β-*Ferric Oxyhydroxide.*

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Summary. The crystallographic properties of the hydrated iron oxide obtained by the hydrolysis of $FeCl_3$ are described. The characterizing X-ray powder pattern can be indexed on a tetragonal unit cell with *a* 10·48 and *c* 3·023 Å. This cell is shown to contain eight formula units of FeOOH but Cl^- or other anions are necessary for the crystallization of the material. The structure is that of hollandite or α-MnO_2. The unit cell has been confirmed by electron diffraction from single crystals having dimensions about 5000 × 500 × 500 Å. and twinning, which produces hexagonal stars, has been studied. On heating, the structure breaks down and recrystallizes as α-Fe_2O_3, probably with an intermediate stage involving a spinel phase.

β-FERRIC oxyhydroxide is one of the less common iron oxides and its study has been somewhat neglected as large crystals have not so far been reported. Its crystal chemistry appears to be markedly different from that of the other iron oxides and deserves a more detailed study than hitherto. Evidence for the formula is presented below, but for brevity it will be used at once. The material under discussion is characterized by the X-ray powder measurements quoted in table I.

Table I. X-ray powder data for β-FeOOH.

hkl.	*d.*	*I.*
110	7·40 Å.	vs
200	5·25	m
220	3·70	vw
310	3·311	vs
400	2·616	m
211	2·543	s
420	2·343	w
301	2·285	m
321	2·097	w
510	2·064	w
411	1·944	ms
440	1·854	vw
600	1·746	m
501 431	1·719	vw
521	1·635	vs
002	1·515	m
611	1·497	w
112 710 550	1·480	w
640	1·459	vw
541	1·438	s
730 312	1·374	m

Indexing then becomes uncertain.

Occurrence. β-FeOOH is produced in the following processes of which the first is the most important:

The hydrolysis of $FeCl_3$ or FeF_3 in solution at 60–100° C. for about

6 hours. If the hydrolysis is very protracted (144 hours) α-Fe_2O_3 results, not α-FeOOH as in the case of all other iron salts examined (except ferrous ammonium sulphate), so that β-FeOOH is presumably metastable at this temperature.

Direct precipitation from 0·5 M $FeCl_3$ at 75° C. by the addition of 3·5 *M* K_2CO_3 has been reported (Hofer *et al.*, 1946).

The damp oxidation of crystals of $FeCl_2.4H_2O$. Crystals of this material accessible to the atmosphere for a year had formed a brown powder identified as β-FeOOH.

The dry oxidation of $3Fe(OH)_2.FeCl_2$ (Keller, 1948, see below).

The damp oxidation of 'white rust' formed on steel under reducing conditions in contact with sea water (Aruja, private communication, 1958).

The hydrolysis of FeOCl (Heller, Kratky, and Nowotny, 1936).

Various natural processes give an iron-containing scum that may be β-FeOOH (Kratky and Nowotny, 1938).

X-ray powder photographs. The spacings listed in table I agree well with those published earlier—ASTM cards numbers 1–0669, 3–0429, and 3–0446; Weiser and Milligan (1935); Kratky and Nowotny (1938); Mackenzie (1952). Weiser and Milligan indexed their data, which did not include the first line at 7·40 Å., on an orthorhombic cell with *a* 5·28, *b* 10·24, and *c* 3·34 Å. Kratky and Nowotny revised this to *a* 10·56, *b* 10·24, and *c* 3·03 Å., having better data from a texture photograph (that is, a powder photograph showing preferred orientation effects), but the spacings can, in fact, be indexed on a body-centred tetragonal cell with *a* 10·48±0·01 and *c* 3·023±0·005 Å. There is no evidence of the doublets such as 200, 020 which might be expected if the material were orthorhombic. The powder lines continue sharp up to the λ/2 cut off (0·895 Å.).

Composition. The principal chemical study of β-FeOOH is by Weiser and Milligan (1935) who established the formula and showed that the compound always contains chlorine. When first precipitated the chlorine content might be as high as 8 % (Fe/Cl = 4·79), but with prolonged washing this can be reduced to any desired value (certainly to Fe/Cl > 45). Analyses kindly made for us at the Building Research Station showed 2 to 4 % chlorine and no ferrous iron. The water content is somewhat uncertain as much of the water is certainly adsorbed. Dehydration curves recorded on a thermo-balance with a rate of heating of 100° C. per hour and an uncontrolled water vapour pressure over the specimen showed a loss of some 10 % water below 100° and a further 13·5 % in a sharp step at about 230° C. A loss of 10 % would be expected from the stoichiometric composition. Weiser and Milligan found that the step occurred over a broader temperature interval as the Cl content was lowered. The product of the dehydration is α-Fe_2O_3. The observed density is 3·0 g./cm.^{3}, whereas if the unit-cell contents were 8FeOOH the calculated density would be 3·6 g./cm.^{3} The large discrepancy can probably be ascribed to adsorbed water, since the crystals are very small.

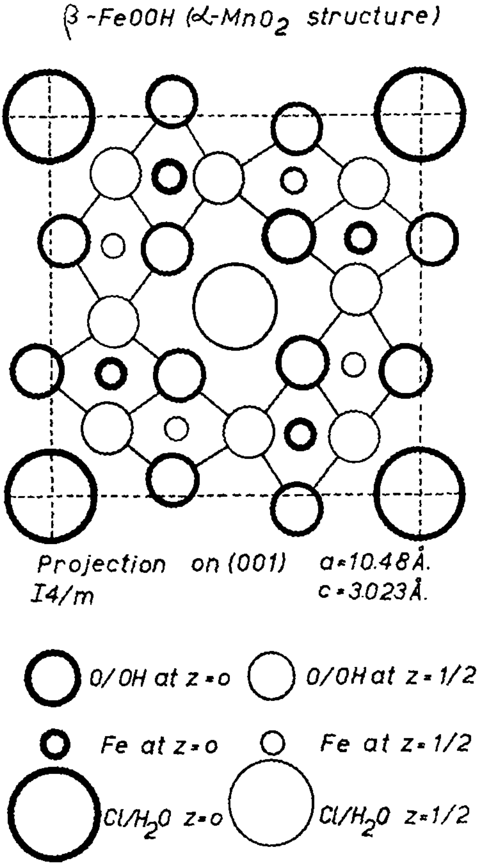

FIG. 1. Projection of the α-MnO_2 structure as determined by Byström and Byström (1950).

Structure. On the basis of the unit-cell dimensions and the observed body-centring of the cell it was suggested (Bernal, Dasgupta, and

Mackay, 1959) that β-FeOOH has essentially the hollandite ($BaMn_8O_{16}$) or α-MnO_2 structure (fig. 1). This has now been confirmed by the comparison of observed and calculated intensities (fig. 2). The intensities

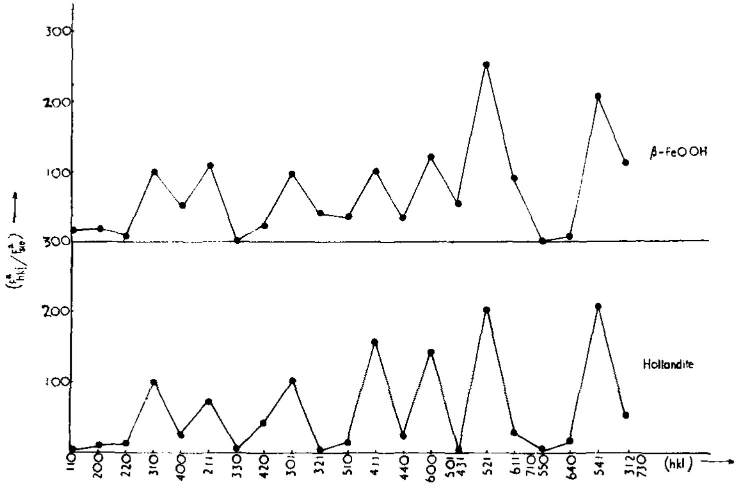

FIG. 2. Comparison of the intensities observed for β-FeOOH (powder photograph) with those calculated for hollandite by Byström and Byström (1950).

were calculated by Byström and Byström (1950), who determined the structure of hollandite, for Mn^{4+} ions (21 electrons) but the agreement did not improve appreciably on recalculating them for Fe^{+++} ions (22 electrons). In view of the uncertainty as to the contents of the channels in the structure (see below) the agreement is satisfactory. The structure analysis could not easily be continued because of the overlapping of the *hk*0 and *kh*0 reflections in the powder photographs and the impossibility of distinguishing between the Laue groups 4/*m* and 4/*mmm*.

Agreement with Byström and Byström's observations implies a space group *I*4/*m* with 8Fe in 8(*h*) positions with parameters (0·348, 0·167, 0) and 16 (O, OH) in 8(*h*) positions with parameters (0·153, 0·180, 0) and (0·542, 0·167, 0). There may be Cl′ ions or H_2O molecules in the 2(*b*) positions.

Crystal chemistry. The Fe^{+++} ions are each surrounded octahedrally by six (O″, OH′) ions. These octahedra are linked to form double strings parallel to the *c*-axis. In each string the octahedra share edges parallel

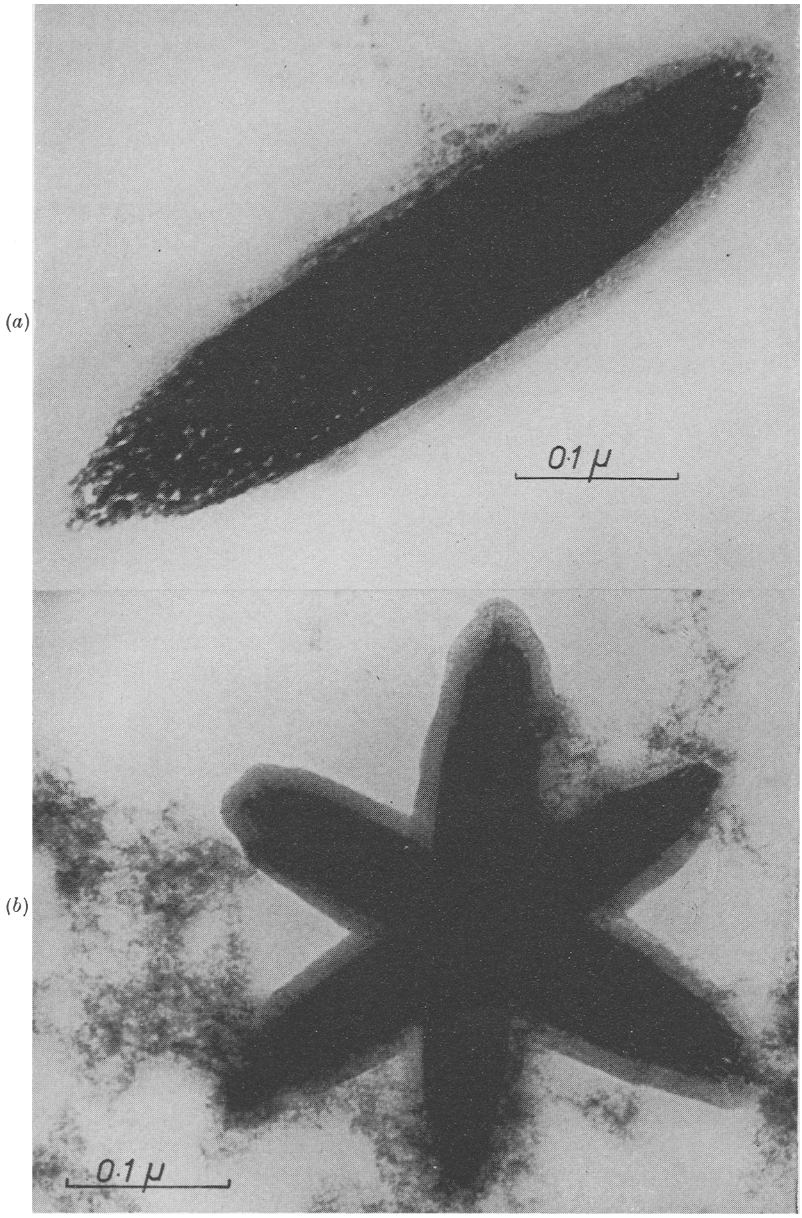

Fig. 3. (a) Single crystal of β-FeOOH. (b) Star-shaped twinned crystal of β-FeOOH.

to *a* and each octahedron shares also two edges with octahedra in the neighbouring string. The double strings are joined by sharing corners. The 2(*b*) positions at (0, 0, 1/2) are surrounded by 8+4 (O″, OH′) ions. If the 2(*b*) positions were filled by oxygen atoms the structure would

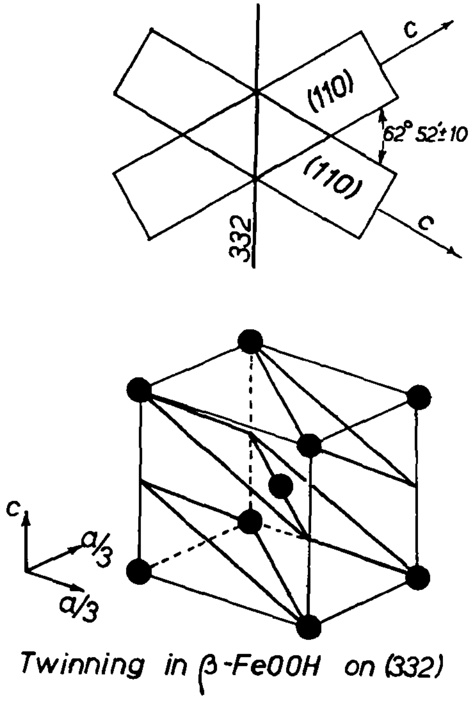

FIG. 4. The twin law for β-FeOOH.

consist of approximately body-centred close-packed oxygen. The parameters would be (0·167, 0·167, 0) and (0·500, 0·167, 0) instead of those quoted above. In hollandite the 2(*b*) positions are occupied statistically to the extent of 50 % by Ba^{++} ions. In β-FeOOH these positions will be available for the large Cl′ ions but the diameter of such an ion (3·62 Å.) is greater than the *c*-dimension of the cell (3·02 Å.) so that they could only be accommodated statistically. The maximum chlorine content (Fe/Cl = 4·79; Weiser and Milligan, 1935) would correspond to about 84 % occupation of the 2(*b*) positions, and, if all the 2(*b*) positions were occupied by H_2O molecules after washing, the formula would correspond to $Fe_2O_3.3/2H_2O$, more in accord with the dehydration data.

Hollandite is reported to have ion exchange properties. The F′-containing β-FeOOH had exactly the same cell dimensions as the Cl′-containing samples and no changes dependent on Cl′ content were found. Presumably some OH′ ions replace O″ ions to compensate for the extra negative charge of the Cl′. It is interesting to compare the 'ferroxdure' compounds ($BaFe_2^{++}Fe_{16}^{+++}O_{27}$ and $Ba_2Fe_2^{++}Fe_{28}^{+++}O_{46}$; Braun, 1957), where Ba replaces O in a close-packed arrangement, with hollandite.

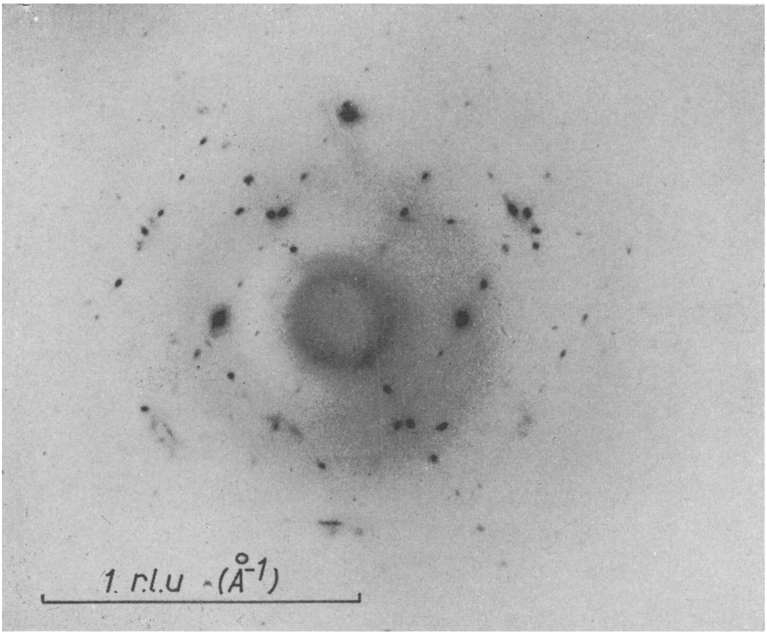

FIG. 5. Electron diffraction pattern from an X-shaped twin of β-FeOOH lying in the orientation shown in fig. 4.

Electron microscopic and diffraction observations. Specimens of β-FeOOH were examined by electron microscopy and were seen to be composed of exceptionally regularly formed spindle-shaped crystals of length about 5 000 Å. (fig. 3*a*). This agrees with Meldau's observations (1957). Many star-shaped and X-shaped twins are found (fig. 3*b*). The crystals obtained by the hydrolysis of FeF_3 occurred in irregular aggregates but nevertheless gave the powder diffraction pattern of β-FeOOH. Single crystal diffraction patterns were obtained from crystals such as that of fig. 3*a* showing that the elongation is along the

c-axis and confirming the cell dimensions. Unfortunately all crystals examined lay with their c-axes parallel to the substrate so that it was not possible to check differences in intensities between hkl and khl reflections. Crystals were found with (100), (110), or (310) parallel to the substrate. The components of the twinned crystals, however, lay only on (110) and the twin plane was shown to be (332) (figs. 4 and 5). It has been shown that the structure is built up of oxygen atoms close-packed in a body-centred cubic lattice, and if referred to the pseudo unit-cell (cubic with cell edge $a/3 = c$) the twin plane has indices (112), which are the indices of the usual twin plane in α-iron and α-tungsten.

Formation of β-FeOOH *from* $Fe_2(OH)_3Cl$. Keller (1948) reported the formation of a compound $Fe_2(OH)_3Cl$, which was isomorphous with one of the four forms of $Cu_2(OH)_3Cl$, probably with atacamite, the orthorhombic form determined by Thoreau and Verhulst (1938), when a solution of $FeCl_2$ was incompletely precipitated with NaOH. When this compound is oxidized dry then β-FeOOH is formed. Fig. 6 shows an oriented texture of needles, which fig. 7 proves to be β-FeOOH, resulting from the decomposition of a flaky crystal, presumably $Fe_2(OH)_3Cl$.

Transformation of β-FeOOH *on heating*. When β-FeOOH is heated in air α-Fe_2O_3 eventually results, but there are several indications that there may be intermediate stages to the process. Firstly, we have observed that sometimes, if the heating is stopped at an intermediate temperature, a magnetic product may result. One explanation was that a disordered form of α-Fe_2O_3, perhaps superparamagnetic like δ-FeOOH, intervened. Further heating in this case would destroy the ferromagnetism by producing recrystallization as normal α-Fe_2O_3. Hilpert, Maier, and Hoffman (1938) also observed ferromagnetism on hydrolysing and then dehydrating FeOCl. By itself β-FeOOH has the abnormally low bulk susceptibility for an iron oxide of $29{\cdot}0 \pm 0{\cdot}5 \times 10^{-6}$ e.m.u. (Hofer *et al.*, 1946). Secondly, Mackenzie (1952) found that the d.t.a. record of the dehydration of β-FeOOH showed an endothermic peak at 250–260° C. corresponding to the loss of water but also an exothermic peak at a higher temperature (420° C.) which was first attributed to recrystallization of the α-Fe_2O_3 but which must now be given another explanation (see below). Thirdly, the state of β-FeOOH immediately on dehydration is certainly peculiar because Fischer-Tropsch catalysts, prepared by the reduction of precipitated oxide in H_2 at 300° C., have no activity if β-FeOOH is the initial material. Other oxides, even if chlorides are present, give catalysts active in promoting the

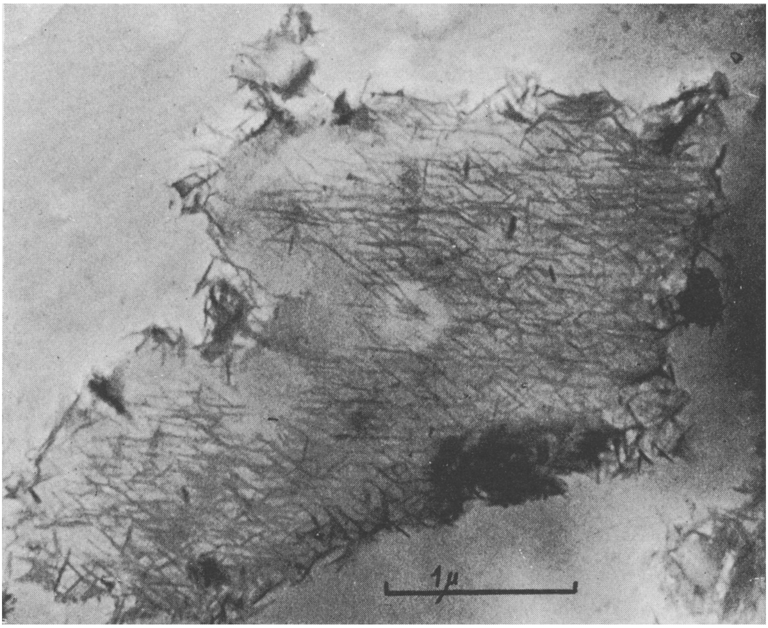

FIG. 6. An oriented texture of needles of β-FeOOH probably deriving from the breakdown of a crystal of $Fe_2(OH)_3Cl$.

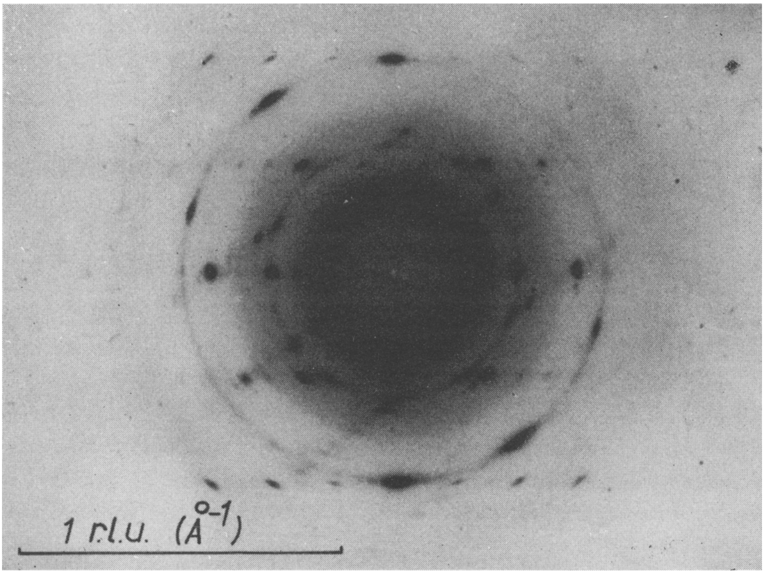

FIG. 7. Electron diffraction pattern from the texture of needles shown in fig. 6.

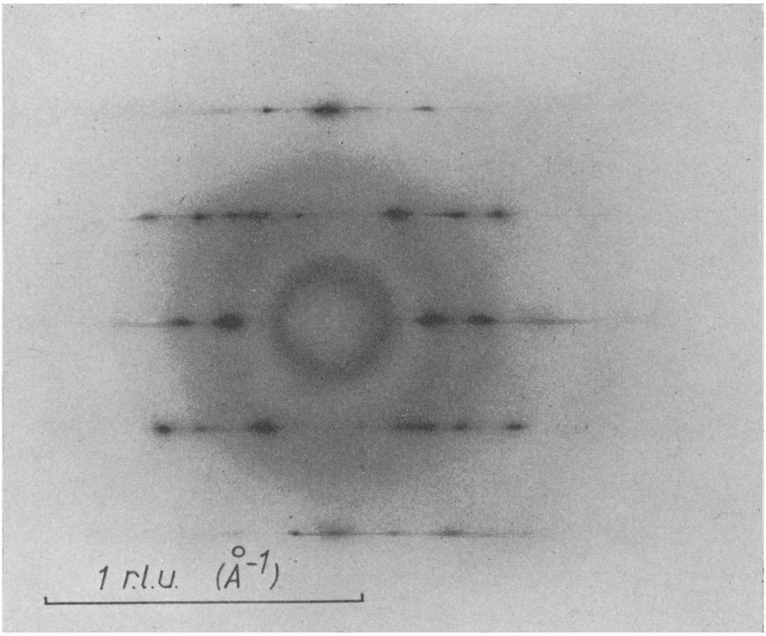

FIG. 8. Electron diffraction pattern from a single crystal of β-FeOOH after heating showing streaks perpendicular to [001].

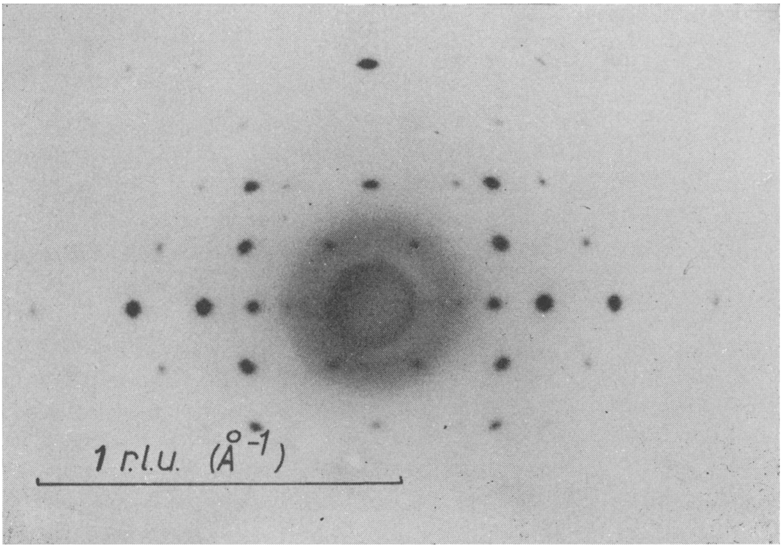

FIG. 9. Electron diffraction pattern from a single crystal of β-FeOOH that has completely transformed to crystals with a spinel structure in two orientations.

combination of CO and H_2. Even if the β-FeOOH is first aged to α-Fe_2O_3 before reduction no catalytic activity is found (Hofer *et al.*, 1946).

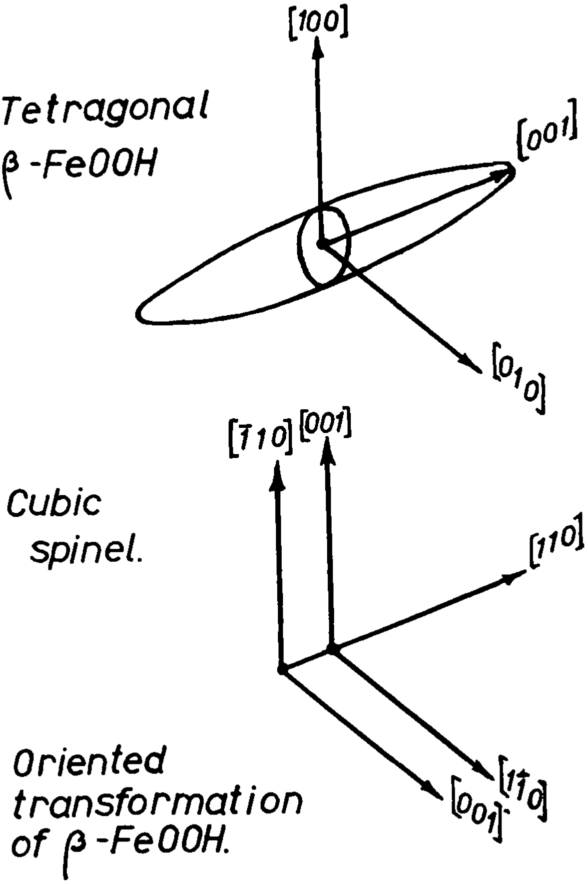

FIG. 10. Diagram of the orientational relationships in the transformation of β-FeOOH.

Single crystals of β-FeOOH have been heated in the beam of the electron microscope and the resulting transformation has been followed by observing the changes in their diffraction patterns. First, the single crystal spot pattern developed streaks along the layers perpendicular to [001] (fig. 8). The 002 reflection became very noticeable and weak intermediate layer lines doubling the c-axis appeared. Mukherjee's observa-

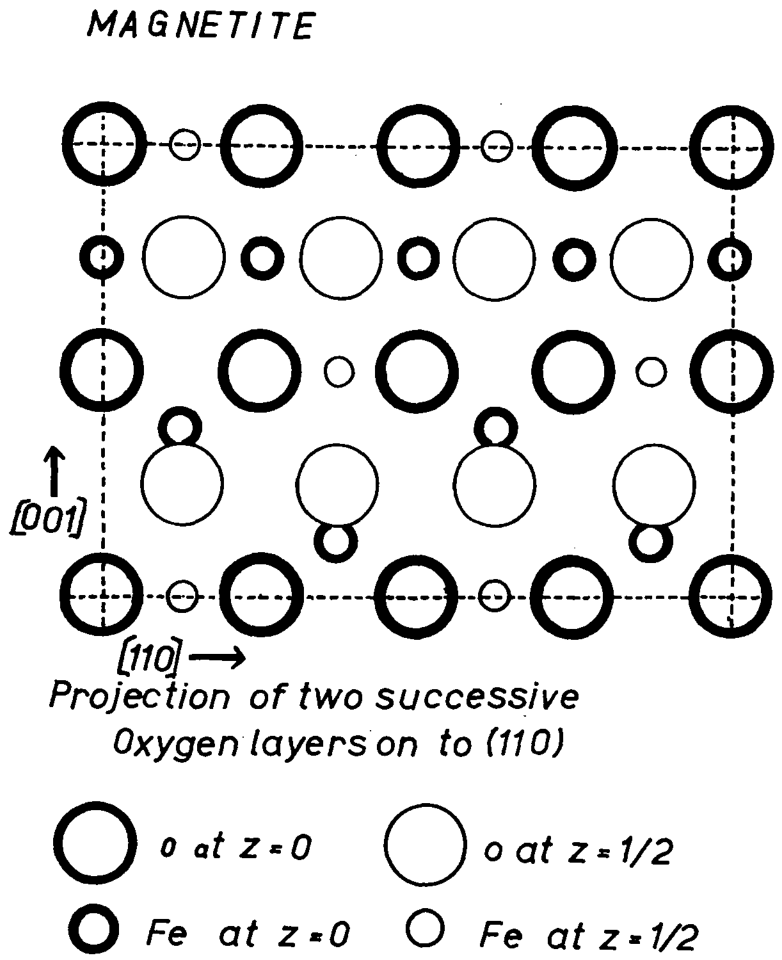

FIG. 11. Plan of a (110)-section through the magnetite structure to show the similarity to the β-FeOOH structure.

tion (1960) of the doubling of the c-axis in hollandite might be recalled in this connexion. The streakiness next cleared and the resulting rectangular pattern (fig. 9) could be indexed as being due to crystals with a spinel structure in two orientations (fig. 10). The two orientations are to be expected as the fourfold axis of β-FeOOH is replaced by a two-fold axis of the cubic phase and by Neumann's principle the overall point group symmetry cannot be lowered by such a transformation.

The spinel is presumably γ-Fe_2O_3 although reduction to Fe_3O_4 under the very low oxygen pressure conditions in the microscope cannot at present be excluded.

The exothermic peak observed by Mackenzie in the d.t.a. curve of the dehydration of β-FeOOH may then be the γ-Fe_2O_3 to α-Fe_2O_3 transformation which releases about 8 kcal./mol.

Examination of fig. 11 shows the similarity between a section through the spinel structure parallel to (110) and the β-FeOOH structure. Only the migration of Fe ions to tetrahedral sites and an expansion of the O–O distance from 3·49 to 4·17 Å. in one direction and a contraction from 3·49 to 2·95 Å. in a perpendicular direction are necessary and these may follow from the migration of the iron.

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