

Magnetic moment of γ -Fe₂O₃ microcrystals: morphological and size effect

H. BATAIS-LANDOULSI*, P. VERGNON

Laboratoire de Catalyse Appliquée et Cinétique Hétérogène de l'Université Claude Bernard (Lyon I) associé au CNRS (L.A. No. 231), 43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

The size of gamma-ferric microcrystals prepared by vapour phase reaction in an oxygen–hydrogen flame may be varied between 17 and 77 nm. Saturation magnetization at 77 K decreases when the surface/volume ratio of particles increases but, for the smallest particles (< 40 nm) exhibiting only {1 0 0} and {1 1 1} planes, the size effect is much greater than for larger particles also exhibiting {1 1 0} faces.

1. Introduction

In spite of severe competition, gamma-ferric oxide remains one of the most important active ingredient in magnetic recording devices. Nevertheless, some aspects of its crystallographic and magnetic structure are unclear and much debated. One reason is certainly that no large monocrystals have been prepared and that the different methods of small particle preparation seem to lead to different gamma-ferric oxides. A magnetic structure of gamma-ferric oxide has been suggested by Néel [1]. Iron ions are divided into two sublattices depending upon their location of octahedral or tetrahedral sites. The atomic moments of each sublattice are parallel, but the moments of the two sublattices are antiparallel. By supposing all the vacancies on the octahedral sites, the excess of cations on octahedral sites leads to a net moment of 1.25 μ B if all the iron ions have a 3d⁵ outer electron configuration. A non-colinear spin configuration on the surface, resulting from the incomplete or different surrounding of surface atoms, should lead to a reduced magnetization of small particles. Experimental evidence for surface or interface effect on the magnetic properties of γ -Fe₂O₃ ultrafine particles has already been established [2–5]. Until now the lack of precise characterization of surface structure has prevented researchers obtaining more data concerning this effect. So, it appears interesting to study the magnetic properties of

γ -Fe₂O₃ submicron particles prepared in a flame by vapour phase reaction and condensation. This method developed in the laboratory, makes it possible to vary the size and morphology of γ -Fe₂O₃ microcrystals and is particularly appropriate to a physical characterization [6, 7].

2. Experimental procedure and results

Ferric oxide is prepared from vapour ferric chloride by reaction in an oxygen–hydrogen flame. The flame reactor has been described elsewhere [6]. The size, morphology and crystalline structure of particles depend on the nucleation, growth and quenching conditions, which, in turn, are governed by the flame temperature, concentration and residence time of reactive species in the flame. The cubic spinel structure of γ -Fe₂O₃ is obtained in hot flames (3000 K). By varying the molar ratio of ferric chloride from 3×10^{-4} to 10^{-3} in the gaseous flow feeding the reactor, the specific surface area of the powder decreases from 72 to 16 m²g⁻¹. The mean particle diameter calculated from the Brunauer, Emmett and Teller (BET) surface and the mean crystallite size calculated from the X-ray line broadening are given in Table I.

The γ form is characterized by its X-ray diffraction pattern. All the reflexions corresponding to the spinel structure are observed and the superstructure extralines are present, except for smallest

*Present address: Université de Tunis, Tunisie.

TABLE I

Sample*	D_{BET} (nm)	D_{RX} (nm)	a^\dagger (nm)	$\Delta H_{\gamma \rightarrow \alpha}$ (kJ mol ⁻¹)	σ_s 77 K (emu cgs)
Fe ₂ O ₃ -72	17	16	0.8347	-8.8	55.4
Fe ₂ O ₃ -50	25	27	0.8359	-9.6	68
Fe ₂ O ₃ -28	44	42	0.8363	-14.2	79
Fe ₂ O ₃ -24	51	>45	0.8362	-13.4	79.2
Fe ₂ O ₃ -16	77	>45	0.8368	-13.8	79.6

*Samples are differentiated by specific surface area expressed in m²g⁻¹.

†Cubic lattice parameter calculated from 220 and 311 lines.

particles (Fe₂O₃-72). The disappearance of these lines has been already observed by Haneda and Morrish [8] and Gillot and Bouton [9] for particle diameters less than 20 nm. The lattice parameter was calculated from the cubic 220 and 311 lines.

The granulometric study of different samples has shown the monodispersion and the narrow size distribution of particles [7]. High resolution electron microscopy and microdiffraction gave evidence for the monocrystallinity of particles with occurrence of twins in the largest particles. A modification of the morphology is observed when the particle size changes as shown in Figs. 1 and 2. Smallest particles (Fig. 1), i.e. particles the diameter of which is less than 30 nm, essentially exhibit projections with six edges or less corresponding to {100} and {111} faces. When the particle size increases (Fig. 2) the {110} faces appears and projections are octagonal. The {110} faces are often stepped by {111} planes and twins are observed.

Mössbauer spectra were taken at room temperature. ⁵⁷Co in a palladium matrix was used as a source of radiation. The spectrum of Fe₂O₃-16

(Fig. 3) exhibits the hyperfine split pattern (sextet) characterizing γ -Fe₂O₃. The hyperfine fields at the iron nuclei on octahedral and tetrahedral sites are almost equal, resulting in the overlap of patterns. The value of the field determined from the spectrum is 502 kOe in agreement with values already obtained [10-12]. In the case of smallest particles (Fe₂O₃-72) the spectrum is modified (Fig. 4). The 1, 2, 5 and 6 lines are well defined, but the two central lines are deformed and no close fit is possible. This deformation can result from the superposition of a central component due to a superparamagnetic phase and a six-line hyperfine structure. At room temperature, particles at sizes below 15 nm can be responsible for the superparamagnetism. Nevertheless with the Fe₂O₃-72 sample this phenomenon plays a relatively small role.

Confirmation of the γ form is provided by the differential thermal analysis performed under an helium flow. From 298 to 900 K one exothermal peak is observed between 720 and 760 K, corresponding to the $\gamma \rightarrow \alpha$ transformation. A morphological effect is clearly emphasized by the differ-

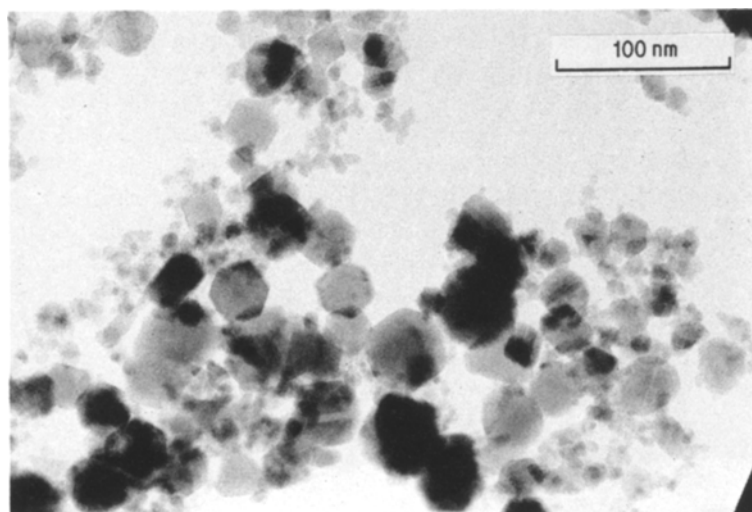


Figure 1 Electron micrograph of γ -Fe₂O₃-72 ($\times 400\,000$).

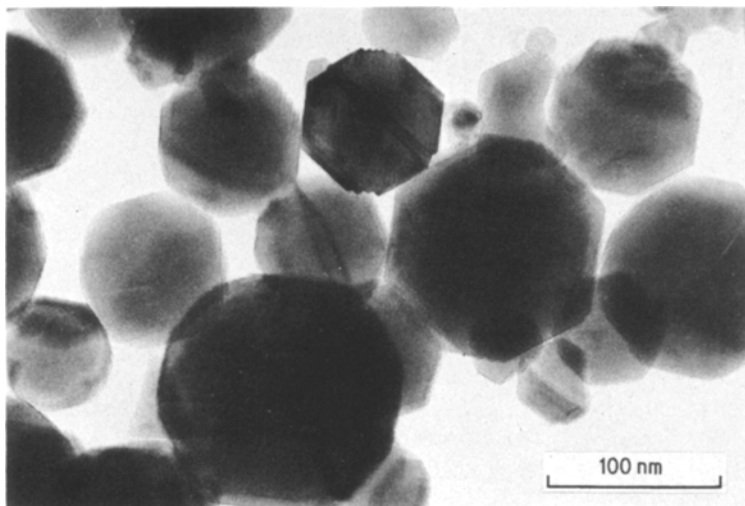


Figure 2 Electron micrograph of $\gamma\text{-Fe}_2\text{O}_3\text{-16}$ ($\times 400\,000$).

ence in the measured exothermicity (see Table I). For particles exhibiting only $\{100\}$ and $\{110\}$ faces (less than 30 nm) the heat of transformation is close to 9 kJ mol^{-1} whereas for larger particles also exhibiting $\{110\}$ faces the heat of transformation is about -14 kJ mol^{-1} .

The specific magnetization σ was obtained at 77 K by measuring the induced flux due to the axial extraction of the sample from a coil in applied fields H up to 21 kOe. For all the samples a linear decrease of σ against $1/H$ was observed. The extrapolation of σ at infinite field gives the value of saturation magnetization at 77 K (see Table I). At this temperature, the weak superparamagnetic effect observed at room temperature on the Mössbauer spectrum can be neglected for particle sizes above 10 nm. The variation of σ_s against the specific surface area is shown in Fig. 5.

As previously mentioned, particles in the 44 to 47 nm range (28 to $16\text{ m}^2\text{ g}^{-1}$) are frequently twinned and the increase of the crystallite size is smaller than the increase of the particle size. Therefore, the variation of the magnetization

with the crystallite surface area, which is unknown, should be slightly more important than the variation obtained by taking the BET particle surface area. Nevertheless, in Fig. 5 two variation ranges of the magnetization versus particle (or crystallite) size appear clearly.

By taking into account only monocrystalline particles ($\text{Fe}_2\text{O}_3\text{-72}$; $\text{Fe}_2\text{O}_3\text{-50}$ and $\text{Fe}_2\text{O}_3\text{-28}$), a linear relation between magnetization and crystallite surface area can be obeyed, as proposed by Mollard *et al.* [13], but the extrapolated value at infinite size (94 emu cgs g^{-1} or $1.33\text{ }\mu\text{B}$ per iron atom) corresponding to the bulk value at 77 K is without meaning with respect to the moment value ($1.25\text{ }\mu\text{B}$) predicted by the Néel structure [1] supposing all the vacancies on octahedral sites. Consequently the surface/volume should not be the only parameter taken into account.

3. Discussion

Mollard *et al.* [5] have found that the specific saturation magnetization σ_s (s) of small crystallites of $\gamma\text{-Fe}_2\text{O}_3$ decreases linearly with specific surface

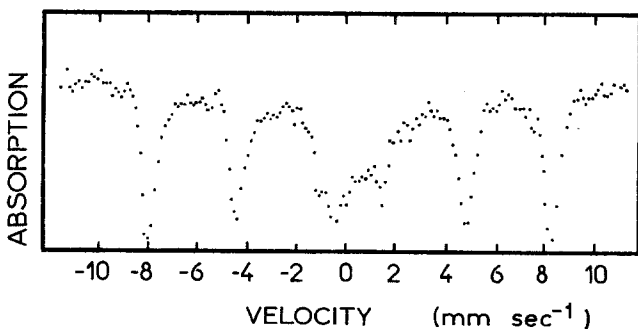


Figure 3 Mössbauer spectrum from $\gamma\text{-Fe}_2\text{O}_3\text{-16}$ taken at room temperature. Dots correspond to experimental values and continuous line to calculated values after the fit of hyperfine fields.

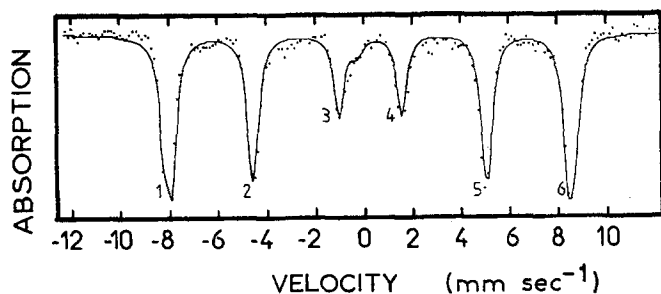


Figure 4 Mössbauer spectrum from $\gamma\text{-Fe}_2\text{O}_3\text{-72}$ taken at room temperature.

area s from the bulk value $\sigma_s(\infty)$. Using a set of samples, the value extrapolated for the bulk magnetization is $1.215 \mu\text{B}$ close to the theoretical value. For the surface layer the Néel's colinear structure is not valid and its magnetization is lowered so, Mollard *et al.* suggested that an electron transfer with the O and OH layers and oxidation of some cations can explain the decrease in magnetization. Under these conditions the external surface of a particle must be considered as different from that of crystallite boundaries. Moreover, some changes in the morphology and particularly the development of new exposed planes will result in a change of the surface magnetization. Results shown in Fig. 5 establish clearly that the surface effect is different according to the size range. For the smallest crystallites exhibiting only $\{100\}$ and $\{111\}$ faces, the size effect is more important than for larger particles also exhibiting $\{110\}$ faces. In fact, it seems that, below a critical size, close to 20 or 30 nm, a stable morphological configuration of individual monocrystalline particles cannot be developed and some discontinuity must appear in physico-chemical

properties as illustrated by the heat of the $\gamma \rightarrow \alpha$ transformation. This "morphological metastability" leads to some variations in crystalline field, which contributes to explaining the size effect on the physical adsorption of CO_2 , previously reported [14], and of other molecules [15]. The discontinuity does not appear in polycrystalline samples where grain boundaries act as stabilizing interfaces.

4. Conclusion

These results emphasize the dependence of physico-chemical properties of solid in a divided state on their preparative conditions. Therefore, more information than the specific surface area is necessary to characterize such solids. As the surface/volume ratio becomes greater, size effect rises, leading to modifications in the measured values, but in most cases size variation below a critical value results in morphological or structural modifications. In the case of $\gamma\text{-Fe}_2\text{O}_3$ microcrystals evidence is given for the decrease in the magnetization of the surface layer, but the importance of this decrease depends on the morphological configuration.

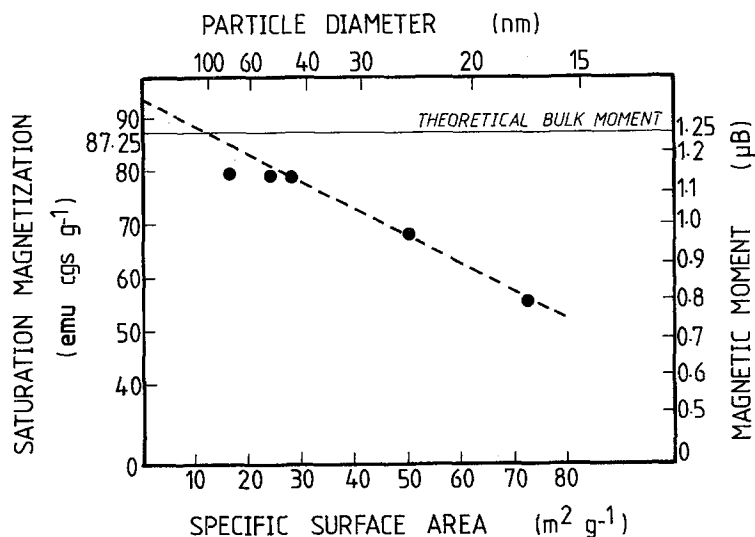


Figure 5 Influence of the particle size on the saturation magnetization of $\gamma\text{-Fe}_2\text{O}_3$ at 77 K.

Acknowledgements

The authors are very grateful to Drs P. Bussière, G. A. Martin and J. A. Dalmon for their contribution to the Mössbauer spectra and magnetic measurements and to Mrs Ch. Leclercq for the micrographs of γ -Fe₂O₃.

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*Received 1 March
and accepted 17 March 1983*