Hydrogen Bonds of γ-FeOOH

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The crystal structure of Lepidocrocite, γ-FeOOH, was determined by Ewing[1] using X-ray diffraction methods. The compound has a layer crystal structure where close-packed FeO_6-octahedra are held together by 2.70 Å hydrogen bonds. Olés, Szytula and Wanic[2] reinvestigated the structure using neutron diffraction powder methods and found that the hydrogen atom was centered in the hydrogen bond, and that the diffraction pattern had a magnetic contribution of the (020) reflection at 4.2 K.

In the previously accepted space group for the structure of γ-FeOOH,[1,2] *Cmcm* (No. 63) a centered O−H−O bond has the hydrogen atom in site 4*a*. Another possibility for the position of the hydrogen atom would be in site 8*f* with ½H in this site. The hydrogen bond is rather long for a centered hydrogen bond (the hydrogen atom placed in the centre of the O−H−O bond), and a more likely structure would be the above suggested statistical arrangement with ½H atom in site 8*f* of space group *Cmcm*, or a structure described in the non-centrosymmetric space group $Cmc2_1$ (No. 36). This paper describes a reinvestigation of the crystal structure of γ-FeOOH using neutron powder diffraction methods. Two samples of γ-FeOOH were investigated, a mineral from Glendon, Pa., U.S.A., supplied by Petersen[3] and a synthetic sample supplied by Janes.[4] The powder patterns were measured at Risø using neutrons with wave length $\lambda = 0.998$ Å.

γ-FeOOH (mineral). The diagram was measured in the 2θ interval 5.0−56.0° in steps of 0.2°. The diagram showed that the specimen contained α-FeOOH (goethite) as a major impurity. Some of the reflections of γ-FeOOH overlapped with reflections of α-FeOOH and the diagram could thus not be used in a profile refinement procedure.[5,6]

γ-FeOOH (synthetic). Data I. The diagram was measured at 300 K in the 2θ interval 2.0−91.0° in steps of 0.2°. The diagram had 16 resolved peaks with contributions from 108 reflections (see Fig. 1).

Table 1. Results of the refinement of the structure of γ-FeOOH in space group $Cmc2_1$. $a = 3.08(1)$ Å, $b = 12.50(1)$ Å, $c = 3.87(1)$ Å.

Atom	*x*	*y*	*z*	*B*(Å²)
Data I, 108 reflections. $R = 13.24\ \%$ [c]				
Fe	0	−0.323(1)	0.25	0.8(2)
O1	0	0.295(1)	0.266(19)	0.7(4)
O2	0	0.072(1)	0.250[a]	0.6(3)
H	0.5	0.525(3)	0.452(12)	0.8(6)
Data II. 54 reflections. $R = 8.51\ \%$				[b]
Fe	0	−0.322(1)	0.25	0.2(1)
O1	0	0.294(1)	0.264(11)	0.2(1)
O2	0	0.074(1)	0.282(9)	0.2(1)
H	0.5	0.523(2)	0.458(11)	0.2(1)

[a] Coordinate due to oscillation in refinement.
[b] Overall temperature factor. [c] *R* (profile) for definition, see Ref. 6.

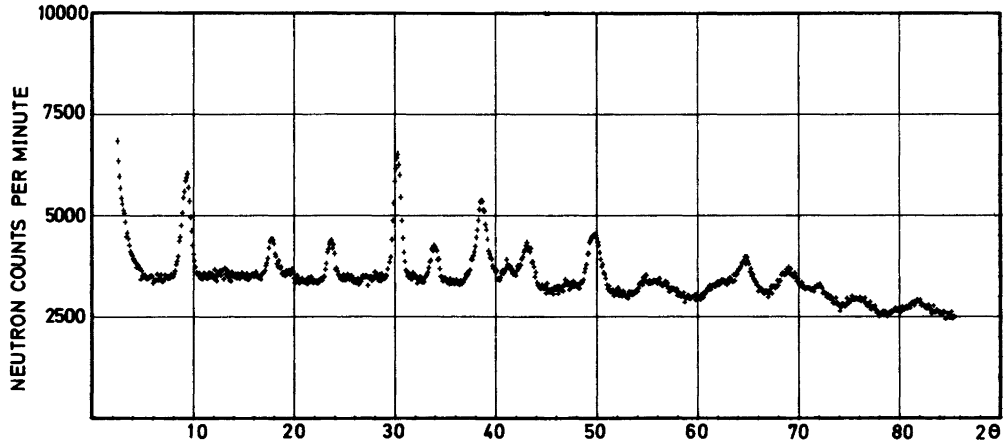

Fig. 1. Neutron diffraction powder patterns of γ-FeOOH, Data I. $\lambda = 0.998$ Å of incident neutrons.

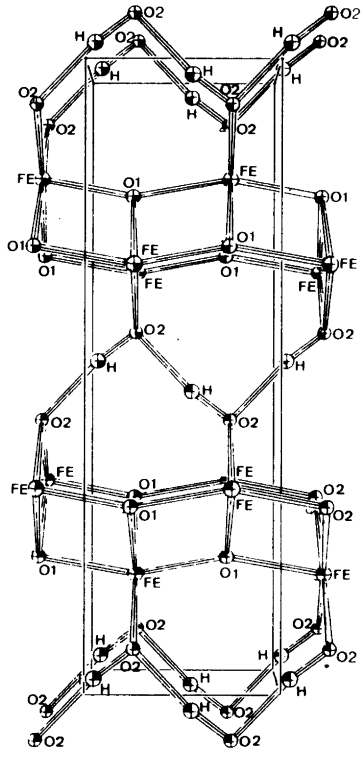

Fig. 2. Projection of the structure of γ-FeOOH along the 100-direction.

γ-FeOOH (synthetic). Data II. The diagram was measured at 7.5 K in the 2θ interval 7.5–62.0° in steps of 0.1°. The diagram had 12 resolved peaks with contributions from 54 reflections. None of the observed peaks in this diagram had scattering contributions from magnetic reflections.

The structure of γ-FeOOH was refined in the space groups *Cmcm* and $Cmc2_1$, using the Rietveld refinement programme for powder intensities.[5,6] The scattering lengths used were (in 10^{-12} cm): $b_{Fe}=0.951$, $b_O=0.580$, and $b_H=-0.374$.[7] The best agreement between observed and calculated intensities was obtained when the structure was refined in space group $Cmc2_1$ (see Table 1). In the space group *Cmcm* the agreement factor R was 16.15 % (Data I), when the hydrogen atom was placed in site 4*a* and the Debye-Waller factor for the hydrogen atom was 4.41 Å^2. With half-hydrogen atoms placed in site 8*f* the agreement factor was $R=13.71$ % and the Debye-Waller factor became negative (−2.19 Å^2). It is thus only the space group $Cmc2_1$ that gives a physically meaningful model for the structure of γ-FeOOH.

For Data II an R-value of 8.51 % was obtained. In order to restrict the number of parameters, an overall isotropic temperature factor parameter was used in this refinement. Fig. 2 is a projection of the structure along the 100 direction. It shows the hydrogen bonds placed between the oxygen atoms named O2. This oxygen atom is tetrahedrally coordinated with two Fe atoms and one H atom and has thus a vacant sp^3 hybride orbital for hydrogen bonds. The hydrogen bond is non-centered and the distances in it are O–H···O: 2.68(2) Å, O–H: 0.93(2) Å, and H···O: 1.75(2) Å, in acceptable agreement with hydrogen bond distances found for other oxide hydroxides.[8] The present investigation gave no indication of a magnetic structure of γ-FeOOH a 7.5 K.

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