

THE OXIDES AND HYDROXIDES OF IRON AND THEIR STRUCTURAL INTER-RELATIONSHIPS

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ABSTRACT

The transformations in the iron oxide-hydroxide system have been interpreted in a rational crystallochemical manner, some being characterized as topotactic and some as non-topotactic. Crystallographic measurements have been made on the more reactive or metastable phases, particularly on the "green rusts." The oxyhydroxides β -FeOOH and δ -FeOOH have been examined more fully, but data on all the phases have been checked. New data on transformations, such as $\text{FeCO}_3 \rightarrow \text{FeO}$ and $\text{Fe}(\text{OH})_2 \rightarrow \text{FeO}$ are reported.

INTRODUCTION

The iron oxides and hydroxides have recently been reinvestigated with the aim of elucidating the nature of their mutual transformations, with special reference to magnetic properties. Most of these transformations are examples of a phenomenon which has been named *topotaxy*;^{*} this signifies the transformation of one solid crystalline phase to another, by rearrangement of the atoms, so that, even if a certain fraction of the material is taken into or expelled from the system, the two phases have a definite structural relationship to each other.

The iron oxide/hydroxide system has been investigated in part several times previously (Sidgwick, 1950) and many of the transformations are well known. However, some have been examined which, so far as can be ascertained, have not been previously reported and it is believed that the whole set of transformations can now be interpreted in a rational crystallochemical way. A chart outlining the relationships of the phases to each other is shown in Fig. 1 and brief data on the structures are given in Table 1. These summarize the present state of our investigations which will now be described in more detail. Certain transformations, such as that of Fe_3O_4 to α -FeOOH (which was deduced from the examination of natural pseudomorphs of α -FeOOH after magnetite) are not included in Fig. 1, because the conditions necessary for accomplishing them are unknown.

* This name is due to Dr. E. W. Gorter, and is derived from the Greek *τοπος*—place, *ταξις*—arrangement.

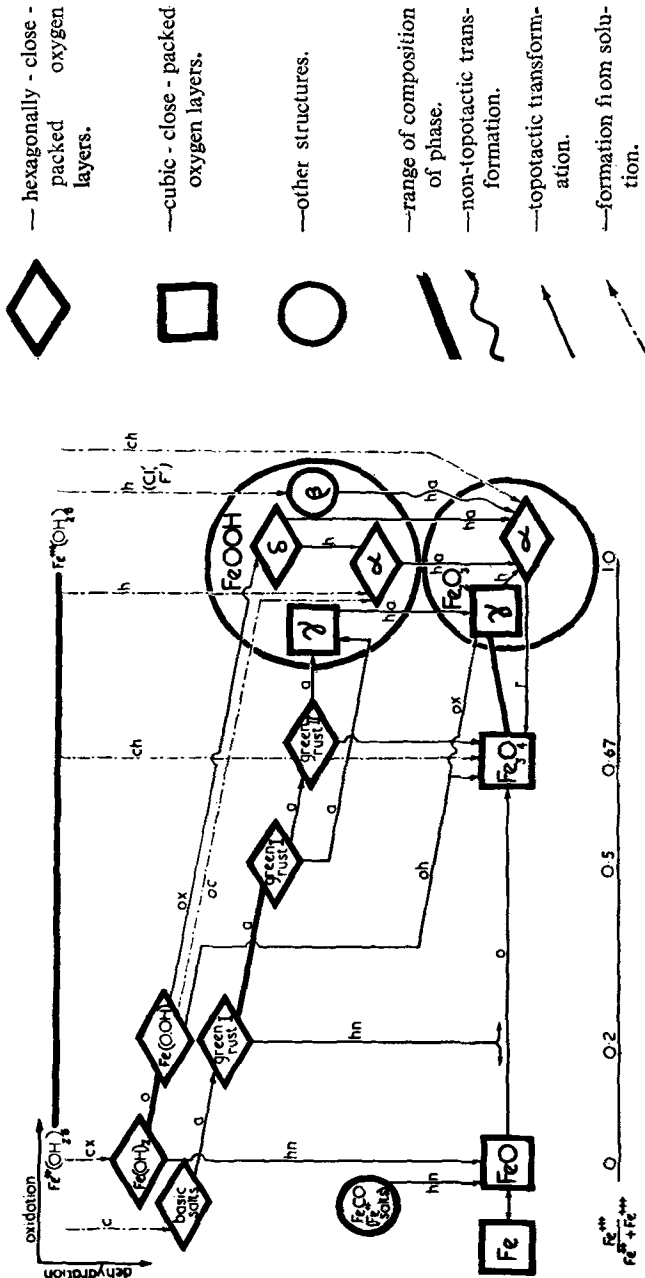


Fig. 1.—Structural transformations in the iron oxide/hydroxide system. KEY: a—on exposure to air; c—in alkali; h—on heating; n—in nitrogen or *in vacuo*; o—on oxidation; r—on reduction; x—in excess.

TABLE I—Summary of the crystal structures of oxides and hydroxides of iron.

Composition	Mineral Name	Space Group	Dimensions (Å)	Z	d _{obs}	Notes
α -Fe ₂ O ₃	Hematite	<i>R</i> 3c	<i>a</i> = 5.0345, <i>c</i> = 13.749	6 (hex.)	5.2	H.c.p. oxygen with Fe ³⁺ in octahedral positions.
Fe ₃ O ₄	Magnetite	<i>Fm</i> 3d	<i>a</i> = 8.3963 (18°C)	8		Inverse spinel.
γ -Fe ₂ O ₃	Maghemite	<i>P</i> ₂ ¹ / ₃ or <i>P</i> ₄ ¹ / ₃ 2	<i>a</i> = 8.338	10½		Spinel—various degrees of ordering.
FeO	Wüstite	<i>P</i> ₄ ² / ₁ 2 <i>Fm</i> 3m	<i>c</i> = 3 <i>a</i> <i>a</i> = 4.302 (high Fe) 4.275 (low Fe)	32 4 4		"
		Tetragonal	<i>a</i> = 6.04, <i>c</i> = 8.54	16		Martensitic transformation.
α -FeOOH	Goethite	<i>P</i> bnm	<i>a</i> = 4.587, <i>b</i> = 9.937, <i>c</i> = 3.015	4	4.28	Based on h.c.p. oxygen.
β -FeOOH		<i>I</i> 4/ <i>m</i> (?)	<i>a</i> = 10.48, <i>c</i> = 3.06	8		Laue group <i>I</i> 4/ <i>m</i> or <i>I</i> 4/ <i>mmm</i> . F or Cl necessary for formation. α -MnO ₂ structure likely.
γ -FeOOH	Lepidocrocite	<i>C</i> mc <i>m</i>	<i>a</i> = 3.87, <i>b</i> = 12.51 <i>c</i> = 3.06	4	4.09	Based on c.c.p. oxygen.
δ -FeOOH		<i>P</i> 312 (?) hex.	<i>a</i> = 2.941, <i>c</i> = 4.58	1		H.c.p. oxygen; disordered CdI ₂ structure.
Fe(OH) ₂ Fe(OH) ₃ Variable	Green rust I	<i>P</i> 31 Gel (existence doubtful—no X-ray photographs) <i>R</i> ... (not <i>c</i>)	<i>a</i> = 3.262, <i>c</i> = 4.596 <i>a</i> = 3.18 <i>c</i> = 24.4-27.4 (SO ₄ ²⁻) <i>a</i> = 3.22, <i>c</i> = 24 (Cl ⁻) <i>a</i> = 3.18, <i>c</i> = 22.8 (Br ⁻) <i>a</i> = 3.17, <i>c</i> = 10.9 (hex.)	1		CdI ₂ -type structure.
FeCO ₃	Chalybite (Siderite)	<i>R</i> 3c	<i>a</i> = 4.711, <i>c</i> = 15.436	2 6 (hex.)	3.89	"Green basic iron (II, III) chloride or sulphate"—Keller (1948). (9 layers of O). (4 layers of O).

Abbreviations used: c.c.p.—cubic-close-packed; h.c.p.—hexagonally-close-packed; hex.—hexagonal; oct.—octahedral; tet.—tetrahedral.

STRUCTURES OF CLOSE-PACKED OXYGEN SHEETS

The common feature of the group of iron oxides and hydroxides is that they are composed of different stackings of close-packed oxygen/hydroxyl sheets, with various arrangements of the iron ions in the octahedral or tetrahedral interstices. The X-ray diffraction effects from these structures are best calculated by taking their Fourier transforms. The transform of a single extended oxygen/hydroxyl sheet is a system of rods perpendicular to the sheet. Consequently, X-ray powder photographs from a random assembly of such sheets would show a set of bands beginning at 2.83 \AA ($10\bar{1}l$), 1.63 \AA ($11\bar{2}l$), 1.42 \AA ($20\bar{2}l$), etc., if the side a of the hexagonal cell is 3.26 \AA (as in $\text{Fe}(\text{OH})_2$) or at 2.55 \AA , 1.47 \AA , 1.28 \AA , etc., if $a=2.94 \text{ \AA}$ (as in $\delta\text{-FeOOH}$), since the sheet dimensions change slightly with hydrogen content. When these sheets are stacked regularly, the transform will be modified by the distribution function of the stacking, but each compound based on such sheets will have strong lines associated with these bands.

Iron oxides can be obtained in the amorphous state and also in states where the layers must be largely intact but disordered. When potassium ferricyanide is hydrolyzed a magnetic precipitate is obtained which shows only two broad lines corresponding to the ($10\bar{1}l$) and ($11\bar{2}l$) bands. The same sort of disordered material results from the oxidation of $\text{Fe}(\text{OH})_2$ by solutions of hydrogen peroxide or ammonium persulphate before the crystals of the oxyhydroxide can grow, *e.g.*, when a ferrous solution is poured into a mixed solution of sodium hydroxide and hydrogen peroxide. The green complexes or *green rusts* (see below) on rapid oxidation give forms of $\delta\text{-FeOOH}$ which may be extremely disordered.

THE OXIDATION PRODUCTS OF $\text{Fe}(\text{OH})_2$

$\text{Fe}(\text{OH})_2$ is best obtained by adding a ferrous solution to excess alkali with the strict exclusion of oxygen. The precipitate is white, although some grains may be bluish, and gives very sharp powder photographs. The X-ray data in Table 2 indicate a hexagonal cell with $a=3.258 \text{ \AA}$ and $c=4.605 \text{ \AA}$, which are close to previously published values (Natta and Casazza, 1928; Clark, Hedley and Robinson, 1944; Keller, 1948) and particularly to those of Clark, Hedley and Robinson (1944). The structure is of the CdI_2 type containing two hexagonally-packed oxygen layers. Although extremely sensitive to oxygen, the $\text{Fe}(\text{OH})_2$ structure is surprisingly stable. Keller (1948) reports that the structure is maintained until

the Fe^{3+} content is 10 per cent. of the total iron. Specimens prepared here by oxidation of $\text{Fe}(\text{OH})_2$ with ammonium persulphate were brown and strongly magnetic and gave excellent powder photographs of $\text{Fe}(\text{OH})_2$ although oxidized to the extent of about 20 per cent. $\text{Fe}(\text{OH})_2$ is also obtained by precipitation with other alkalis, such as ammonium hydroxide, but may appear grey or green. It is stable to boiling, but if the $\text{Fe}(\text{OH})_2$ precipitate is washed in oxygen-free water (which has been passed through a de-oxygenating resin) to

TABLE 2—X-ray powder data for $\text{Fe}(\text{OH})_2$ and $\delta\text{-FeOOH}$.*

$\text{Fe}(\text{OH})_2$			$\delta\text{-FeOOH}$		
<i>hkl</i>	<i>d</i>	I	<i>hkl</i>	<i>d</i>	I
0001	4.597	vs	0001	4.61	vw
10 $\bar{1}$ 0	2.817	s	10 $\bar{1}$ 0	2.545	vs
10 $\bar{1}$ 1	2.403	vs	10 $\bar{1}$ 1	2.255	vs d
10 $\bar{1}$ 2	1.782	s	10 $\bar{1}$ 2	1.685	vs vd
11 $\bar{2}$ 0	1.629	s	11 $\bar{2}$ 0	1.471	vs
11 $\bar{2}$ 1, 0003	1.535	m			
20 $\bar{2}$ 0	1.411	vw	20 $\bar{2}$ 0	1.271	vw
10 $\bar{1}$ 3, 20 $\bar{2}$ 1	1.349	m	11 $\bar{2}$ 2	1.223	vw
20 $\bar{2}$ 2	1.203	vw	20 $\bar{2}$ 2	1.104	vw vd
0004	1.148	vw			
11 $\bar{2}$ 3	1.115	vw			
10 $\bar{1}$ 4, 21 $\bar{3}$ 0	1.067	w d	21 $\bar{3}$ 0	0.965	vw d
20 $\bar{2}$ 3, 21 $\bar{3}$ 1	1.040	m	21 $\bar{3}$ 1	0.943	vw d
21 $\bar{3}$ 2	0.968	m d			
11 $\bar{2}$ 4, 30 $\bar{3}$ 0	0.941	m d			
0005, 30 $\bar{3}$ 1	0.923	w			

*Prepared from ferrous sulphate by adding excess sodium hydroxide and excess ammonium persulphate.

remove salts, and is then heated to dryness under nitrogen, it decomposes to FeO at about 200°C . The observations of Goodman (1958) on the decomposition of $\text{Mg}(\text{OH})_2$ to MgO indicate that this must be a topotactic reaction. Some magnetite may also be formed either from oxidized $\text{Fe}(\text{OH})_2$ or by disproportion of the FeO . It is shown below that FeO and Fe_3O_4 are topotactically related. On oxidation in hot suspension by a dilute solution of hydrogen peroxide or ammonium persulphate added very slowly $\gamma\text{-Fe}_2\text{O}_3$ can be formed from $\text{Fe}(\text{OH})_2$. The $\gamma\text{-Fe}_2\text{O}_3$ is of the cubic modification with the lines 110, 200, 210 and 211 present (see below).

If oxygen is passed through a strongly alkaline suspension of $\text{Fe}(\text{OH})_2$, α - FeOOH is produced. It appears that γ - FeOOH is never formed directly from $\text{Fe}(\text{OH})_2$. Although $\text{Fe}(\text{OH})_2$ may become green on oxidation, when there is excess alkali the green colour is due to changes maintaining the CdI_2 structure and not to the green complexes described below.

DELTA FERRIC OXIDE

The most interesting product to be obtained from $\text{Fe}(\text{OH})_2$ is produced by very rapid oxidation with an excess of a strong solution of hydrogen peroxide or ammonium persulphate. The resulting brown strongly-magnetic material was first described as " δ - Fe_2O_3 " by Glemser and Gwinner (1939). This compound has been examined in some detail, most of the observations paralleling those of Francombe and Rooksby (1959), which were made simultaneously.

The X-ray data in Table 2 indicate a hexagonal unit cell with dimensions $a=2.941\pm 0.005 \text{ \AA}$ and $c=4.49\pm 0.05 \text{ \AA}$, which are similar to those of $\text{Fe}(\text{OH})_2$ where $a=3.26 \text{ \AA}$ and $c=4.60 \text{ \AA}$. The best-crystallized material gives ten powder lines, none with an l index greater than 2. Lines with $l=0$ are sharpest and those with $l=1$ and $l=2$ are increasingly diffuse. More poorly-crystallized specimens, giving only the four strongest lines, have the $10\bar{1}1$ line diffuse and the $10\bar{1}2$ line very diffuse. Some material gives only the prism reflexions $10\bar{1}0$ and $11\bar{2}0$. On heating, about 10 per cent. water is lost above 100°C (and up to 10 per cent. below 100°C) and the material transforms to hematite. A dehydration curve together with a measurement of the magnetic susceptibility, which was obtained by a recording thermobalance, is shown in Fig. 2. The temperature of the specimen was given by a non-magnetic Pd/Au alloy thermocouple embedded in the specimen, the weight of which was about 250 mg. From these observations the composition is FeOOH and it is clear from the relationship to hematite—the main lines of δ - FeOOH can be obtained from the pattern of hematite by choosing only those lines for which l is a multiple of 3—that the structure is an arrangement of hexagonally-close-packed oxygen/hydroxyl layers with Fe^{3+} between adjacent layers. Feitknecht and Bucher (1943) have observed almost the same structure for $\text{Cd}(\text{OH})\text{F}$ where the Cd^{2+} ions are distributed equally between the two octahedral sites in a hexagonally-close-packed lattice of mixed OH^- and F^- . Francombe and Rooksby (1959) have shown it to be likely that about 20 per cent. of the Fe^{3+} is in tetrahedral sites. The main feature of

interest is that δ -FeOOH has a very high magnetic susceptibility. The powder has an extremely small remanence and a very low hysteresis loss; the saturation magnetization, not reached until about 3000 oersted, is up to 19 e.m.u./g.* The powder is flaky and the anisotropy in the magnetization is strikingly visible when a suspension of the powder is held in a strong magnetic field. The changes in the reflectivity of the suspension show that the flakes are most easily magnetized in their planes. This might, however, be

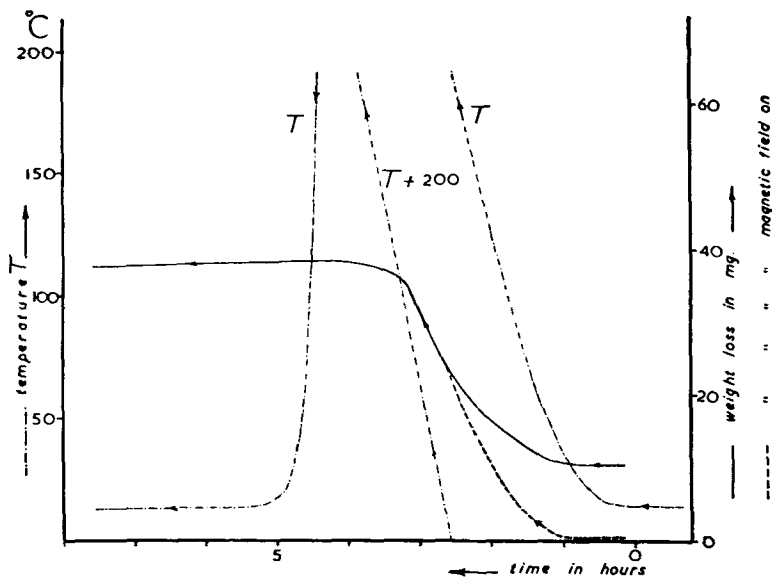


FIG. 2—Thermobalance record of the dehydration of δ -FeOOH (248 mg sample): — weight change of the specimen; - - - weight change measured in a magnetic field so that a force proportional to the susceptibility is added to the weight; - · - · temperature of specimen as recorded by a thermocouple embedded in it.

simply an example of extreme shape demagnetization. Fuller magnetic observations on this and other phases will be reported elsewhere.

The time of heating has a considerable influence on the temperature of dehydration. To investigate this aspect specimens were heated in air for periods of a week in a device which may have

*The magnetic properties of the powder were measured by Dr G. Haigh, Imperial College of Science and Technology.

applications in fields other than iron oxides. A well-lagged vertical steel bar about 1 metre long is heated electrically at the top and cooled with water at the bottom. It has 25 holes drilled into it at regular intervals along its length to accommodate 25 portions of the preparation in glass tubes. Thermocouples record the temperature at each hole.

On heating δ -FeOOH a steady decrease in the a -dimension was found, this amounting to 1 per cent. by 130°C. Broadened lines of α -Fe₂O₃ appeared above 120-130°C, but the lines of δ -FeOOH persisted up to 180°C. At 200°C the material was completely converted to α -Fe₂O₃. When α -FeOOH was present in the initial specimen, heating for 10 days at 96°C converted the δ -FeOOH. Heating in coal gas converted the δ -FeOOH to α -Fe₂O₃ at 200°C and this was then reduced to Fe₃O₄ and further to α -Fe and Fe₃C.

The behaviour of Fe(OH)₂ on oxidation can be summarized as follows. In strongly alkaline suspension oxidation takes place before dehydration, initially the CdI₂ structure is retained but later it breaks down to the hexagonally-close-packed α - and δ -oxyhydroxides. These can be subsequently dehydrated to α -Fe₂O₃ in topotactic transformations (Goldsztaub, 1931). If dehydration occurs before oxidation, cubic FeO is first formed. On boiling Fe(OH)₂ with a dilute oxidant cubic γ -Fe₂O₃ is produced non-topotactically.

THE GREEN OXIDATION COMPLEXES—THE "GREEN RUSTS"

If insufficient alkali to precipitate all the Fe²⁺ as Fe(OH)₂ is added to a solution of ferrous ions under oxygen-free conditions and air is bubbled through the suspension, blue-green compounds result. X-ray powder photographs have been taken at various stages of oxidation. In all instances aerial oxidation gave γ -FeOOH as the end product. The following compounds were distinguished from their powder photographs.

Green rust I has been described by Keller (1948) who gives it a composition between 4Fe(OH)₂.FeOCl and 2.17Fe(OH)₂.1.83FeOOH.FeOCl, or recalculated to 9 (O,OH,Cl) per cell, a composition between Fe²⁺_{3.6}Fe³⁺_{0.9}(O,OH,Cl)₉ at 20 per cent. oxidation and Fe²⁺_{1.95}Fe³⁺_{2.55}(O,OH,Cl)₉ at 57 per cent. oxidation. He assigns dimensions to the hexagonal unit cell of $a=3.22 \text{ \AA}$, $c=24.0 \text{ \AA}$ if the material is a basic chloride, $a=3.18 \text{ \AA}$, $c=22.96 - 22.25 \text{ \AA}$ if the chloride is hydrolyzed to an unstable double

hydroxide $4 \text{Fe}(\text{OH})_2 \cdot \text{FeOOH}$, and $a=3.18 \text{ \AA}$, $c=24.37 \text{ \AA}$ (28 per cent. Fe^{3+}) - 27.38 \AA (56 per cent. Fe^{3+}) if the green complex is produced from a sulphate solution. In each instance there are rhombohedral extinctions so that the structure must have nine close-packed oxygen layers stacked ABC BCA CAB. The results in Table 3 confirm the dimensions of the complex from chloride solutions but give $a=3.23 \text{ \AA}$ and $c=22.5 \text{ \AA}$ for the complex from sulphate solutions. Green rust I has a dark blue-green colour.

Green rust II has not previously been reported. It has a hexagonal unit cell with $a=3.17 \text{ \AA}$ and $c=10.9 \text{ \AA}$ (see Table 3), and is presumably built up of four close-packed oxygen-hydroxyl layers in an ABAC sequence. The material has a slightly dulled dark green colour.

Green rust I can be produced by the aerial oxidation of a ferrous chloride solution buffered with ammonium chloride, to which excess ammonium hydroxide has been added, or by the oxidation of a ferrous chloride solution partially precipitated with sodium hydroxide. Sulphate solutions give substantially the same results except that on oxidation green rust I gives $\gamma\text{-FeOOH}$ via green rust II instead of giving $\gamma\text{-FeOOH}$ directly. Bromide and fluoride solutions also give green rust I.

On violent oxidation with a strong solution of hydrogen peroxide both complexes give $\delta\text{-FeOOH}$ in disordered form. The preparation from green rust II gave the four main X-ray powder lines of $\delta\text{-FeOOH}$ plus a line at 10.9 \AA while that from green rust I gave only the $10\bar{1}0$ and $11\bar{2}0$ lines of $\delta\text{-FeOOH}$ plus a line at 7.3 \AA . It is possible that the latter pattern represents a disordered 3-layer structure. On heating the green rusts to dryness they break down, principally to Fe_3O_4 and some FeO .

Electron diffraction data from a green rust have been given by Yoshioka (1948) and correspond to green rust I with dimensions $a=3.15 \text{ \AA}$ and $c=22.6 \text{ \AA}$. The very strong reflections 0003 and 0006 are missing because of the preferential orientation of the flaky material on the specimen carrier.

The green rusts I and II have been prepared in 10-gram quantities by the electrolytic solution of iron anodes in N/20 solutions of ammonium chloride or ammonium sulphate, respectively. On electrolysis in more oxidizing conditions $\gamma\text{-FeOOH}$, Fe_3O_4 or $\alpha\text{-Fe}_2\text{O}_3$ can be produced in quantity and the green-rust layer is confined to the surface of the anode. In oxygen-free conditions $\text{Fe}(\text{OH})_2$ can be formed.

TABLE 3—X-ray powder data for green rust.

<i>hkl</i>	Green rust I						Green rust II*		
	From chloride		From sulphate		From bromide		<i>hkl</i>	<i>d</i>	I
	<i>d</i>	I	<i>d</i>	I	<i>d</i>	I			
0003	8.02	vs	7.49	vs	7.64	vs	0001	10.92	vs
0006	4.01	s	3.84	s	3.79	m	0002	5.48	s
10 $\bar{1}$ 2	2.701	m	2.72	m	2.683	m	0003	3.65	s
10 $\bar{1}$ 4					2.479	vvw	0004, 10 $\bar{1}$ 0	2.747	m
10 $\bar{1}$ 5	2.408	m	2.47	m	2.357	m	10 $\bar{1}$ 1	2.660	ms
10 $\bar{1}$ 7					2.103	vvw	10 $\bar{1}$ 2	2.459	ms
10 $\bar{1}$ 8					1.982	w	0005, 10 $\bar{1}$ 3	2.195	ms
10 $\bar{1}$, 10	2.037	w	2.029	w	1.752	vw	10 $\bar{1}$ 4	1.938	ms
10 $\bar{1}$, 11	1.805	vw			1.653	vw	10 $\bar{1}$ 5	1.712	w
11 $\bar{2}$ 0	1.716	vwd			1.588	w	11 $\bar{2}$ 0	1.587	w
11 $\bar{2}$ 3	1.598	mw	1.616	mw	1.579	w	11 $\bar{2}$ 1	1.570	w
11 $\bar{2}$ 3	1.567	mw	1.579	mw	1.556	w	11 $\bar{2}$ 2	1.525	w
10 $\bar{1}$, 13	1.541	vvw							
11 $\bar{2}$ 6	1.487	w			1.479	vvw			
20 $\bar{2}$ 4	1.355	vvw			1.318	vvw			
	1.040	vvw							
					1.264	vvw			
					1.216	vvw			
					1.014	vvw			
					0.990	vvw			

Unit cell dimensions of green rust I (rhombohedral): from chloride $a=3.198 \text{ \AA}$, $c=24.21 \text{ \AA}$;

from sulphate $a=3.23 \text{ \AA}$, $c=22.5 \text{ \AA}$;

from bromide $a=3.18 \text{ \AA}$, $c=22.8 \text{ \AA}$.

Unit cell dimensions of green rust II (hexagonal): $a=3.174 \text{ \AA}$, $c=10.94 \text{ \AA}$; note that $4/3 \cdot 1/a^2 \approx (4/c)^2$.

*Prepared by oxidation of precipitate from solutions of ferrous sulphate and sodium hydroxide mixed in 1:1 proportions.

BASIC CHLORIDES

Keller (1948) reports three basic chlorides obtained by partial precipitation from ferrous chloride solution in various concentrations. They are:

- I. $\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$ with $a=3.40 \text{ \AA}$ and $c=16.92 \text{ \AA}$ (a rhombohedral CdCl_2 -type structure with 6 layers).
- II. $2\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$ with $a=3.32$ and $c=5.52$ (a CdI_2 -type structure).
- III. $3\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$ with a non-layer atacamite-type structure.

The basic chloride II has been examined and the presence of an unindexed line at $d=2.32 \text{ \AA}$ has been confirmed. These basic chlorides are presumably the precursors of green rust I when produced by partial precipitation.

SPINEL PHASES

When a ferrous solution buffered with ammonium sulphate and containing excess ammonium hydroxide, which would yield one of the green complexes if air were passed through it, is oxidized by boiling with the stoichiometric quantity of ammonium persulphate, a black precipitate of magnetite results. If the oxidant is in excess, $\gamma\text{-Fe}_2\text{O}_3$ results. If the oxidation is carried out under alkaline conditions $\delta\text{-FeOOH}$ and amorphous material are produced instead.

$\gamma\text{-Fe}_2\text{O}_3$ has been prepared in as many ways as possible and powder photographs taken of the products. Among these can be distinguished several types according to the strengths of the non-magnetite (superlattice) lines present. The indices refer in each instance to the spinel unit cell containing 32 oxygen atoms (here $N=a^2/d^2$ where $d=\lambda/2 \sin \theta$). The varieties are:

1. Completely ordered $\gamma\text{-Fe}_2\text{O}_3$ with extra lines corresponding to $c=3a$ —the tetragonal modification found by van Oosterhout and Rooijmans (1958). It had no 200 ($N=4$) reflection but had $N=10/9$, $13/9$, $16/9$, $22/9$, $61/9$, as well as the $N=2$, 5, 6 lines of maghemite and the $N=3$, 8 of magnetite. This is the magnetic ferric oxide of commerce, produced in acicular pseudomorphic polycrystals from $\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$.

2. Cubic $\gamma\text{-Fe}_2\text{O}_3$ with 110, 200, 210, 211 (lines with $N=2$, 4, 5, 6) present. This is the form produced by the oxidation of $\text{Fe}(\text{OH})_2$ by dilute peroxide or ammonium persulphate. Also in this class may be single crystals of Fe_3O_4 heated in air which still have the a -dimensions of magnetite but which show streaky reflections and anomalous 200 reflections.

3. Specimens with $N=2, 4$ (110 and 200) absent but $N=5, 6$ present. This variety has been described by Braun (1952) and is found in the material used in certain recording tapes. He explained this structure as paralleling the ordered phase in lithium ferrite. The latter can be written $\text{Fe}_8[\text{Li}_4\text{Fe}_{12}]\text{O}_{32}$; in the same way magnetite would be $\text{Fe}^{3+}_8[\text{Fe}^{2+}_8\text{Fe}^{3+}_8]\text{O}_{32}$ and maghemite between $\text{Fe}_8[\text{H}_4\text{Fe}_{12}]\text{O}_{32}$ and $\text{Fe}_8[(\text{Fe}_{1\cdot33}\square_{2\cdot67})\text{Fe}_{12}]\text{O}_{32}$ according to the amount of H present. The space group would be $P4_132$ with $h00$ absent except for $h=4n$ as the only condition.

4. Specimens with no non-magnetite lines but nevertheless the cell dimension $a=8\cdot35 \text{ \AA}$ appropriate to $\gamma\text{-Fe}_2\text{O}_3$. These were made by dehydrating lepidocrocite, also a toptotactic transformation (Bernal, Dasgupta and Mackay, 1957). They may be $\text{Fe}_8[\square_{2\cdot67}\text{Fe}_{13\cdot33}]\text{O}_{32}$.

The significance of the conditions which lead to these various modifications of $\gamma\text{-Fe}_2\text{O}_3$ is still obscure. The observation that the wet oxidation of natural and synthetic magnetites gives different modifications of $\gamma\text{-Fe}_2\text{O}_3$ implies differences in magnetites prepared in various ways. Some differences would be expected on the basis of magnetic observations.

THE DECOMPOSITION OF CHALYBITE

Single crystals of chalybite, FeCO_3 , which were perfect cleavage rhombohedra, were sealed into tubes under vacuum and heated under their own CO_2 pressure to about 550°C . On cooling rapidly by removal from the furnace they became magnetic and on X-ray examination proved to be oriented textures of FeO and Fe_3O_4 . Although black, the crystals still remained sharp-edged rhombohedra but under high magnification their faces appeared rough. The orientation of both cubic phases was such that one triad axis of the cube was parallel to the triad axis of the chalybite and the three diad axes of the latter phase were maintained. There was no unchanged FeCO_3 and no Fe was detected. The FeO (which has the NaCl structure) must derive from the FeCO_3 lattice (which has formally the NaCl structure also) by expulsion of CO_2 and change of the angles between the sheets of ions from 72° to 90° . It is remarkable that despite the loss of more than half the oxygen atoms from the structure the orientation of the lattice is still preserved. The decomposition takes place at a lower temperature than that of calcite and it is possible that the thermal vibrations at this temperature are not sufficient to cause complete disorganisation of the lattice. The Fe_3O_4 may derive from the FeO either by disproportion or by oxidation by the

CO₂. Pumping off the gas as it formed did not affect the production of magnetite, but it would seem improbable that CO₂ would leave the crystal and then return to be reduced to CO. It would be more likely that the oxygen in question never left the lattice. The topotactic decomposition of chalybite does not seem to have been mentioned previously, but Collongues (1954) showed metallographic evidence for the parallel growth of Fe₃O₄ from FeO.

BETA FERRIC OXYHYDROXIDE

The compound β -FeOOH lies rather outside the main scheme of transformations shown in Fig. 1. It is formed as a light brown deposit when a ferric solution containing Cl⁻ is hydrolyzed by boiling.

TABLE 4—X-ray powder data for β -FeOOH.

<i>hkl</i>	<i>d</i>	I	<i>hkl</i>	<i>d</i>	I
110	7.40	vs	440	1.854	vw
200	5.25	m	600	1.746	m
220	3.70	vw	501, 431	1.719	vw
310	3.311	vs	521	1.635	vs
400	2.616	m	002	1.515	m
211	2.543	s	611	1.497	w
420	2.343	w	112;710,550	1.480	w
301	2.285	m	640	1.459	vw
321	2.097	w	541	1.438	s
510	2.064	w	730;312	1.374	m
411	1.944	ms			

The dimensions of the tetragonal unit cell are: $a=10.48 \pm 0.01 \text{ \AA}$, $c=3.023 \pm 0.005 \text{ \AA}$.

Powder photographs of this material show it to be exceptionally well-crystallized and the pattern (Table 4) can be indexed on a body-centred tetragonal unit cell with $a=10.48 \pm 0.01 \text{ \AA}$ and $c=3.023 \pm 0.005 \text{ \AA}$. Kratky and Nowotny (1938), who studied the substance previously, reported it to be orthorhombic with $a=10.56 \text{ \AA}$, $b=10.24 \text{ \AA}$ and $c=3.34 \text{ \AA}$, but the pattern gives no close pairs, such as 020, 200, and their measurements agree fairly well with those quoted here.

Hydrolysis of ferric salts normally gives a precipitate of α -FeOOH (this was confirmed for the nitrate, sulphate and bromide) but hydrolysis of $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O} + 6\text{KCl}$ gives β -FeOOH. If the chloride in this solution is replaced by bromide then jarosite, $(\text{NH}_4, \text{K})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$, is formed. Ferric alum by itself gives jarosite. It was found, however, that solutions containing fluoride

(e.g., $\text{Fe}_2(\text{SO}_4)_3 + \text{KF}$ or $\text{Fe}(\text{NO}_3)_3 + \text{KF}$) gave $\beta\text{-FeOOH}$ on hydrolysis. The dimensions of the product were, within 1 per cent., the same as those of $\beta\text{-FeOOH}$ from chloride solutions. Keller (1948) reports that the basic chloride III (p. 25), when dry, decays on aerial oxidation to $\beta\text{-FeOOH}$. Aruja (private communication) has found $\beta\text{-FeOOH}$ among the oxidation products formed when "white rust" (a corrosion product formed on steel reinforcing bars embedded in concrete which had been laid down in sea-water) was exposed to the air. $\beta\text{-FeOOH}$ has been reported to be inactive in comparison to $\alpha\text{-FeOOH}$ as a catalyst for the Fischer-Tropsch synthesis. Published analyses show an appreciable Cl^- content (about 2 per cent.) which can be reduced indefinitely on prolonged washing (Weiser and Milligan, 1935). On heating, $\beta\text{-FeOOH}$ is transformed at about 280°C to $\alpha\text{-Fe}_2\text{O}_3$. Heating on a thermobalance showed a rapid loss of 13 per cent. H_2O at 230°C in a sharp step—rather more than the 10 per cent. loss which would correspond to the formula FeOOH . Boiling with water for 6 days converts $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$.

$\beta\text{-FeOOH}$ probably has a structure like that of hollandite or $\alpha\text{-MnO}_2$ (Byström and Byström, 1950). This compound has a unit cell with dimensions similar to those of $\beta\text{-FeOOH}$ and space group $I4/m$. The metal ions are at the centres of MO_6 octahedra and the oxygen ions are approximately close-packed in a cubic body-centred arrangement, except that there are open channels parallel to the c -axis. In the hollandite structure Ba^{2+} ions are statistically distributed in these channels. For $\beta\text{-FeOOH}$ $c=3.02 \text{ \AA}$, whereas the diameter of Cl^- is 3.62 \AA so that Cl^- which seems essential, at least for the formation of the structure, can only be accommodated statistically. The atacamite structure, from which the $\beta\text{-FeOOH}$ structure may also be derived (Wells, 1949), is notable in that it is not built of close-packed oxygen sheets as are almost all the compounds in Fig. 1. We conclude, therefore, that $\beta\text{-FeOOH}$ lies outside the field of hexagonally- and cubic-close-packed oxygen/hydroxyl compounds which we have delineated. As additional evidence that, on heating, the $\beta\text{-FeOOH}$ structure breaks down and later crystallizes as $\alpha\text{-Fe}_2\text{O}_3$, two observations can be adduced. First, the differential thermal curve of a specimen of $\beta\text{-FeOOH}$ showed an endothermic peak at $250\text{-}260^\circ\text{C}$ corresponding to loss of water and an exothermic peak at 420°C which could be explained by recrystallization of $\alpha\text{-Fe}_2\text{O}_3$. Secondly, a specimen heated to an intermediate temperature (about 300°C) was found to be magnetic $\alpha\text{-Fe}_2\text{O}_3$ and therefore, presumably disordered structurally.

Despite the observations of Abe (1951) the authors consider that no crystalline $\text{Fe}(\text{OH})_3$ has been observed; his data correspond to a mixture of $\beta\text{-FeOOH}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

CONCLUSIONS

All the reactions of solid phases shown in Fig. 1 are topotactic in character except $\beta\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3$, $\text{Fe}(\text{OH})_2 \rightarrow \alpha\text{-FeOOH}$, and $\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_3\text{O}_4$. $\beta\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ seem to have dissimilar structures and renucleation is necessary for the transformation process. The two other transformations may be explained as follows.

The solubility products of iron hydroxides are $[\text{Fe}^{2+}][\text{OH}]^2 = 1.6 \times 10^{-14}$ and $[\text{Fe}^{3+}][\text{OH}]^3 = 1.1 \times 10^{-36}$. In strong alkali ($> \text{N}$) the concentrations of both ferrous and ferric ions are extremely small, being $\sim 10^{-14}$ g-ion/l and $\sim 10^{-36}$ g-ion/l, respectively, and hence solid $\text{Fe}(\text{OH})_2$ is stable and on attack with a rapid oxidizing agent reacts as a solid being oxidized up to about 20 per cent. Fe^{3+} content, at which point the structure becomes unstable. Further oxidation gives $\delta\text{-FeOOH}$. On slow oxidation by oxygen dissolved in the solution the attack on the solid phase is inappreciable and Fe^{2+} is oxidized in solution and precipitated as ferric oxyhydroxide (in fact as $\alpha\text{-FeOOH}$ which is the normal hydrolysis product of a ferric salt). The $\alpha\text{-FeOOH}$, although built of hexagonally-stacked close-packed oxygen layers, does not derive from the $\text{Fe}(\text{OH})_2$ but is nucleated afresh. The oxidation must be slow enough for the solid $\text{Fe}(\text{OH})_2$ to remain in equilibrium with the solution, supplying fresh Fe^{2+} ions as they are removed by oxidation and precipitation.

In neutral solution solid $\text{Fe}(\text{OH})_2$ will be in equilibrium with a high concentration ($\sim \text{N}$) of Fe^{2+} . Slow oxidation under these conditions will transform Fe^{2+} to Fe^{3+} in the solution. In neutral solution the concentration of Fe^{3+} ions will be 10^{-15} g-ion/l and it must be assumed that there is a ferrous-ferric phase, of composition perhaps $\text{Fe}^{2+} \cdot 2\text{Fe}^{3+}(\text{OH})_8$ which is in equilibrium with an even lower concentration of Fe^{3+} . This hydroxide, with $[\text{Fe}^{2+}][\text{Fe}^{3+}]^2[\text{OH}]^8 < 10^{-86}$ and composition about $\text{Fe}_3(\text{OH})_8$, must be presumed to pass over to Fe_3O_4 on heating to 100°C in water as the hypothetical $\text{Fe}(\text{OH})_3$ ages to $\alpha\text{-FeOOH}$ or $\alpha\text{-Fe}_2\text{O}_3$. Further strong oxidation will alter the solid $\text{Fe}_3(\text{OH})_8$ or Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$. If oxidation takes place before dehydration this green complex of approximate composition $\text{Fe}_3(\text{OH})_8$ must transform to $\gamma\text{-FeOOH}$. This process is confirmed by the normal procedure for preparing

Fe_3O_4 : $\text{Fe}^{2+} + 2\text{Fe}^{3+}$ in solution are precipitated together with alkali and on boiling Fe_3O_4 , and not $\text{Fe}(\text{OH})_3$, is formed.

In a purely ferrous solution, buffered with ammonium chloride, ammonium hydroxide gives no precipitate as $[\text{OH}^-]$ does not reach the solubility product of $\text{Fe}(\text{OH})_2$. If air is passed through this solution green rust I is precipitated and the Fe^{3+} produced by slow oxidation is removed from solution as fast as it is formed and before its concentration can exceed that required to precipitate $\text{Fe}(\text{OH})_3$. Further work on the green rusts is in progress.

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