Crystal Structure of Synthetic Feroxyhite δ-FeOOH Studied with Neutron Diffraction

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The synthetic polycrystalline sample of δ-FeOOH was investigated by means of neutron diffraction. Based on these data, the parameters of the crystal structure are determined. This compound crystallizes in the hexagonal structure described by the space group $P\bar{3}m1$, in which the oxygen O^{2-} ions in the $2d$ site form the octahedral network. The Fe^{3+} ions randomly occupy the $1a$ (53%) and $1b$ (47%) sites, and the hydrogen atoms half-occupy two positions in the $2d$ site. The magnetic contribution to the neutron diffraction pattern is very small and does not give possibility to determine the magnetic structure.

topics: feroxyhite δ-FeOOH, crystal structure, neutron diffraction

1. Introduction

The oxydroxides of iron FeOOH form four structural phases described by the letters α, β, γ, δ. The crystal structure and magnetic properties of the first three phases are already determined. The α [1] and γ [2] phases have a orthorhombic, while β phase [3] has a tetragonal crystal structure. The phases α, β and γ are antiferromagnets with a collinear magnetic order of the Fe^{3+} ions [1–3]. The crystal structure of the δ-FeOOH phase was investigated by X-ray diffraction method by different authors [4–8]. All these investigations suggest the hexagonal crystal structure similar to $Fe(OH)_2$ with unit cell parameters equal to $a = 2.95(1)$ Å and $c = 4.53(1)$ Å. The results of these measurements are not consistent with each other concerning the distribution of the Fe^{3+} ions in the network of the oxygen O^{2-} ions. Okamoto [4] suggests that Fe^{3+} ions statistically occupy two octahedral positions, i.e., $1a$: $(0, 0, 0)$ and $1b$: $(0, 0, \frac{1}{2})$, while for Francombe and Rooksby [5] Fe^{3+} ions occupy both octahedral (40%) and tetrahedral (5%) sites, i.e., $(\frac{1}{3}, \frac{2}{3}, 0)$, $(\frac{2}{3}, \frac{1}{3}, 0)$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. Eggleton and Fitzpatrick [6] indicate that 36% of Fe^{3+} ions is in a tetrahedral site.

According to Patrat et al. [7] the crystal structure of δ-FeOOH is described by the space group $P\bar{3}m1$. This crystal structure based on a close packed hexagonal oxygen lattice is similar to that of $Fe(OH)_2$. Oxygen is in the $2d$ sites, i.e., $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, -z)$ with $z = 0.246$ and hydrogen occupies half of the tetrahedral intersites $2d$ with $z' = 0.51$ and iron occupies half of the $1a$ and $1b$ sites. Drits et al. [8] confirmed this model.

Magnetic measurements indicate ferrimagnetic properties with the small value of saturation moment equal to 0.3 μ_B [9]. The change of magnetization at 360 K is connected with the decomposition of the sample. The magnetic properties were investigated by the Mössbauer spectroscopy by Dezsi et al. [10]. Two internal magnetic fields with different temperature dependence were observed in the Mössbauer spectrum. They confirm the distribution of the Fe^{3+} ions on two sites. Preliminary data on neutron diffraction at room temperature confirm the antiferromagnetic ordering [11].

In order to determine the parameters of the crystal and magnetic structure, the neutron diffraction measurements at 77 and 300 K are performed.

2. Experimental

The powder sample was obtained by the method originally used by Glemser and Gwinner [12]. The single-phase nature of the compound was checked by analyzing the X-ray diffraction pattern obtained at room temperature using a diffractometer DRON-1 and Fe K_α radiation. Neutron diffraction patterns were obtained on a diffractometer at Institute of Nuclear Studies Vinča using a neutron wavelength
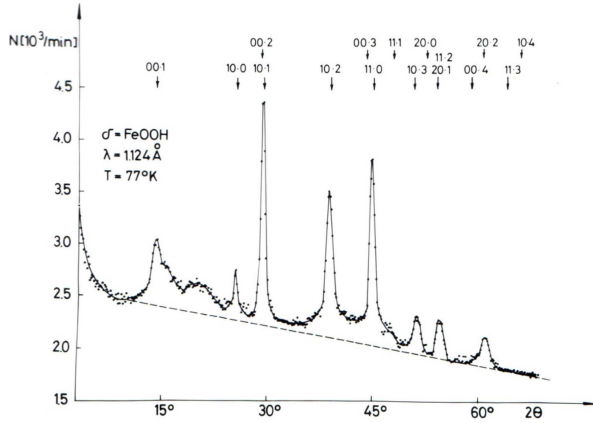
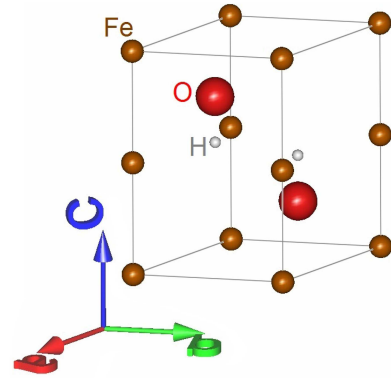Fig. 1. Neutron diffraction pattern of δ-FeOOH at 77 K.

Fig. 2. Crystal unit cell of δ-FeOOH [13].

TABLE I

X-ray powder intensities for the Fe^{3+} ions distributions in δ-FeOOH.

Indices	One octahedral site filled	Both octahedral site filled	Randomly in octahederal and tetrahedral	Exper. data
001	29	0	0	0
100	11	26	10	19
002	2	2	6	0
101	33	14	36	26
102	17	40	4	36
003	1	0	2	0
110	7	18	43	19

of 1.124 Å at temperature of 77 and 300 K. In order to separate the magnetic and nuclear contributions to the total scattering, a field of 9 kOe was applied parallel to the scattering vector.

3. Results

X-ray data at room temperature confirms the hexagonal crystal structure similar to that proposed in previous works [4–8]. Four reflections of d_{hkl} were detected, equal to 2.546, 2.22, 1.69, and 1.47 Å, described by the (hkl) indices (100), (101), (102), and (110), and corresponding to the hexagonal cell with $a = 2.95(1)$ Å and $c = 4.53(1)$ Å. In addition, two broad maxima are observed. The analysis of the intensities of Bragg reflections is performed assuming that the O^{2-} ions occupy the $2d$ sites $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ and with assuming different occupancy distributions of the Fe^{3+} ions, i.e.,

(i) all in octahedral site $1a$: $(0,0,0)$;
(ii) randomly in two octahedral sites $1a$: $(0,0,0)$ and $1b$: $(0, 0, \frac{1}{2})$;
(iii) randomly in both octahedral and four tetrahedral sites: $(\frac{2}{3}, \frac{1}{3}, \frac{1}{8})$, $(\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$, $(\frac{2}{3}, \frac{1}{3}, \frac{3}{8})$, $(\frac{1}{3}, \frac{2}{3}, \frac{5}{8})$.

TABLE II

Results of the neutron diffraction, i.e., comparison of the calculated and observed intensities for δ-FeOOH. The intensity of the reflections is normalized to the intensity of the (101) and (002) reflections.

Indices	I(calc.)	I(obser.)
001	9.0	10.0
100	6.0	7.7
101, 002	100	100
102	61.3	62.4
110, 003	57.2	68.8
111	5.5	3.0
103	15.8	15.3
200	1.0	0
112, 201	31.5	23.1
004, 202	24.8	21.2
$R[\%]$	11.8	–

Table I presents the results of the calculated (for these models) and observed intensities. All intensities are normalized to their total sum. Good agreement between the calculated and observed intensities is noticed for (ii) model, in which the Fe^{3+} ions occupy randomly $1a$ and $1b$ sites with the occupancy of 53% and 47%, respectively.

Since there is no difference in the neutron diffraction patterns with and without an external magnetic field and the patterns measured at 77 and 300 K, the neutron diffraction data obtained at 77 K (see Fig. 1) is used to determine the parameters of the crystal structure, as well as the distribution of Fe^{3+} ions, the values of the z parameter of the oxygen atom and the location of the hydrogen atom.

Based on the crystal structure of the $Fe(OH)_2$ compound described by the space group $P\bar{3}m1$ (no. 164) with two O atoms in $2d$: $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, -z)$ and two H atoms in $2d$ site with a different value of the z parameter. The oxygen and hydrogen parameter z were determined by means of minimization of the disagreement factor. The best

fit (with $R = 11.8\%$ was obtained for the parameters $z_O = 0.245$ and $z_H = 0.45$ and for half of the occupied $2d$ sites by hydrogen atoms. Crystal unit cell of δ-FeOOH figure made in FullProf studio [13] is shown in Fig. 2. The comparison between the observed and calculated intensities is shown in Table II.

4. Conclusions

Results presented in this work indicate that the crystal structure of δ-FeOOH has a similar distribution of oxygen ions O^{2-}, while the Fe^{3+} ions randomly occupy two sites $1a$ and $1b$. Hydrogen half-occupies two positions in the $2d$ site. The calculated interatomic distances of 2.83 Å for O–O and of 1.13 and 2.4 Å for O–H atoms are similar to those observed in the α- and β-FeOOH compounds [1, 3].

There was no observed difference between the diffraction patterns of neutrons with and without a magnetic field, indicating that the magnetic contribution is very small and it is not possible to provide a credible model of the magnetic structure.

The magnetic moment value of 0.3 μ_B per molecule determined from magnetic measurements suggests that the magnetic structure is probably formed of ferromagnetic layers in the (001) plane and antiferromagnetic coupling between them. Pernet et al. [11] suggest that the magnetic moment is parallel to the c-axis similar to those of $Ni(OH)_2$ [14], while Miyamoto et al. [15] suggest that in $Fe(OH)_2$ the magnetic moment is perpendicular to the c-axis. Weak intensity of the (001) reflection confirms the model of magnetic structure proposed in [11].

Acknowledgments

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