

A temperature and magnetic field dependence Mossbauer study of (-Fe₂O₃)

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Abstract

(-Fe₂O₃ was synthesized as nanoparticles by a pre-vacuum heat treatment of yttrium iron garnet (Y₃Fe₅O₁₂) in a silica matrix at 300-C followed by sintering in air at 1,000-C for up to 10 h. It displays complex magnetic properties that are characterized by two transitions, one at 480 K from a paramagnet (P) to canted antiferromagnet (CAF1) and the second at ca. 120 K from the canted antiferromagnet (CAF1) to another canted antiferromagnet (CAF2). CAF2 has a smaller resultant magnetic moment (i.e. smaller canting angle) than CAF1. Analysis of the zero-field Mossbauer spectra at different temperatures shows an associated

discontinuity of the hyperfine field around 120 K. In an applied field, the different

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magnetic sublattices were identified and the directions of their moments were assigned. The moments of the two sublattices are antiparallel and collinear at 160 K but are at right angle to each other at 4.2 K.

Key words : Mossbauer spectra . nanoparticles . complex magnetic properties

1 Introduction

(-Fe₂O₃, a rare orthorhombic polar form of iron oxide, was recently prepared as nanoparticles in silica [1–4] and its structure from powder neutron diffraction was successfully modeled to that of the iso-structural AlFeO₃ [1]. It was shown to exhibit interesting magnetic properties such as a very high coercive field of $\delta 2$ T at 300 K and displays a very complex phase diagram with at least three ground states [1–3].

In our previous study of the magnetic properties and Mossbauer spectroscopy of (-Fe₂O₃ as a function of temperature [1], we observed two sharp discontinuities; one at 480 K and the other centered at ca. 120 K. It is clear from the magnetization data that the transition at 480 K is from a paramagnet to an ordered state and that at 120 K is accompanied by a severe loss of magnetic hardness and a change in canting angle from a wide angle at high temperature to a narrow one at low temperature. However, the compositions and orientations of the magnetic moments in the respective sublattices remained unresolved. However, due to the similar behavior found for α -Fe₂O₃, we associated this discontinuity to a Morin-like transition. The present work deals principally with the study of the temperature dependence of the Mossbauer spectra in an external applied magnetic field in an attempt to clarify the origin of the change of canting angle at 120 K.

2 Preparation and characterization

The compound was reproducibly prepared as nanoparticles in a silica matrix by the sol-gel technique. The procedure for the production of (-Fe₂O₃ is quite specific and was described elsewhere [1]. Although the amount of parasitic α -Fe₂O₃ can be minimized by the choice of the sintering temperature between 900 and 1,000-C and the period (5–10 h), no absolute optimization has been reached. Therefore, for all the samples prepared to date Mossbauer spectroscopy suggests the presence of a variable fraction of α -Fe₂O₃.

Powder X-ray diffraction was recorded at room temperature using the Bragg-

Brentano geometry on a Siemens D500 employing Co Ka₁ radiation (1.789 Å). Variable temperature (2–300 K) neutron powder diffraction was recorded on the D20 High flux multiple detector diffractometer at the Institut Laue Langevin at

Grenoble employing an excitation wavelength of 2.41 Å.

Magnetization data were measured using a Quantum Design SQUID magnetometer operating in the temperature range 2 to 400 K and field of up to 50 kOe. All measurements we performed on samples immobilized in polymethylmethacrylate polymer, in their virgin state, to prevent motion of the particles in high applied

fields [5]. Susceptibility at high temperatures was measured using a Faraday balance equipped with a variable temperature oven operating between 300 and 1,300 K and a field of up to 10 kOe.

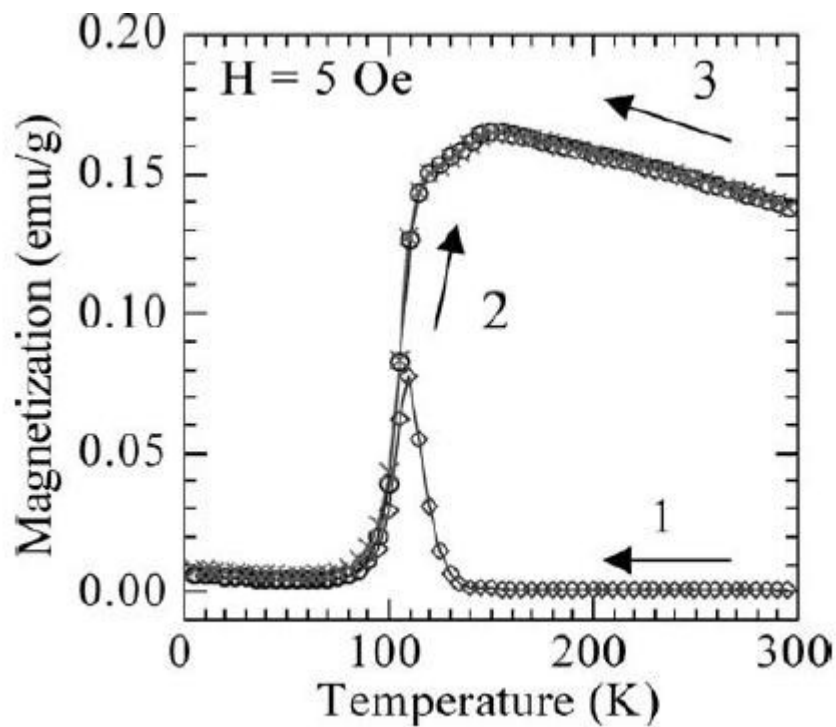


Figure 1 Temperature dependence of the magnetization in 5 Oe on first-cooling (1) and warming (2) and second-cooling (3).

The ^{57}Fe powder absorption Mossbauer spectra in zero-field were recorded at different temperatures and those in 3 and 5 T applied perpendicular to the g-ray at

4.2, 120, and 160 K by use of a Janis cryosystem. A $^{57}\text{Co}/\text{Rh}$ source and a conventional constant acceleration mode were employed. The raw spectra were summed and treated using either DASUM or NORMOSS or MOSFIT [6]. The isomer shift values are relative to that of iron metal at 293 K. The sample contains a small amount of $\alpha\text{-Fe}_2\text{O}_3$ (about 10% mol) that was fitted to a sextet with its characteristic parameters. For the evaluation of the angle α_1 between the direction of the applied magnetic field B_{app} and of the effective hyperfine field B_{eff} , we used the equation below:

$$B_{\text{hf}} = \frac{1}{4} B_2 \left[B_2 - 2B_{\text{eff}} \cos \alpha_1 \right]$$

where B_{hf} is the hyperfine field in zero applied field.

3 Results and discussion

X-ray diffraction of the samples (annealed at 1,000-C for 6 h) exhibits very weak Bragg peaks on a high background. In contrast, the variable temperature neutron

powder diffraction ($\lambda = 2.41 \text{ \AA}$) exhibits a better resolution and a proportionally higher intensity of the sharp peaks compared to the background. Starting from the unit cell parameters of AlFeO_3 [7], we successfully performed a pattern matching using FULLPROF [8]. The fitted unit-cell parameters within $\text{Pna}2_1$ space group are

$a = 5.1104(5)$, $b = 8.7362(7)$, $c = 9.466(1) \text{ \AA}$ [$R_p = 13.6$ and $R_{wp} = 12.2$] and these values are in good agreement with those reported in the literature [4, 9–11]. In the structure of $\alpha\text{-Fe}_2\text{O}_3$ iron occupies four different crystallographic positions; Fe_1 , Fe_2 and Fe_3 have octahedral coordination and Fe_4 is tetrahedral [1]. By valence

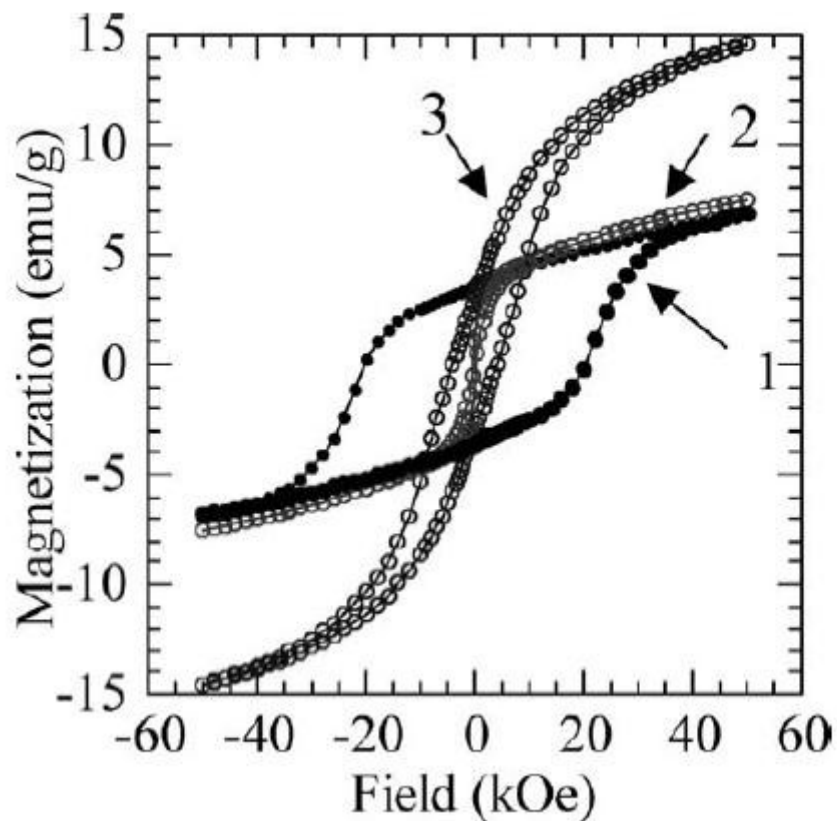


Figure 2 Hysteresis loops at 200 K (1), 100 K (2) and 2 K (3).

consideration all the iron ions are trivalent and are expected to be high spin (5/2) due to the weak oxygen ligand field.

The magnetic properties are quite unusual. Above 480 K the sample is paramagnetic and below it is in an ordered magnetic state. Below 300 K, the evolution of the magnetization as a function of temperature is quite sensitive to the field strength and to the history of the sample as well as the temperature at which the measuring field is applied. On cooling a virgin sample in a small field (<5 Oe) we first observed a sharp peak at 110 K and upon warming in the same field there is a sudden increase around 100 K to two anomalies (120 and 150 K) and then it decreases linearly up to 400 K (Figure 1). Subsequent cooling and warming of the sample in the same field follows the initial warming run.

Measurements of the isothermal magnetization were measured by performing hysteresis loops between +50 kOe and -50 kOe at different temperatures (Figure 2). We note first an unexpectedly wide hysteresis loop at 300 K, similar to that observed by Jin et al. [2, 3]. In addition, on cooling the sample the hysteresis loop disappears

at 110 K. In all cases, we notice that the maximum field of 50 kOe of our magnet is not enough to achieve complete saturation of the magnetization of this sample. However, the linear dependence of the magnetization with field is indicative of an antiferromagnetic ground state with a canting [12, 13]. This is also consistent with the low magnetization values in an applied field of 50 kOe. The large change in magnetic hardness is an indication of a change of magneto-crystalline anisotropy that may result from either a change of geometry of the iron sites, or a re-orientation of the moments as found for α -Fe₂O₃. Further analysis of our neutron scattering data should reveal which of the two possibilities is correct.

The Mossbauer spectrum originating from α -Fe₂O₃ (Figure 3) has contribution from four different Fe sites but two of them (Fe₂ and Fe₃) have very close hyperfine

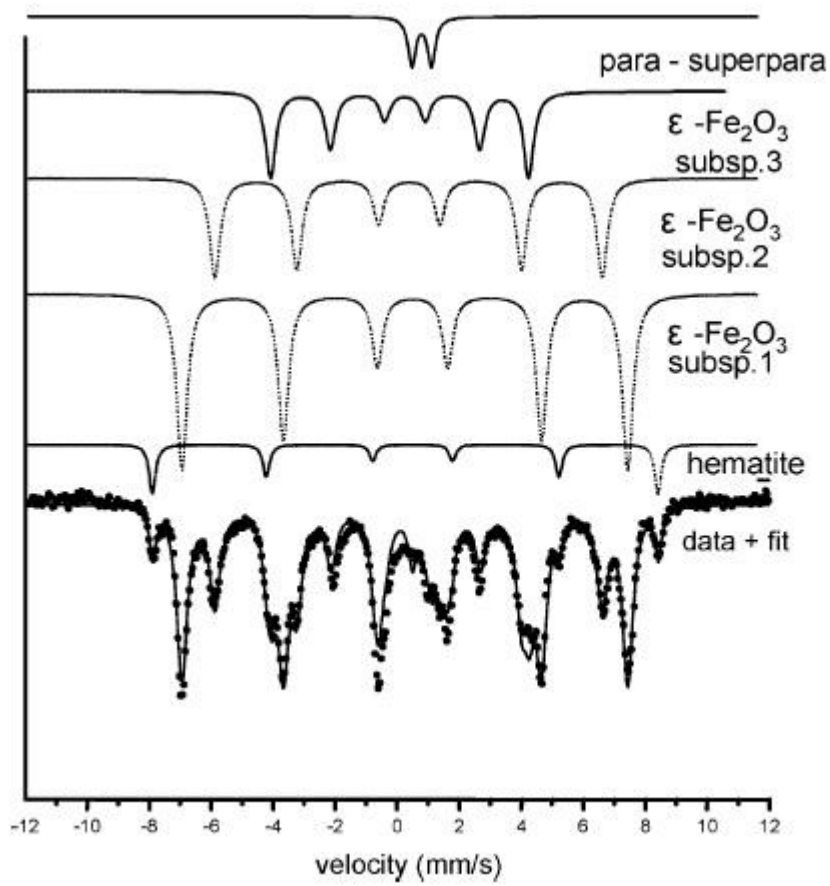


Figure 3 Experimental Mossbauer spectrum and the components as described in the text.

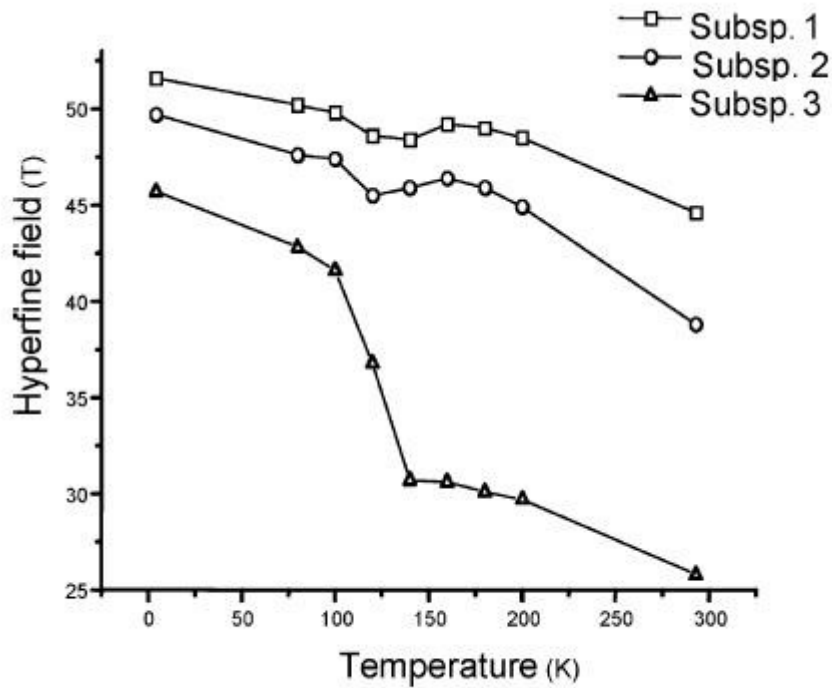


Figure 4 Temperature dependence of the hyperfine field for the three subspectra (subsp. 1 and 2 for octahedral Fe; subsp. 3 for tetrahedral Fe).

fields and chemical shifts and cannot be distinguished (labeled here as subsp. 1). Both Fe2 and Fe3 occupy octahedral sites with similar environment and form the edge-sharing double chains. One Fe (Fe1, labeled subsp. 2) is octahedral and is attached on top of the double chains while the fourth Fe is tetrahedral (Fe4, labeled subsp. 3). Each of the spectra was fitted by these three independent sextets (Fe1, Fe2 + Fe3 and Fe4) and one further sextet due to a small amount of residual hematite. The Mossbauer spectra during cooling are presented in [1]. A plot of the

Table I Isomer shift, quadrupole splitting, effective field and magnetic orientation of the different sublattices of (-Fe₂O₃ at 4.2 and 160 K

	Isomer shift d (mm/s)	Quadrupole splitting DEQ (mm/s)	Effective field Beff (T)	a1 (-)
4.2 K; 0 T				
Fe2	0.48	-0.02	51.8	
Fe3	0.51	-0.09	51.7	
Fe1	0.47	-0.03	50.5	
Fe4	0.31	-0.03	45.9	
4.2 K; 5 T				
Fe2	0.49	-0.04	55.8	35
Fe3	0.45	-0.02	48.1	136
Fe1	0.40	-0.02	49.5	99
Fe4	0.43	-0.04	46.4	81
160 K; 0 T				
Fe2	0.47	-0.17	49.3	
Fe3	0.46	-0.35	49.0	
Fe1	0.44	0.01	46.3	
Fe4	0.27	-0.14	30.5	
160 K; 5 T				
Fe2	0.45	-0.09	54.0	19
Fe3	0.45	-0.17	44.7	148
Fe1	0.44	-0.01	42.4	139
Fe4	0.24	-0.18	34.4	36

hyperfine fields of the three sites as a function of temperature (Figure 4) shows a small kink for sextets 1 and 2 leading to a linear extrapolated-zero-temperature value of 51.87 and 50.52 T, respectively. However, variations of the hyperfine field for sextet 3 (tetrahedral Fe4) show a sudden change at the transition near 120 K suggesting a change in the geometry associated with the transition. Subsequently, similar observations were reported by other authors [14].

Therefore, Mossbauer experiments were performed at 160, 120 and 4 K in

external applied magnetic field of 3 and 5 T perpendicular to the g-ray beam propagation. From the fitting procedure the respective hyperfine fields and angles were derived. The fitted parameters of each component are gathered in Table I.

Two magnetic sublattices were identified (Fe2 + Fe3) and (Fe1 + Fe4). The magnetic moments of the two sublattices are antiparallel to one another at 160 K and collinear to the applied magnetic field. At 4.2 K the moments of the (Fe1 + Fe4) sublattice tend to orient perpendicularly to B_{app}. The results can be interpreted as follows: the anisotropy at 160 K is strong, as already experienced by the magnetic

measurements while at 4.2 K it is weak. Thus, the moment is easily flopped as also observed by the presence of metamagnetism below 50 K.

4 Conclusion

We have prepared the rare (γ -Fe₂O₃) as nanometer size particles by the decomposition of yttrium iron garnet in silica in air. The proposed crystal structure has been

confirmed from pattern matching of the powder neutron diffraction data. The magnetic properties show unusual behaviors, viz: temperature dependence magnetic hardness ranging from zero to 22 kOe, three ground states separated by a Neel transition at 480 K and one associated with a change in the canting angle similar to that of a Morin transition below 150 K. The Mossbauer spectra under magnetic field

indicate a collinear two-sublattice antiferromagnet above 120 K where one is easily flopped to the perpendicular direction below 120 K.

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