

X-ray diffraction and ^{57}Fe Mössbauer spectra of the system $\text{Fe}_2\text{O}_3\text{-Ga}_2\text{O}_3$

S. MUSICIĆ*, S. POPOVIĆ*†, M. RISTIĆ*

**Rudjer Bošković Institute, P.O. Box 1016, 41001 Zagreb, Croatia, Yugoslavia*

†*Department of Physics, Faculty of Science, University of Zagreb, P.O. Box 162, 41001 Zagreb, Croatia, Yugoslavia*

The influence of gallium substitution on the chemical and structural properties of haematite, $\alpha\text{-Fe}_2\text{O}_3$, has been studied using X-ray diffraction and ^{57}Fe Mössbauer spectroscopy. The presence of only $\alpha\text{-(Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ phase is detected for the compositions with x between 0.01 and 0.90. A gradual decrease of the unit-cell parameters of $\alpha\text{-(Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ with the increase of gallium substitution is measured. ^{57}Fe Mössbauer spectra showed that the value of the magnetic hyperfine field of pure $\alpha\text{-Fe}_2\text{O}_3$ decreases with increasing gallium for iron substitution. The hyperfine magnetic structure, which is observed for $\alpha\text{-(Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ at room temperature, collapsed for the composition with $x \approx 0.50$. The changes in the ^{57}Fe Mössbauer spectra of the $\alpha\text{-(Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ phase are discussed in the sense of the electronic relaxation and the superparamagnetic effects.

1. Introduction

In the last decade significant attention has been paid to the investigation of the chemical and structural properties of haematite, $\alpha\text{-Fe}_2\text{O}_3$, in which some iron ions are substituted by other metal ions. These systems have been investigated using different experimental techniques, such as X-ray diffraction, neutron diffraction, IR spectroscopy and Mössbauer spectroscopy.

Taylor and Schwertmann [1] investigated the influence of Al^{3+} on the precipitates formed by aerial oxidation of FeCl_2 , FeSO_4 or FeCO_3 solution at pH 5.5 to 7 to 20°C . They found that the presence of aluminium at levels $\text{Al}/(\text{Al} + \text{Fe}) = 0.09$ to 0.30 inhibited the formation of lepidocrocite, $\gamma\text{-FeOOH}$, and maghaemite, $\gamma\text{-Fe}_2\text{O}_3$, in favour of goethite, $\alpha\text{-FeOOH}$. The formation of ferrihydrite ("amorphous" iron(III) hydroxide) was favoured at higher levels of aluminium. This effect of aluminium was explained by a decrease in the hydrolysis-oxidation rate of the Fe(II) system.

De Grave, Bowen and Weed [2] studied the relation between the aluminium content and the average magnetic hyperfine field at room temperature for $\alpha\text{-(Fe}_{1-x}\text{Al}_x)_2\text{O}_3$ over a large composition range up to $x = 0.32$.

Murad and Schwertmann [3] recorded, at room temperature, the Mössbauer spectra of 15 haematite samples with aluminium substitution up to 10 mol %. The Mössbauer spectra showed that the magnetic hyperfine field decreases both with increasing the aluminium for iron substitution and with decreasing crystal size.

Fysh and Clark [4] found that the Mössbauer recoil-free fraction at room temperature increased from 0.64 for pure $\alpha\text{-Fe}_2\text{O}_3$ to 0.82 for the sample having

14 mol % of iron substituted by aluminium. This result was confirmed by Murad [5].

Fysh and Fredericks [6] investigated synthetic aluminium containing haematites by FTIR spectroscopy. They found that for aluminium containing haematites prepared at 950°C a linear relationship exists between aluminium content (up to 10 mol % Al substitution) and the location of the IR band near 470 cm^{-1} .

Vandenbergh, Verbeeck and De Grave [7] used Mössbauer spectroscopy to study the Morin transition in manganese-substituted haematites. The magnetic behaviour of manganese-substituted haematites is qualitatively similar to aluminium-substituted haematites, although manganese affects the Morin transition temperature more than aluminium. Since the manganese substitution did not change the crystal structure parameters, it was concluded that in manganese-substituted haematites the Morin transition is mainly influenced by the magnetocrystalline contribution of Mn^{2+} ions to the anisotropy.

Barron and Torrent [8] found that the affect of both particle size and particle morphology on the colour of haematite is unimportant compared to that of aluminium substitution.

In the present study the influence of gallium substitution on the chemical and structural properties of haematite is determined. The $\text{Fe}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system has been investigated using X-ray diffraction and ^{57}Fe Mössbauer spectroscopy as experimental techniques.

2. Experimental procedure

2.1. Preparation of samples

Mixed hydroxides of Fe(III) and Ga(III) were coprecipitated at pH 7, and this pH value was kept constant during the precipitation process. The coprecipitates

TABLE I Crystallographic data for α -Fe₂O₃, α -Ga₂O₃ and β -Ga₂O₃ [9]

JCPDS PDF Card No.	Compound	Space group	Unit-cell parameters (nm)
13-534	α -Fe ₂ O ₃	$R\bar{3}c(167)$	hexagonal axes: $a = 0.5034$ $c = 1.3752$
6-503	α -Ga ₂ O ₃	$R\bar{3}c(167)$	hexagonal axes: $a = 0.4979$ $c = 1.3429$
11-370	β -Ga ₂ O ₃	$A2/m(12)$	monoclinic axes: $a = 0.580$ $b = 0.304$ $c = 1.223$ $\beta = 103.7^\circ$

were washed at near neutral pH (bidistilled water plus a few drops of NH₃ · aq), and then dried. Samples S1 to S13 were thermally treated for 1 h at 200°C, for 1 h at 300°C, for 1 h at 400°C and for 5 h at 600°C (“step-by-step” heating). Two Ga₂O₃ samples, supplied by Koch-Light and Merck, were also analysed by X-ray diffraction.

2.2. Instrumentation

X-ray diffraction patterns were taken at room temperature using a counter diffractometer with monochromatized CuK α radiation (Philips diffractometer, proportional counter, graphite monochromator). The phases found in our samples (α -Fe₂O₃, α -Ga₂O₃, β -Ga₂O₃) were easily identified according to the data contained in the Powder Diffraction File (JCPDS) [9].

Mössbauer spectra were recorded using a commercial Mössbauer spectrometer produced by Wissenschaftliche Elektronik GmbH (D-8130 Starnberg, West

Germany). A ⁵⁷Co–Rh source was used. The standard absorbers, α -Fe, α -Fe₂O₃ and ⁵⁷Fe–Rh were also used.

3. Results and discussion

The ionic radii of Fe³⁺ and Ga³⁺ are similar (0.067 nm for Fe³⁺ and 0.062 nm for Ga³⁺), and for this reason the unit-cell parameters of α -Fe₂O₃ and α -Ga₂O₃ are also similar. These compounds belong to the same space group, i.e. they are isostructural having rhombohedral symmetry. β -Ga₂O₃ possesses monoclinic symmetry. Crystallographic data for α -Fe₂O₃, α -Ga₂O₃ and β -Ga₂O₃ are given in Table I. For α -Fe₂O₃ and α -Ga₂O₃ the difference in the a parameters is 1.09%, and the difference in the c parameters is 2.35%.

The unit cell parameters of α -Fe₂O₃ (sample S1) and α -Ga₂O₃ (sample S2), measured in this work, were practically equal to the literature data [9]. For this reason, the measured data were used for calibration of the angular scale of the diffractometer.

The results of X-ray diffraction phase analysis are shown in Table II. Samples S3 to S12 are α -phase, α -(Ga _{x} Fe _{$1-x$})₂O₃, which is isostructural with α -Fe₂O₃ and α -Ga₂O₃. The replacement of Fe³⁺ with Ga³⁺ ions is manifested in gradual small shifts of diffraction lines toward higher Bragg angles, i.e. a decrease of the unit-cell parameters takes place (Figs 1 and 2). The relative decrease of the c parameter is more than two times as large as the decrease of the a -parameter. Diffraction patterns do not show 001 diffraction lines at higher Bragg angles for calculation of the c parameter. Instead, one can make use of diffraction lines hkl , for which the index l is dominant in relation to the indices h and k . Fig. 1 shows a gradual separation of diffraction lines 212 and 108 of the α -phase with the

TABLE II X-ray diffraction phase analysis of the system Fe₂O₃–Ga₂O₃

Sample	Molar fraction of Ga, x	Composition	Note	Colour (visually)
S1	0	α -Fe ₂ O ₃		brown–violet
S3	0.01	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃		brown–violet
S4	0.03	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃		brown–violet
S5	0.05	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃		brown–violet
S6	0.10	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃		brown
S7	0.15	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃		brown
S8	0.20	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	brown
S9	0.30	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	brown–violet
S10	0.50	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	brown–ochre
S11	0.70	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	brown–ochre
S12	0.90	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	ochre
S13	0.95	α -(Ga _{x} Fe _{$1-x$}) ₂ O ₃	broadened diffraction lines	white–yellow
S2	1	β -(Ga _{x} Fe _{$1-x$}) ₂ O ₃ + β -Ga ₂ O ₃ + α -Ga ₂ O ₃	broadened diffraction lines	white
Ga ₂ O ₃ (Koch-Light)		β -Ga ₂ O ₃	broadened diffraction lines	white
Ga ₂ O ₃ (Merck)		β -Ga ₂ O ₃	broadened diffraction lines	white

TABLE III Hyperfine magnetic fields measured for samples S1 and S3 to S10

Sample	$H_{5/2}$ (kOe)	
S1	517	
S3	517	
S4	514	
S5	508	
S6	503	
S7	497	
S8	488	
S9	466	
S10	M_1	397
	M_2	366

increase of gallium substitution. Also, Fig. 1 shows a gradual increase of the diffraction line intensities with the increase of gallium substitution. This is a consequence of a decrease of the absorption coefficient, as well as the increase of the average structural factors, as gallium replaces iron.

The increase of the gallium content results in a small broadening of diffraction lines. The spectral doublet components $K\alpha_1\alpha_2$ are not resolved at higher Bragg angles for $x \geq 0.20$.

Sample S13 ($x = 0.95$) is a mixture of the dominant α - $(\text{Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ phase and the β - $(\text{Ga}_x\text{Fe}_{1-x})_2\text{O}_3$ phase. The actual stoichiometry of sample S13 is not investigated, and for this reason it is supposed that the x fraction of gallium for iron substitution has the same value in both α and β phases. Sample S2 is a mixture of the dominant β - Ga_2O_3 phase and the α - Ga_2O_3 phase. The commercial Ga_2O_3 samples, supplied by Koch Light and Merck, show only β - Ga_2O_3 with broadened diffraction lines.

The characteristic Mössbauer spectra of α - Fe_2O_3 and the Fe_2O_3 - Ga_2O_3 solid solutions, recorded at room temperature, are shown in Figs 3, 4 and 5. Sample S1 (Fig. 3) is characterized by a typical sextet in which the peak intensity ratios are close to 3:2:1:2:3. The Mössbauer spectrum of sample S1 can be ascribed to well crystallized α - Fe_2O_3 . The corresponding value of the hyperfine magnetic field is not changed for a small gallium substitution ($x = 0.01$). However, with further increase of the Ga^{3+} content in the α - Fe_2O_3 structure the hyperfine magnetic field (average) reduces. The measured values of the hyperfine magnetic fields are given in Table III. The line-widths increase gradually with increasing

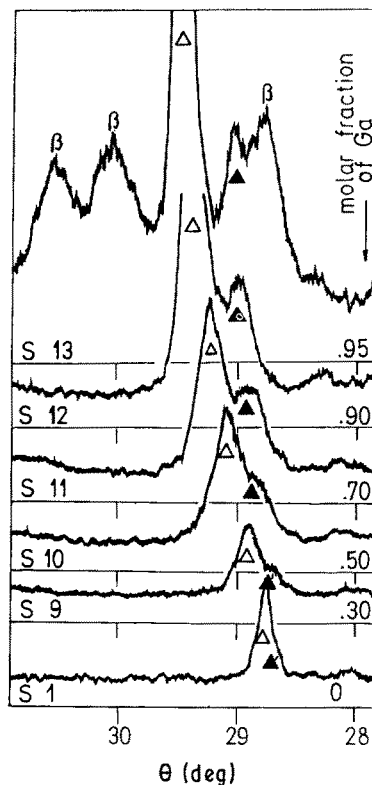


Figure 1 A characteristic part of X-ray diffraction patterns in the system Fe_2O_3 - Ga_2O_3 (Radiation: monochromatized $\text{CuK}\alpha$). A gradual separation of diffraction lines 212 (\blacktriangle) and 108 (Δ) (α -phase), with the increase of the gallium content, is shown.

Ga^{3+} content in the Fe_2O_3 - Ga_2O_3 solid solutions. Also, there is a corresponding increase of the inner absorption lines from sample S4 to sample S10. The Mössbauer spectrum of sample S10 shows the separation of one sextet into two (or more) sextets. Two sextets are relatively well resolved and their hyperfine magnetic fields are given in Table III. There are no hyperfine magnetic splitting components in the Mössbauer spectra of samples S11, S12 and S13 at room temperature.

The Mössbauer spectrum of sample S12 indicates the central quadrupole doublet with very small asymmetry. However, this asymmetry is more pronounced in the Mössbauer spectrum of sample S13, thus indicating the presence of the superposition of two doublets. Their parameters are the following: $\delta_1 = 0.319 \text{ mm sec}^{-1}$ and $Q_1 = 0.482 \text{ mm sec}^{-1}$ for the first doublet, and $\delta_2 = 0.337 \text{ mm sec}^{-1}$ and $Q_2 =$

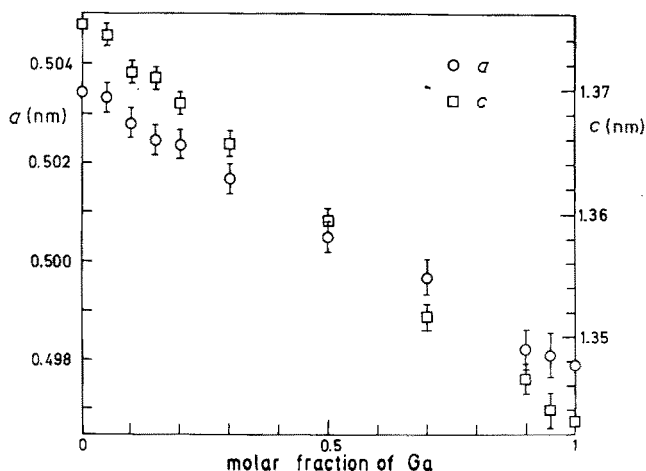


Figure 2 Variation of the unit-cell parameters of the α -phase, in the system Fe_2O_3 - Ga_2O_3 , as a function of the molar fraction of gallium. Vertical bars indicate the estimated experimental errors.

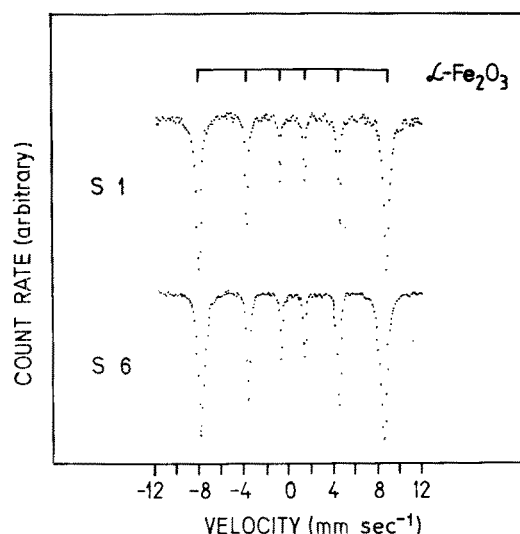


Figure 3 Mössbauer spectra of samples S1 and S6 recorded at room temperature.

0.655 mm sec⁻¹ for the second doublet. Isomer shifts δ_1 and δ_2 are given relative to α -Fe. This result indicates the presence of the ⁵⁷Fe resonant atoms in two different structural environments, which is in agreement with the X-ray diffraction results (α -(Ga_xFe_{1-x})₂O₃ and β -(Ga_xFe_{1-x})₂O₃ were detected).

In the particles of the (Ga_xFe_{1-x})₂O₃ solid solutions there is a non-uniform (statistic) distribution of dopant ions. Also various lattice defects can exist as a result of the experimental procedure by itself ("wet" precipitation and solid state transformation at elevated temperature). In these particles the ⁵⁷Fe resonant atoms have different types of nearest-neighbour (n.n.) configuration (electronic environment). For this

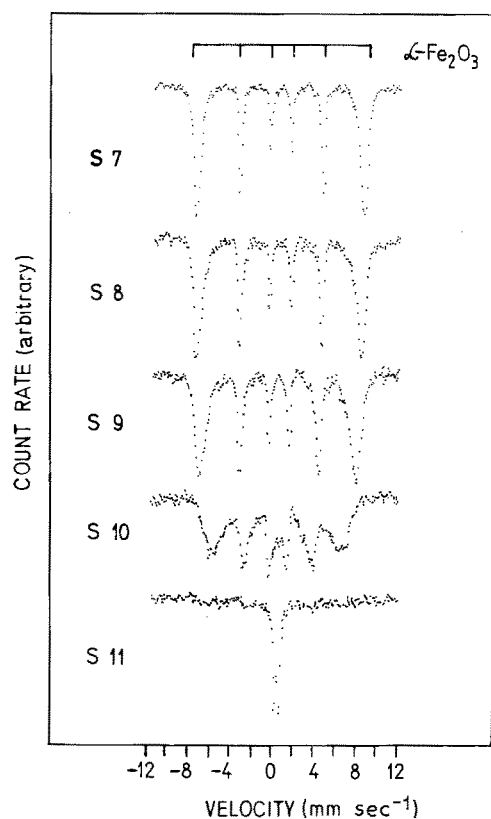


Figure 4 Mössbauer spectra of samples S7, S8, S9, S10 and S11 recorded at room temperature.

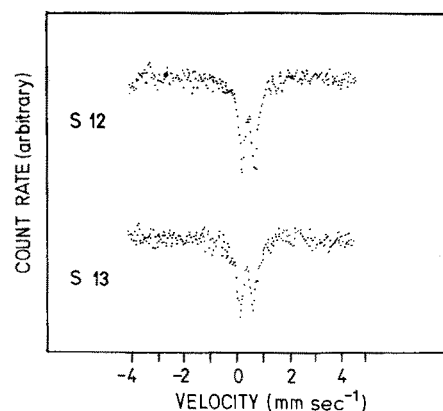


Figure 5 Mössbauer spectra of samples S12 and S13 recorded at room temperature.

reason, the ⁵⁷Fe resonant atoms are characterized with different contributions to the Mössbauer effect.

Generally, the Mössbauer spectra of iron oxides doped with foreign metal ions have been interpreted in the sense of the electronic relaxation and the superparamagnetic effects [10, 11]. The distributions of the hyperfine magnetic fields have been explained as a result of the local variations in the environment of the γ -resonant atoms. In specific cases, the influence of particle size must also be taken into account. Coey showed [12, 13] that for certain concentrations of statistically substituted diamagnetic ions, the magnetic ions should be found in magnetic clusters of various size. Ishikawa suggested [14, 15] that such clusters might behave superparamagnetically. Iron ions in different magnetic clusters are expected to have a different magnetic ordering temperature (Curie temperature or Neel temperature), as well as a different temperature dependence of the hyperfine magnetic field. Recently, Chadwick and coworkers [16] studied the superparamagnetism in aluminium substituted ferrihydrite. Their experimental results could not be explained only by the superparamagnetism, and for this reason the relaxation effects were also considered.

References

1. R. M. TAYLOR and U. SCHWERTMANN, *Clays Clay Miner.* **26** (1978) 373.
2. E. DE GRAVE, L. H. BOWEN and S. B. WEED, *J. Magn. Magn. Mater.* **27** (1982) 98.
3. E. MURAD and U. SCHWERTMANN, *Clays Clay Miner.* **34** (1986) 1.
4. S. A. FYSH and P. E. CLARK, *Phys. Chem. Miner.* **8** (1982) 257.
5. E. MURAD, *Phys. Lett.* **111A** (1985) 79.
6. S. A. FYSH and P. M. FREDERICKS, *Clays Clay Miner.* **31** (1983) 577.
7. E. DE GRAVE, D. CHAMBAERE and L. H. BOWEN, *J. Magn. Magn. Mater.* **30** (1983) 349.
8. V. BARRON and J. TORRENT, *Clays Clay Miner.* **32** (1984) 157.
9. International Centre for Diffraction Data, Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, Pa. 19081, USA.
10. S. MORUP, J. A. DUMESIC and H. TOPSOE, in "Application of Mössbauer Spectroscopy", Vol. II (Academic Press, New York, 1980).
11. R. NAGARAJAN and J. K. SRIVASTAVA, *Phys. Status Solidi (b)* **81** (1977) 107.

12. J. M. D. COEY, *Phys. Rev. B* **6** (1972) 3240.
13. J. M. D. COEY and D. KHALAFALLA, *Phys. Status Solidi (a)* **11** (1972) 229.
14. Y. ISHIKAWA, *J. Phys. Soc. Jpn* **17** (1962) 1877.
15. Y. ISHIKAWA, *J. Appl. Phys.* **35** (1964) 1054.
16. J. C. CHADWICK, D. H. JONES, M. F. THOMAS and M. DEVENISH, *Hyperfine Inter.* **28** (1986) 537.

*Received 11 July
and accepted 18 November 1988*