy constants determined from the theoretical spectra were $K = 0.75 \times 10^6$ erg/cm^3 for the 100 Å particles and $K = 1.30 \times 10^6$ erg/cm^3 for the 60 Å particles. These anisotropy constants are much larger than those of macroscopic crystals. Furthermore, the anisotropy energy seems to increase when the particle size decreases. It has been pointed out by Néel [10] and verified experimentally that surface effects may contribute to the anisotropy energy [11-13]. In order to investigate whether this could be the explanation of the large value of K, 60 Å Fe_3O_4 particles were exposed to oleic acid, stearic acid, and acetone. The spectra obtained at 205 K are shown in figure 4. These

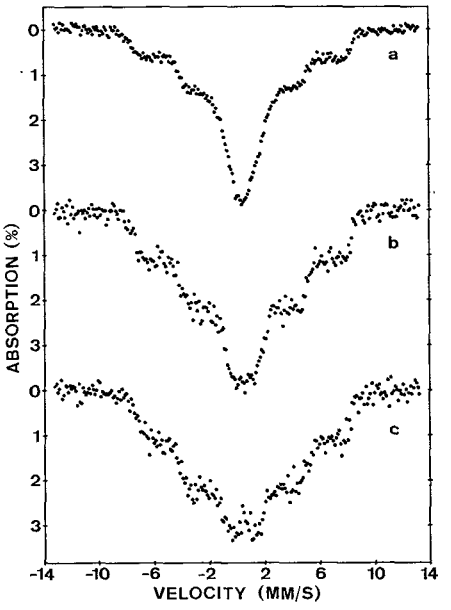

FIG. 4. — Mössbauer spectra of 60 Å Fe_3O_4 particles at 205 K exposed to *a*) acetone ; *b*) oleic acid, and *c*) stearic acid.

measurements show that the relaxation time depends on the kind of molecules chemisorbed and therefore surface effects do seem to contribute to the anisotropy energy of the Fe_3O_4 particles.

In earlier studies [14, 15] it has been shown that surface ions have a smaller hyperfine field than the ions in the interior. It has been proposed that this could explain some of the observed asymmetric line shapes of samples of small particles. For instance, Mössbauer spectra of small particles of goethite exhibit highly asymmetric line shapes which have been explained by this effect [16].

However, the present model for a particle size dependent reduction in the hyperfine field explains such

anomalous line shapes and shows that in all practical cases where a distribution of particle sizes will be present, asymmetric line shapes will be expected. To illustrate this, theoretical spectra with only one magnetically split component have been calculated. Figure 5 shows computer simulated spectra based on a hyperfine field of 490 kOe and a particle size distribution similar to that of the 100 Å Fe_3O_4 particles. The asymmetry of the lines agrees with that observed in the experimental spectra of goethite. Thus the line shape

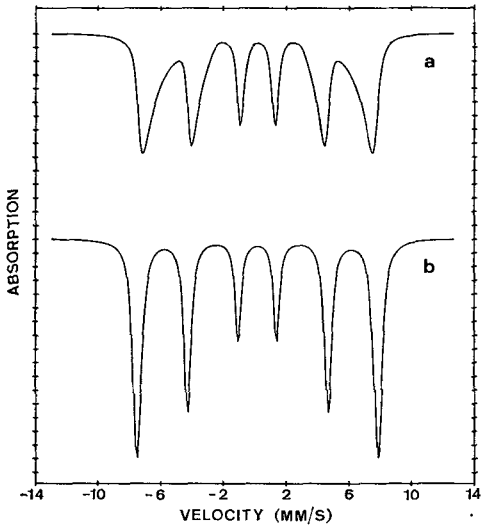

FIG. 5. — Theoretical Mössbauer spectra of α-FeOOH with a broad particle size distribution : *a*) $< KV/kT >_{av} = 6.7$; *b*) $< KV/kT >_{av} = 26.8$.

can be explained by the present theory without taking into account the influence of smaller hyperfine fields of surface ions.

5. **Discussion.** — The results show that the computer simulated spectra based on simple uniaxial anisotropy and a temperature independent anisotropy constant were able to give a good fit to the experimental data over a wide temperature region. The results also indicated that collective magnetic excitations have a great influence on the spectra. When a particle size distribution is present, the effect will generally result in asymmetrically broadened lines. For example, spectra of the small particles of magnetite showed apparent features completely different from the spectra of large crystals which at first sight could indicate deviations from the spinel structure, large surface effects, large changes in the « electron hopping », a. s. o.

However, the present results show that the Mössbauer parameters describing the different particle sizes within the distribution need not be very different from the parameters of large crystals.

The particle size distribution used in the computer fit is in fact a distribution in KV. The mismatch with the experimentally determined curve at low temperature also indicates the increase in K with decreasing particle size.

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