

to apply adequate significance tests (Lipson & Cochran, 1953, p. 309) to bondlengths, especially if detailed interpretations are given to results obtained from few data (as, e.g. in the prochlorite analysis). The present discussion suggests that trial structures for layer silicates may now be proposed which include some degree of distortion, the amount depending on the calculated misfit of the layers, and the direction on the attractive forces due to assumed residual charges.

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Morphology of Synthetic Submicroscopic Crystals of α and γ FeOOH and of γ Fe₂O₃ Prepared from FeOOH

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The orientation of the needle axis of synthetic acicular crystals of α and γ FeOOH with respect to the unit cell has been determined by selected-area electron diffraction. The needle axis is [001] for α FeOOH ($c = 3.03 \text{ \AA}$) and γ FeOOH ($c = 3.06 \text{ \AA}$) and [110] for γ Fe₂O₃ prepared either by dehydration of γ FeOOH or by reduction of α FeOOH or γ FeOOH followed by oxidation.

The results are compared with previous work on this subject and the possible causes of the discrepancies between the results of Osmond and of Campbell and those obtained in the present paper are discussed.

Introduction

Knowledge of the orientation of the needle axis of acicular γ Fe₂O₃ with respect to the unit cell is necessary for a discussion of the magnetic properties of these crystals as they are used in magnetic recording

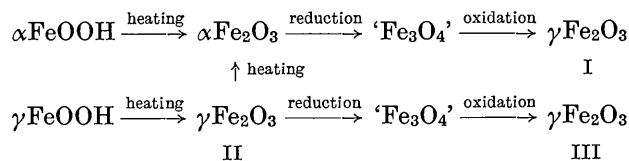
devices. Several papers have already been published on this subject (Osmond, 1953; Campbell, 1957*a, b, c*). Because they report contradictory results it was considered desirable to publish our own results with a discussion of those of the other authors in order to trace the origin of these discrepancies.

Briefly the situation is as follows. Osmond (1953) derived the direction of the needle axis of $\gamma\text{Fe}_2\text{O}_3$ from the isomorphism of αAlOOH (diaspore, Dana 7121) and αFeOOH using data on the transformation $\alpha\text{AlOOH} \rightarrow \alpha\text{Al}_2\text{O}_3$ from a paper by Ervin (1952). Unfortunately he overlooked an essential statement in Ervin's paper and arrived at the—in our opinion—erroneous result that the needle axis is in the [111] direction.

Afterwards Campbell (1957*a, b, c*) investigated sub-microscopic acicular single crystals of $\gamma\text{Fe}_2\text{O}_3$ experimentally, using the selected-area electron diffraction method.* He arrived at the rather unexpected result that the needle axis does not correspond to one definite crystallographic direction but that in general any low order direction may occur.

In an investigation on the morphology of $\gamma\text{Fe}_2\text{O}_3$ it should be borne in mind that $\gamma\text{Fe}_2\text{O}_3$ and even acicular $\gamma\text{Fe}_2\text{O}_3$ can be prepared by several methods starting with different materials. This might conceivably lead to different results. At present the most important materials for the preparation of $\gamma\text{Fe}_2\text{O}_3$ are αFeOOH and γFeOOH (both in acicular form).

These compounds may be transformed into $\gamma\text{Fe}_2\text{O}_3$ by the following processes.



In this scheme 'Fe₃O₄' symbolizes a ferrous-ferric oxide having the spinel lattice but not exactly the composition Fe₃O₄. $\gamma\text{Fe}_2\text{O}_3$ I and III give a sharp X-ray diagram. These types are used in magnetic tapes. $\gamma\text{Fe}_2\text{O}_3$ II gives a very poorly developed X-ray diagram.

The oxidation and reduction process has been described by Abraham & Planiol (1925).

The following methods may be used to determine the crystallographic direction of the needle axis.

- Direct determination of the needle direction of $\gamma\text{Fe}_2\text{O}_3$ by means of selected-area electron diffraction (Campbell, 1957*a, b, c*).
- Direct determination of the needle direction of α and γFeOOH by means of selected-area electron diffraction.

From this we can derive the direction for $\gamma\text{Fe}_2\text{O}_3$ by using the results of Goldstaub (1935) and Bernal (1957), the mineralogical data on intergrowth of $\alpha\text{Fe}_2\text{O}_3$ and magnetite and the plausible assumption that $\gamma\text{Fe}_2\text{O}_3$ behaves in this last respect as the other spinels.

- Using the isomorphism of αAlOOH and αFeOOH and the fact that the elongated direction of

acicular αAlOOH is the *c* axis—a result obtained by Ervin (1952)—we can derive the direction in the same way as described under (b). This in fact is Osmond's method in a slightly improved form.

- On the assumption that the fibre direction of natural αFeOOH corresponds to the needle axis of synthetic αFeOOH the needle direction can be determined from purely mineralogical data.

Methods (b), (c) and (d) for $\gamma\text{Fe}_2\text{O}_3$ give less conclusive evidence than (a) but we will show that they all lead to the same result.

Review of the existing crystallographical and mineralogical data on

αFeOOH , γFeOOH , $\alpha\text{Fe}_2\text{O}_3$ and $\gamma\text{Fe}_2\text{O}_3$

(A) The structures

αFeOOH . Goethite (Dana 7122).

Unit cell: orthorhombic, $a=4.64$, $b=10.0$, $c=3.03$ Å.

γFeOOH . Lepidocrocite (Dana 6121).

Unit cell: orthorhombic, $a=3.87$, $b=12.51$, $c=3.06$ Å.

$\alpha\text{Fe}_2\text{O}_3$. Hematite (Dana 4412).

Unit cell: rhombohedral $a_{\text{rh}}=5.42$ Å; $\alpha=55^\circ 17'$ or $a=5.03$, $c=13.73$ Å in the hexagonal description.

$\gamma\text{Fe}_2\text{O}_3$. Maghemite (Dana 721.10).

Unit cell: cubic $a=8.33$ Å.

$\gamma\text{Fe}_2\text{O}_3$ is practically cubic. Recently it has been shown (van Oosterhout, Rooymans, 1958) that a number of very weak reflexions are due to a tetragonal superstructure with cell dimensions $a=a_{\text{cub.}}$, $c=3.00a$. The spacings and indices of the 'non-cubic' lines are:

<i>d</i>	<i>hkl</i>	<i>d</i>	<i>hkl</i>
7.93	101	3.20	214
6.95	102		205
6.27	004	3.13	008
5.76	111	2.87	222
5.34	112	2.72	207
4.29	114		302
	105	2.58	312
4.12	201		217
3.82	115	2.43	305
3.28	107		314

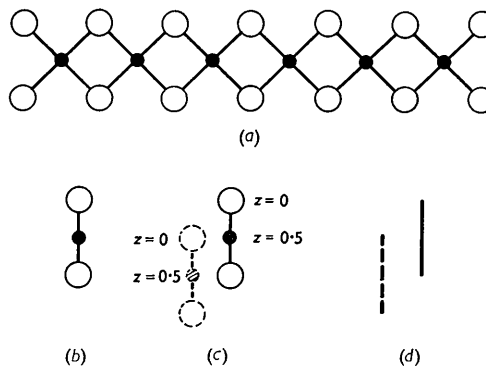


Fig. 1. (a) 'FeO₂' chain. (b) Side view of 'FeO₂' chain. (c) Side view of combination of two parallel 'FeO₂' chains. (d) Schematic representation of Fig. 1(c).

* For a description of this method see van Dorsten *et al.* (1950).

In order to obtain a simple description of the structures of α and γ FeOOH we make use of the scheme shown in Fig. 1(a), (b), (c), (d).

The structures of α and γ FeOOH are shown with this notation in Figs. 2(a) and 2(b).

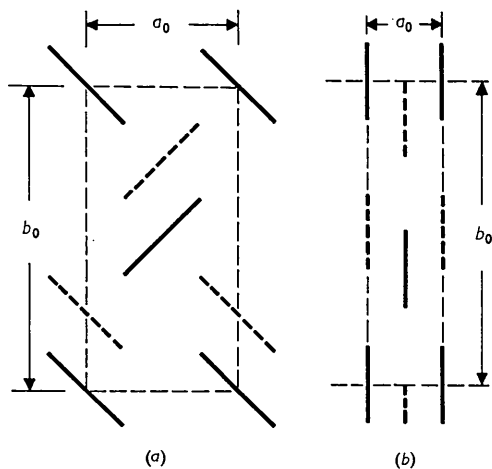
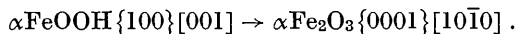


Fig. 2. Schematic representation of the crystal structures of (a) α FeOOH and (b) γ FeOOH (for an explanation see Fig. 1(d)).

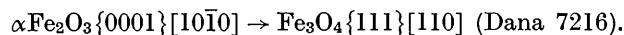
The positions of the protons are not given in these pictures. The essential point for the present paper is that the direction of the 'FeO₂' chain in both α and γ FeOOH is the c axis with c equal to about 3.0 Å.

(B) The transformations

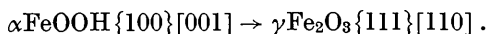
The transformation α FeOOH \rightarrow α Fe₂O₃ has been investigated thoroughly by Goldsztaub (1935). He found that the a axis of α FeOOH becomes the trigonal axis of α Fe₂O₃ and the c axis of α FeOOH becomes the [11 $\bar{2}$] axis of α Fe₂O₃ described in rhombohedral coordinates. This is the hexagonal [10 $\bar{1}$ 0] direction. This transformation is represented by:



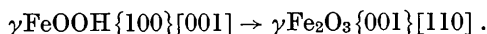
It is known from mineralogy that α Fe₂O₃ and spinels (e.g. magnetite) intergrow according to:



Assuming that the pseudomorphous reduction of α Fe₂O₃ to 'Fe₃O₄' obeys the same law as the intergrowth and that the oxidation of 'Fe₃O₄' to γ Fe₂O₃ does not change the orientation we arrive at the result:



The transformation γ FeOOH \rightarrow γ Fe₂O₃ has been studied by Bernal (1957) and his collaborators. They arrived at the result that the corresponding directions are:



In both cases the FeO₂ chain direction becomes the [110] direction of the spinel structure.

(C) Orientation

There are, apart from Campbell's work (1957a, b, c), some data in the literature which allow an indirect determination of the orientation.

In his paper on the α AlOOH- α Al₂O₃ transition Ervin concludes from optical evidence: '... artificial diaspore which was predominantly in the shape of laths elongated on the c axis'.

This conclusion apparently has been overlooked by Osmond (1953), who writes: 'It follows that each acicular iron-oxide particle must be considered to consist of a collection of crystallites all having their [111] cubic directions of easy magnetization aligned in the same sense most probably parallel to the long dimension of the particle'.

We will see below that there is no need for this extra assumption. According to Ervin the long dimension is the c axis, and the c axis of α FeOOH becomes the cubic [110] direction in γ Fe₂O₃; so the elongated dimension corresponds to the cubic [110] direction contrary to Osmond's results.

The only assumption made here is that of analogy between diaspore and goethite which is also the basis of Osmond's method.

α FeOOH in nature often occurs in a fibrous or striated form with fibre direction [001] (Dana 7122).

It is therefore very likely that the needle axis is also [001] for synthetic acicular α FeOOH.

Direct determination of the direction of the needle axis of α FeOOH, γ FeOOH and γ Fe₂O₃

Although the arguments given above are very plausible, a direct determination of the orientation is obviously preferable. Diffraction patterns of α FeOOH, γ FeOOH and γ Fe₂O₃ have therefore been made by means of selected-area electron diffraction with a Philips EM 100B electron microscope. The patterns are reproduced in Figs. 3(a), 4(a), 5(a), 6(a).

The bars indicate the direction of the needle axis. Calibration has been done with a vapour-deposited gold film. The diagrams have been indexed completely and lattice periods and directions of axes have been determined. The results are shown in Figs. 3(b), 4(b), 5(b), 6(b), and lead to the following conclusions:

- For γ Fe₂O₃ prepared from α FeOOH or from γ FeOOH by reduction and oxidation and for γ Fe₂O₃ prepared from γ FeOOH by dehydration the direction of the needle axis is one of the cubic $\langle 110 \rangle$ directions. In the last case the electron-diffraction pattern is the same as Fig. 5(a). It has therefore not been reproduced here.
- For α FeOOH the needle axis is the c axis. The c axis thus becomes one of the cubic $\langle 110 \rangle$ direc-

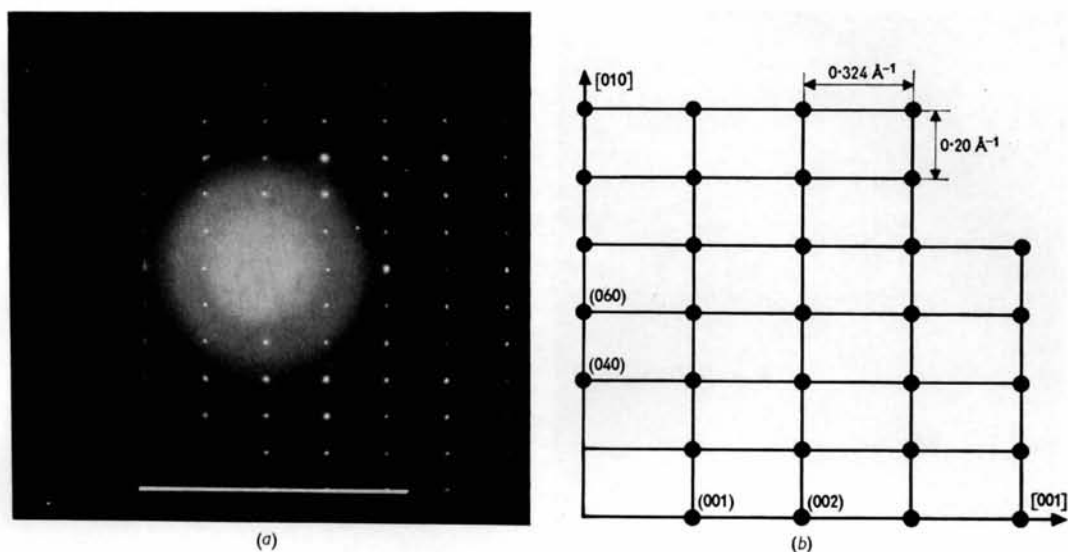


Fig. 3. (a) Electron diffraction pattern of a single crystal of synthetic goethite (αFeOOH). 80 kV. Beam \perp (100). (b) Drawing of the upper right-hand part of Fig. 3(a). The periods correspond to lattice periods of 3.09 \AA ($=c$) and 5.0 \AA ($=\frac{1}{2}b$).

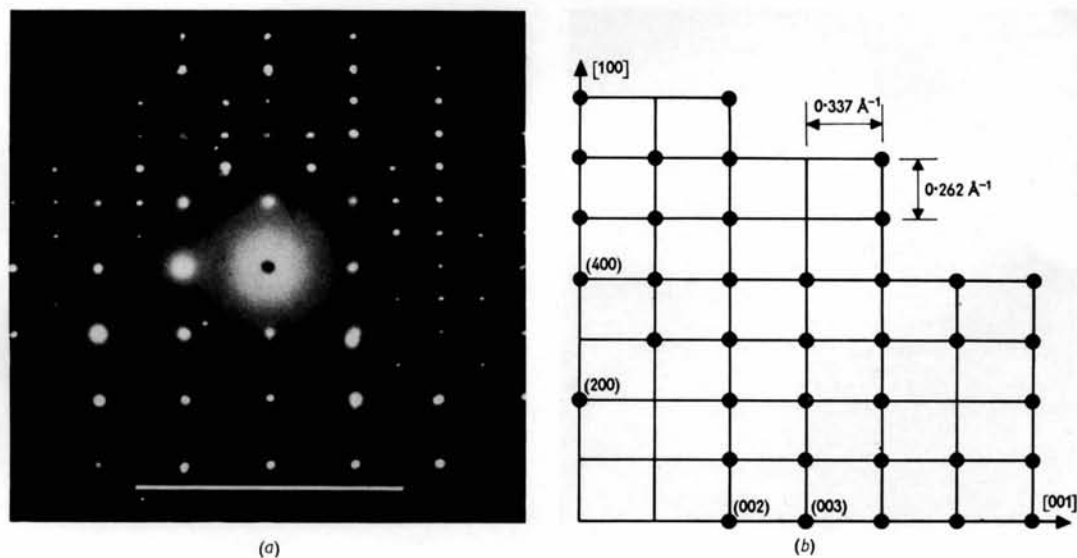


Fig. 4. (a) Electron-diffraction pattern of a single crystal of synthetic lepidocrocite (γFeOOH). 80 kV. Beam \perp (010). (b) Drawing of the upper right-hand part of Fig. 4(a). The periods correspond to lattice periods of 2.97 \AA ($=c$) and 3.81 \AA ($=a$).

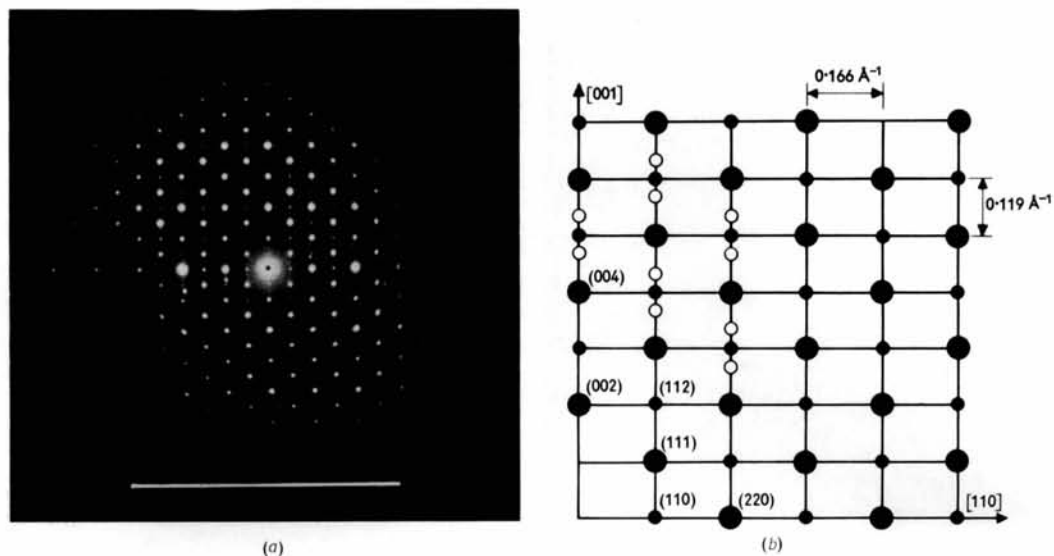


Fig. 5. (a) Electron-diffraction pattern of $\gamma\text{Fe}_2\text{O}_3$ prepared from γFeOOH by reduction and oxidation 80 kV. Beam \perp $(1\bar{1}0)$. (b) Drawing of the upper right-hand part of Fig. 5(a). The periods correspond to lattice periods of 8.4 Å ($= [001]$) and 6.0 Å ($= [110]$). The very weak spots indicated by open circles gave the first indication of $c/a=3$ in the tetragonal superstructure.

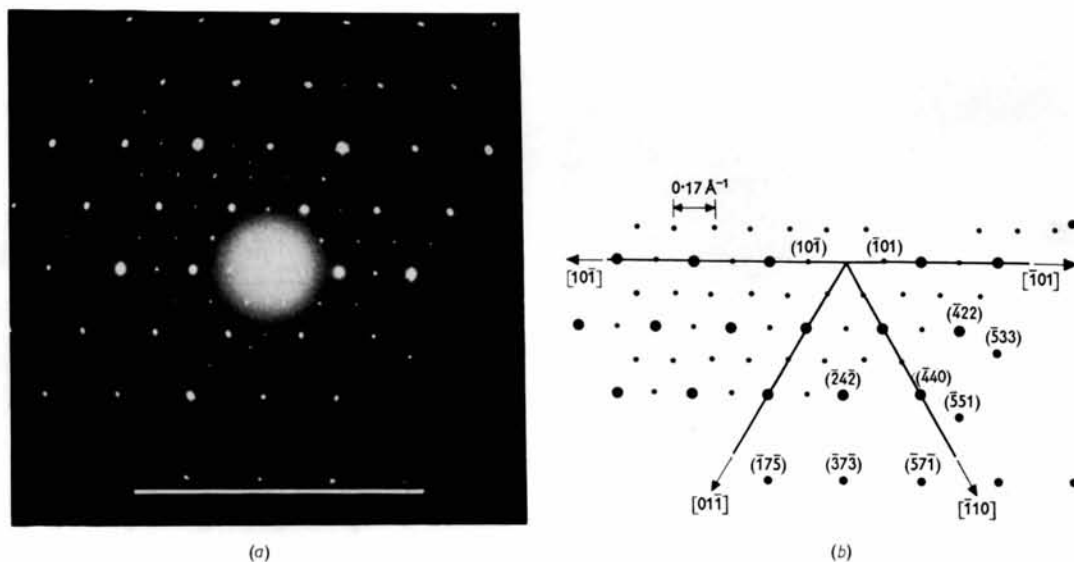


Fig. 6. (a) Electron-diffraction pattern of $\gamma\text{Fe}_2\text{O}_3$ prepared from αFeOOH by reduction and oxidation. 80 kV. Beam \perp (111) . (b) Drawing of the lower part of Fig. 6(a). The period corresponds to a lattice period of 5.9 Å ($= [1\bar{1}0]$).

tions, just as would be expected from the mineralogical data.

- (c) For γFeOOH the needle axis is the c axis. The relation between γFeOOH and $\gamma\text{Fe}_2\text{O}_3$ is the same as found by Bernal.

Discussion

The results arrived at are mutually consistent and in agreement with the existing mineralogical data. They do not agree, however, with the results of Osmond and of Campbell. Because the crystallographic relationships treated in this paper are used in the discussion of the magnetic properties of gamma ferric oxide it seems of importance to discuss the origin of this discrepancy.

As we have seen Osmond's results involve an assumption about the direction of the needle axis of αAlOOH ; but no additional assumption is needed, because Ervin explicitly concludes from optical evidence that it is the c axis. Taking Ervin's results into account, Osmond's method leads to the same result as we obtained.

It is not so easy to see why our results differ from those of Campbell. In αFeOOH as well as in γFeOOH the c direction is very typical as it is the direction of the 'FeO₂' chains. It would be very surprising if such a direction did not have a constant relation to the outer form of the crystals or if there were no constant relation between the axes of α and γFeOOH on the one hand and those of $\gamma\text{Fe}_2\text{O}_3$ prepared from it on the other. Campbell (1957*a, b, c*) suggests, however, that in this case the unexpected does happen: he writes that the directions of the long axes of the particles 'were usually of low order e.g. $\langle 111 \rangle$, $\langle 211 \rangle$, $\langle 221 \rangle$, $\langle 331 \rangle$, etc.' Fig. 4(*a*) of Campbell's paper (1957*c*) compares very nicely with our Fig. 5(*a*), from which we concluded that the direction of the needle axis was $\langle 110 \rangle$. Although it is one of Campbell's best diagrams, $\langle 110 \rangle$ was not mentioned in his results. In a private letter, however, he stated that $\langle 100 \rangle$ and $\langle 110 \rangle$ do also occur.

Unfortunately the other patterns of Campbell's paper do not show sufficient detail for an independent

interpretation. Although we made some twenty patterns we never found other directions than $\langle 110 \rangle$. Two possible reasons for the discrepancies can be easily suggested.

The first is the rather trivial one that the diffraction pattern is not due to the observed needle but to a fragment attached to it in a different orientation. The second is that of a slight tilt of the needle in such a way that the plane perpendicular to the electron beam is not a low-index plane. This may result in a certain deformation of the pattern, not of much importance for our method of indexing, but possibly giving rise to misinterpretations in the method of Campbell, who apparently attaches much importance to the use of tables of interplanar angles (1957*b, c*).

In conclusion I should like to thank Dr A. J. v. Bommel and Dr P. B. Braun for their interest and valuable criticism, Mr J. Govers for the chemical preparations, Mr J. Hornstra for the elucidation of some crystallographic difficulties, Mr H. B. Haanstra and Mr J. M. Nieuwenhuizen for the painstaking and patient preparation of the diffraction patterns and last but not least all those others who by their help at the right moment have made the writing of this paper possible.

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