THE EFFECT OF THE PARTICLE MORPHOLOGY ON THE MÖSSBAUER EFFECT IN αFe_2O_3

A.E. VERBEECK, E. DE GRAVE* and R.E. VANDENBERGHE
Laboratorium voor Magnetisme, Rijksuniversiteit Gent, Proeftuinstraat 86, B-9000 Gent

Several samples of hematite, one a natural specimen, are considered in order to study the specific effect of the morphology on the magnetic structure and especially on the Morin transition. It seemed that mainly the weak-ferromagnetic contribution is affected by the morphology, as well as the transition temperature and region.

As it is known that the spin structure and especially the spin reorientations in hematite, αFe_2O_3, are determined to a large extent by the presence of impurities or substitutions /1,2/ and by the particle size /3/, a detailed study of the influence of the particle morphology, as a whole, on the magnetic structure is presented. For that purpose, several types of αFe_2O_3 were considered. A natural, rather well-crystallized specimen (HN1), a synthetic hematite (H500), prepared by thermal decomposition (500 °C) of goethite, and a series of hematites (H600-H900), resulting from thermal annealing of the latter sample at temperatures T_a between 600 °C and 900 °C, were studied in comparison with a commercial bulk hematite. The samples were characterized by transmission electron microscopy(TEM) and X-ray diffraction (XRD). The electron micrographs for H500 and H600 show cigar-shaped particles with a long axis of about 1500 Å and 500 Å across, containing large macropores. At T_a = 700 °C the macropores become smaller and at T_a = 800 °C, the particles have grown together to form hexagonal platelets. The latter also constitute the morphology of the natural sample HN1. The narrowing of the X-ray diffraction lines as T_a increases reveal an increasing crystallinity. The original broadening of the 104-line with respect to the 110-line, expressed in Table 1 by the ratio R = W(104)/W(110), disappears as well ($R \to 1$), indicating a more isotropic growth, in this case in the shape of hexagonal platelets. The slightly higher R-value for HN1 points to thinner platelets.

The magnetic behaviour of the hematites was studied by means of Mössbauer spectroscopy at temperatures between 10 K and 360 K, using the apparatus described in a previous paper /1/. From previous studies, /1,2/, it was concluded that below a certain threshold, the so-called Morin transition, two magnetic phases coexist. They have respectively an antiferromagnetic (AF) spin arrangement with the spins parallel with the [111]-axis and a weakly ferromagnetic (WF) spin arrangement with the spins perpendicular to the [111]-axis. Above the transition, the spectra contain only one sextet arising from the remaining WF fraction.

Figs. 1-3 depict the behaviour of some Mössbauer parameters as a function of temperature. The isomer shift curves are left out since no particular variations can be noticed.

* Research Associate of the National Fund for Scientific Research (Belgium).

TABLE 1 : *The ratio W(104)/W(110) of the XRD-line widths, for the different αFe_2O_3 samples.*

Sample	W(104)/W(110)
H500	1.99 (8)
H600	1.71 (8)
H700	1.50 (8)
H800	1.31 (8)
H900	1.07 (8)
BULK	1.05 (8)
HN1	1.66 (8)

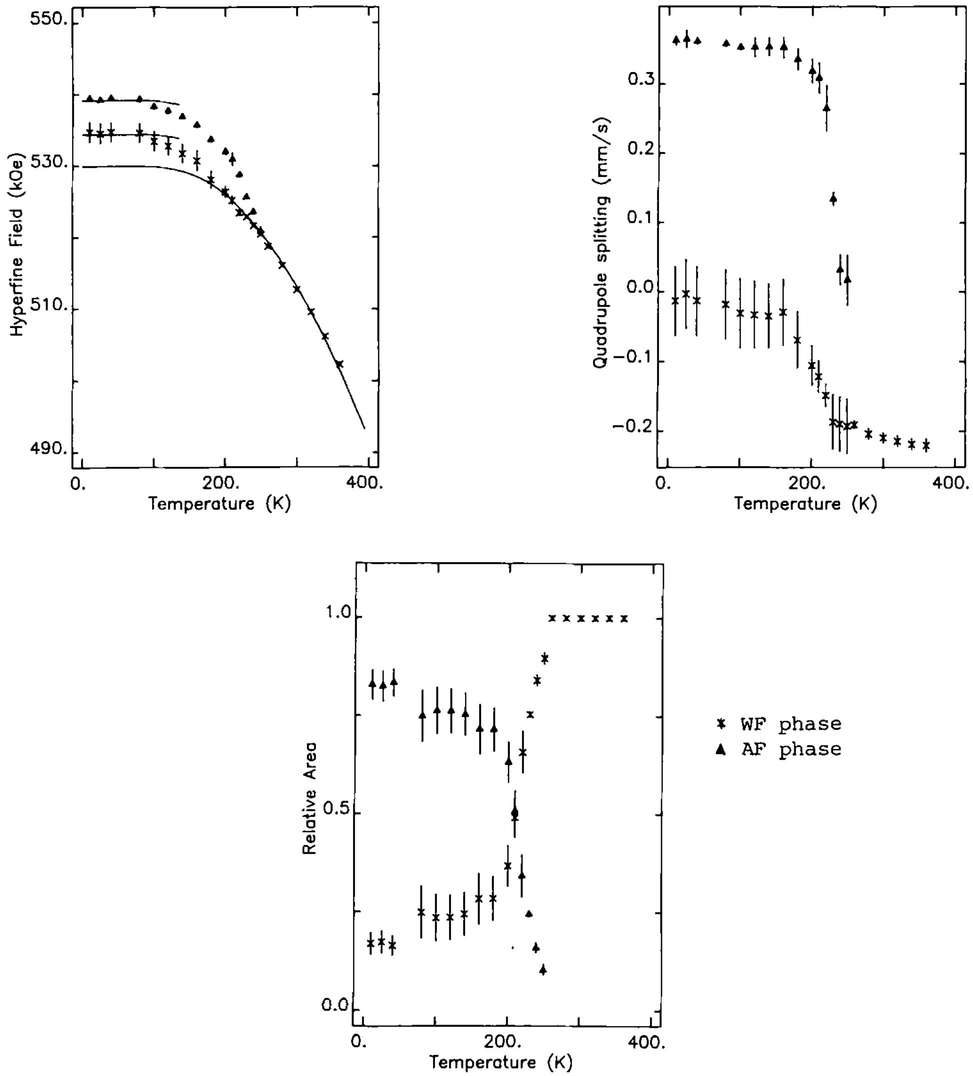

Fig.1-3 : *the temperature dependent behaviour of the hyperfine field, H_{hf}, the quadrupole splitting, $2\varepsilon_Q$, and the relative area, RA, of the synthetic hematite H700.*

Table 2 lists the saturation values of the Mössbauer parameters at low temperatures. It is evident that the low temperature AF saturation hyperfine fields, H_{hf}, are not sensitive to the morphology. Only the WF saturation fields increase with increasing T_a until they "coincide" with the AF values at $T_a = 900$ °C, indicating a decreasing angle between the AF and the WF spins. This is confirmed by the saturation quadrupole splitting values, $2\varepsilon_Q$, obtained from a least squares fit of a straight line to the experimental low temperature data : from the formula $2\varepsilon_Q = e^2qQ.(3\cos^2-1)/4$, the angle Θ between the spins and the [111] axis can be calculated /2/. The behaviour of $2\varepsilon_Q$ versus T_a shows that mainly the WF phase, for which the angle Θ changes by about 20° while for the AF phase a change of only 10° can be noticed, is very sensitive to the altered morphology. The small deviation for H900 may probably be ascribed to a very small contribution of the WF phase at low temperatures, which, however, could not be resolved.

The increasing canting angle, $\pi/2-\Theta_{WF}$, between the WF spins and the basal plane, is accompanied by a decrease of the relative area RA of the latter contribution with increasing T_a. This causes a shift of the Morin transition temperature, T_M, defined as the temperature where RA_{AF} is reduced to half of its low-temperature saturation value, to higher temperatures. Simultaneously a narrowing of the transition region is observed (Table 3). The higher the annealing temperature, the more the samples behave like the BULK material. However T_M and ΔT_M for H900 deviate substantially from the BULK value.

TABLE 2 : *The low temperature saturation values of the hyperfine field, H_{hf}, the quadrupole splitting, $2\varepsilon_Q$, the calculated angles Θ between the spins and the [111] axis, and the relative area for the AF and WF phase.*

Sample	Antiferromagnetic phase				Weakly ferromagnetic phase		
	$2\varepsilon_Q$ (mm/s)	Θ (°)	RA	H_{hf} (kOe)	$2\varepsilon_Q$ (mm/s)	Θ (°)	H_{hf} (kOe)
H500	0.342(14)	11(6)	0.729(50)	539.1(5)	-0.091(40)	66(5)	533.6(12)
H600	0.334(14)	13(4)	0.716(55)	538.8(5)	-0.057(40	62(5)	533.7(12)
H700	0.365(14)	0 (7)	0.844(60)	539.2(5)	-0.007(50)	56(5)	534.4(13)
H800	0.376(14)	0 (7)	0.841(45)	539.0(5)	0.037(40)	51(5)	536.6(14)
H900	0.351(7)	7 (7)	1	539.7(5)	-	-	-
BULK	0.371(7)	0 (4)	1	540.0(5)	-	-	-
HN1	0.370(10)	0 (4)	0.823 (33)	538.6(5)	-0.095(50)	67(5)	531.0(15)

TABLE 3 : *The Morin transition temperature, T_M, the transition region ΔT_M and the width of the first Mössbauer line at 300 K*

Sample	T_M	ΔT_M	Γ_1
H500	200 (10)	40 (20)	0.335 (14)
H600	212 (10)	38 (20)	0.317 (12)
H700	220 (10)	40 (20)	0.315 (9)
H800	226 (10)	35 (20)	0.310 (10)
H900	228 (10)	32 (20)	0.288 (9)
BULK	260 (10)	15 (20)	0.277 (7)
HN1	230 (10)	20 (20)	0.279 (7)

Apparently, the morphology mainly affects the spins in the WF phase and the transition to this phase. Since at higher T_a the particles grow together, it is obvious that the number of particles, which are already WF even at the lowest temperatures, probably due to their size /3/, will have decreased. So the AF fraction increases. Also in the WF phase the spins rotate towards the [111]-axis. Simultaneously the distribution of particle sizes becomes smaller, which might explain the narrowing of the transition region. The slight decrease of the Mössbauer line widths (Table 3) presumably reflects this smaller variety in particle sizes as well. The existence of stable spin directions canted with respect to the [111]-axis and the (111)-plane and the gradual transition, especially for the untreated sample H500, can be explained on a microscopic scale by taking into account second and higher order terms in the expression for the anisotropy energy /2/.

As T_a increases, the higher order terms apparently become more and more negligable, resulting in a smaller canting angle Θ_{AF}. A possible additional effect is the influence of shape anisotropy, which is determined to a large extent by the particle morphology.

The natural sample HN1 behaves rather similar to a hematite single crystal, reflected in a sharp transition, a difference of about 8 kOe between the low-temperature AF saturation value for H_{hf} and the WF saturation value resulting from a Brillouin fit to the H_{hf} data of the remaining WF phase above the transition /5/, and a $2\varepsilon_Q$ saturation value for the AF phase of 0.37 mm/s, corresponding with an angle Θ_{AF} of 0°. However, two magnetic phases are observed at low temperatures and the Morin transition occurs at a much lower temperature (230 K) than expected for a single crystal (265 K). This may be due to the presence of a small amount of impurities, as detected by means of an EDX microprobe.

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