SUPERPARAMAGNETISM OF SMALL α-Fe2O3 CRYSTALLITES STUDIED BY MEANS OF THE MÖSSBAUER EFFECT

A. van Der Kraan

SUPERPARAMAGNETISM OF SMALL α-Fe_2O_3 CRYSTALLITES STUDIED BY MEANS OF THE MÖSSBAUER EFFECT

A. M. van der KRAAN
Interuniversitair Reactor Instituut, Delft, the Netherlands

Résumé. — Les spectres Mössbauer de grains très fins de α-Fe_2O_3 de différents diamètres ont été mesurés en fonction de la température et du champ magnétique externe. Afin d'étudier l'influence des ions de surface sur le spectre Mössbauer, des grains de α-Fe_2O_3 sont employés dont la surface est enrichie en ^{57}Fe jusqu'à 92 %. Les résultats indiquent que les ions de surface ont un temps de relaxation de spin électronique plus grand que ceux de l'intérieur et que le déplacement carré moyen des ions de surface est plus grand.

Abstract. — Mössbauer spectra of ultrafine α-Fe_2O_3 particles with different mean size are measured as a function of temperature and external magnetic field. In order to study the influence of the surface ions on the Mössbauer spectrum, α-Fe_2O_3 crystallites are used the surface of which is enriched in ^{57}Fe up to 92 %. From the results it follows that the surface ions have a faster electron spin relaxation than the inner ones, and that the mean square displacement of the surface ions is larger.

Ultrafine particles of ferro- and antiferromagnetic material show a paramagnetic behaviour below the magnetic transition temperature. This phenomenon is called superparamagnetism by Néel [1] and is due to a fast relaxation of the magnetic moments of the particles. The relaxation time is strongly dependent on the particle volume and the temperature. When this times becomes smaller than the nuclear Larmor precession time the magnetic hyperfine field measured in a Mössbauer spectrum collapses [2-6]. In order to investigate this phenomenon Mössbauer spectra of ultrafine α-Fe_2O_3 particles of different mean size are measured as a function of temperature and external magnetic field.

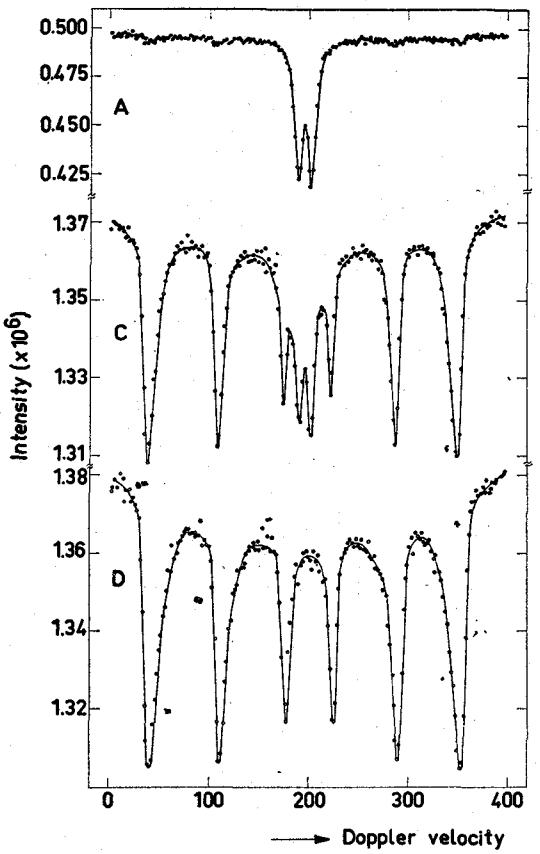

FIG. 1. — MS of α-Fe_2O_3 of various particle size, A (40 Å) C (90 Å) D (120 Å) at 295 °K.

With smaller particle size the internal magnetic field decreases and finally disappears. By decreasing the temperature the magnetic hyperfine splitting appears again (Fig. 1, 2). These results are qualitatively

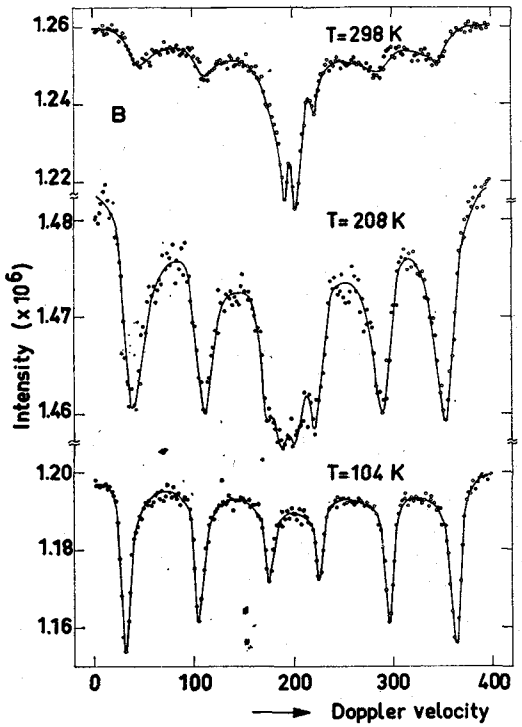

FIG. 2. — MS of sample B (70 Å) at different temperatures.

in agreement with Néel's model of electron spin relaxation and the different models describing the influence of fast electron spin relaxation on the shape of Mössbauer spectra [7, 8]. A quantitative comparison between experiment and theory is complicated by the inevitable volume distribution of the particles in each sample.

By applying an external magnetic field the magnetic moment of a particle is more or less fixed by this field. In this way the relaxation of the spins is retarded

and it is to be expected that the intensity of the hyperfine splitted spectrum increases by increasing external magnetic field. The results of such an experiment shown in figure 3 for sample B are in agreement with those reported in the literature [4, 5]. However the conclusion drawn by Eibschütz [4] that the changes in the relaxation time are less important than the trivial polarization of the superparamagnetic particles by the field does not seem to be correct. Actually increasing polarization is caused by an increasing relaxation time, so that there should be no difference between the two mechanisms. The expression

$$H_{\text{eff}} = - H_{\text{ext}} + H_0 L(\mu H/kT)$$

given by the same author cannot be understood in terms of intensities of magnetic hyperfine spectra. There is just a correlation between the fractional area of the six line pattern, I_{hfs}, and the polarization of the sample which can be given by

$$I_{\text{hfs}}(H_{\text{ext}}) \geqq I_{\text{hfs}}(0) + \{ 1 - I_{\text{hfs}}(0) \} L(\mu H/kT)$$

in the case of an uniform particle size in the sample. However, due to the particle size distribution there will not be one single Langevin function but many of them.

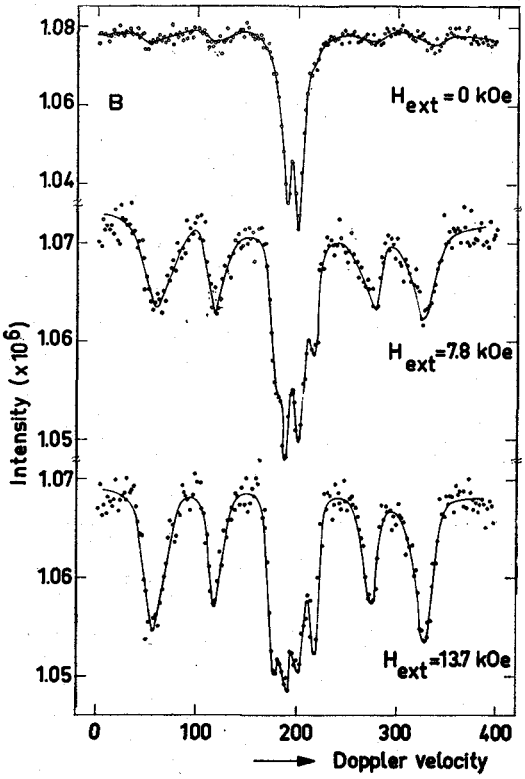

FIG. 3. — MS of sample B (70 Å) at 350 °K and the applied field as parameter.

Since in ultrafine particles of about 100 Å a significant fraction of the atoms are located near or at the surface, the question arises in how far the shape of the Mössbauer spectrum is influenced by the surface ions. In order to investigate this problem it is worthwhile to measure the Mössbauer effect in ultrafine particles the surface of which has been enriched in ^{57}Fe up to 92 %. In order to get such samples, the ultrafine particles are exposed to a solution of ferric nitrate (p$H \approx 2.5$) 92 % enriched in ^{57}Fe and slowly heated up to 140 °C.

In order to prove that the enriched iron is primarily attached to the original particles as α-Fe_2O_3 the same procedure is applied also to particles with a diameter of 500 Å (sample E), which behave like bulk α-Fe_2O_3. When new particles of α-Fe_2O_3 would have been formed, their size would be so small that the Morin transition characteristic for α-Fe_2O_3 should lie below 85 °K. However, whenever α-$^{57}Fe_2O_3$ is attached to the surface of the relatively large particles the whole sample will show the Morin transition. In figure 4 the Mössbauer spectra are given of sample E

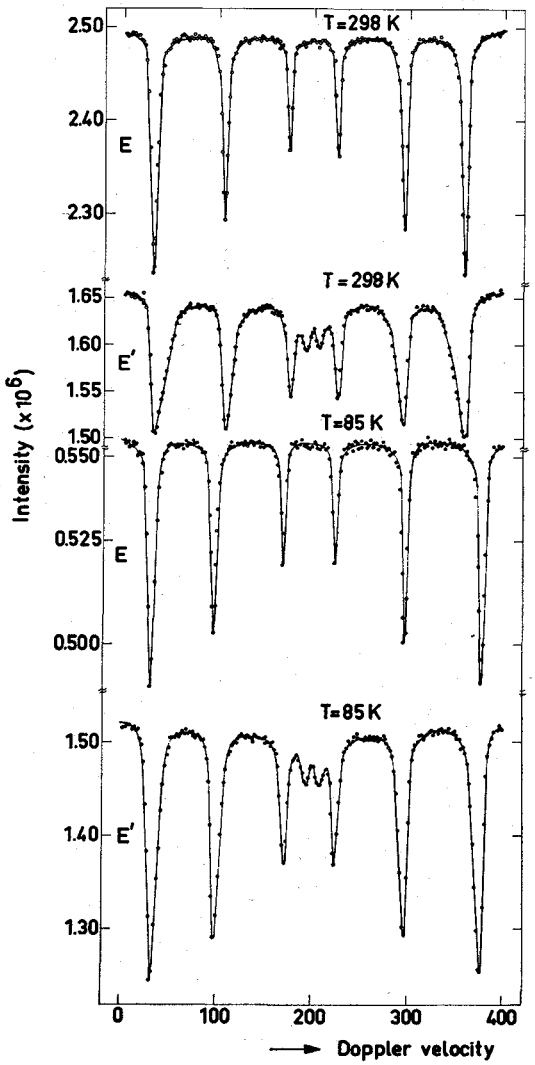

FIG. 4. — MS of α-Fe_2O_3 sample E (500 Å) and the enriched sample E' at 295 °K and 85 °K.

and the enriched sample E' at temperatures of 295 and 85 °K respectively. From these measurements it is concluded that the enriched material should almost completely be attached to the surface of the original particles and that only a small fraction has formed new small particles giving rise to the two small central peaks in the spectra. Samples of ultrafine particles of much smaller size have been enriched with ^{57}Fe in the

same way. In figure 5 Mössbauer spectra are given of sample B′ at temperatures of 295 and 85 °K. Comparing the spectra of samples E, B with E′, B′ respectively, it follows that the effective magnetic field at the nucleus of surface ions is smaller than that of the inner ones.

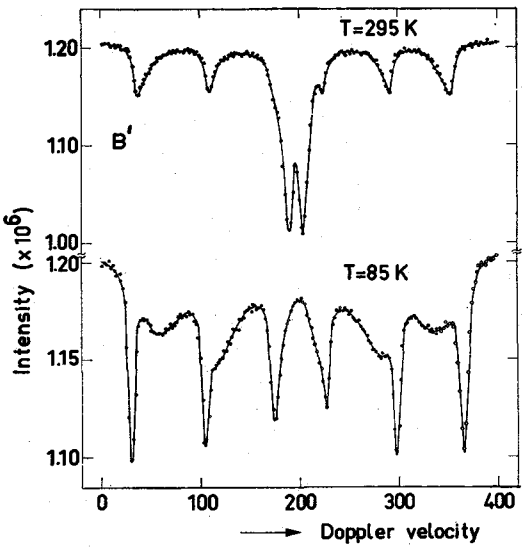

FIG. 5. — MS of α-Fe_2O_3 of the enriched sample B′ at 295 °K and 85 °K.

Furthermore it is calculated [9, 10] that vibrations of surface ions are larger than for inner ones, so the Debye-Waller factor for surface ions will decrease with temperature more rapidly. This has been verified by measuring the total absorption area of the spectra of the original and the enriched samples at 85 °K (f_{85}) and 295 °K (f_{295}) respectively. In table I the

TABLE I

Sample	$\Delta f_T \times 10^{-2}$	$\Delta f_s \times 10^{-2}$
E	17 ± 1	
E′	17 ± 1	
B	21 ± 1	
B′	32,5 ± 1	45 ± 5

results are given in terms of $\Delta f_t = (f_{85} - f_{295}).f_{85}^{-1}$. For the rather large particles (sample E, E′) there is no difference within the experimental error. By taking now for bulk ions $\Delta f = 17$ %, Δf_s for the surface ions in sample B′ can be derived from Δf_T and the intensity ratio of the sharp and very broad six line patterns observed in the spectrum at $T = 85$ °K (Fig. 5). The result is given in the last column of the table.

It can be concluded that ferric ions on the surface of a particle of α-Fe_2O_3 experience a weaker magnetic interaction than bulk ions. Therefore the ionic spins of the former relax faster with the result that both the magnetic hyperfine field is smaller and the motional narrowing effects are more pronounced. In addition the mean square displacement of surface ions is larger than that of ions in the bulk. It turns out that the influence of surface ions on the shape op the Mössbauer spectrum of 500 Å α-Fe_2O_3 crystallites is small while it is rapidly increasing with decreasing particle size.

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