Acta Cryst. (1979). A**35**, 197–200

Structural Changes in β-FeOOH Caused by Radiation Damage

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(*Received* 5 *June* 1978; *accepted* 15 *August* 1978)

Abstract

A high-resolution electron-microscope study of β-FeOOH (akaganéite) has been carried out. Examination of intact crystals and ultrathin sections provided no evidence for the hollow-rod structure proposed by earlier workers. It was found also that features, such as mottling and striations, previously thought to be indicative of a porous structure, were due to radiation damage. It is concluded that the β-FeOOH crystals are not porous, but are, in fact, crystallographically homogeneous.

1. Introduction

β-Iron(III) hydroxide oxide (β-FeOOH) was first isolated by Bohm (1925) but was not studied in detail until 1960, when a series of papers (Mackay, 1960, 1962*a*,*b*) described the occurrence, preparation, crystal structure and morphology of β-FeOOH. It occurs in nature as the mineral akaganéite and can also be prepared by various synthetic methods. The most important of these is the hydrolysis of a dilute solution of $FeCl_3.6H_2O$, and when prepared by this method, the β-FeOOH is found to consist of cigar-shaped crystals, 1000–5000 Å long and 400–600 Å wide with square or circular cross sections.

X-ray powder diffraction studies (Mackay, 1960) showed that the crystals had the hollandite ($BaMn_8O_{16}$) structure, with a tetragonal unit cell ($a = 10{\cdot}48$, $c = 3{\cdot}023$ Å) and space group $I4/m$. This is shown schematically in Fig. 1. The small central tunnel, which in hollandite contains Ba^{2+}, is in the case of β-FeOOH occupied by Cl^- or H_2O in non-stoichiometric amounts. Single-crystal electron-diffraction patterns (Mackay, 1960) showed that the cigar-shaped crystals were elongated along the crystallographic *c* axis.

Watson, Cardell & Heller (1962) used the technique of ultrathin sectioning to investigate the internal structure of β-FeOOH. Longitudinal sections showed striations with a repeating distance of about 30 Å, and when the crystals were cut at 90° to the *c* axis, electron micrographs of the cross sections were seen to display a mottled appearance. On the basis of these observations, Watson *et al.* (1962) proposed that the crystal could be described as a bundle of rods (subcrystals), each of which was hollow, with an internal diameter of 30 Å and an external diameter of 60 Å.

Gallagher & Phillips (1969) used the nitrogen adsorption method of Barrett, Joyner & Halenda (1951) to calculate the pore-size distribution in β-FeOOH. The mean pore diameter was found to be 28·4 Å, in very good agreement with that proposed by Watson *et al.* (1962). Gallagher (1970) was then able to formulate a detailed atomic structure for the tubular subcrystal.

There have been no high-resolution studies on this material up to the present work, but Bursill & Wilson (1977) have examined the crystallographically analogous compound $BaMgTi_7O_{16}$. In this case thin perfect crystals were tilted to the requisite orientation for examination, and structural details down to 3 Å in size were observed. In the present work, the morphology of the crystals prevented direct deposition in the requisite orientation for unit-cell resolution.

Furthermore, tilting the crystals was not possible for two reasons, the first being that to achieve the extensive contrast transfer-function envelope with the low spherical aberration lens used, a tilting stage could not be used, and secondly the susceptibility of the material to radiation damage precluded extensive specimen manipulation in the microscope.

The present paper describes a high-resolution electron-microscope study of the internal structure of β-FeOOH crystals, and a reassessment of the early

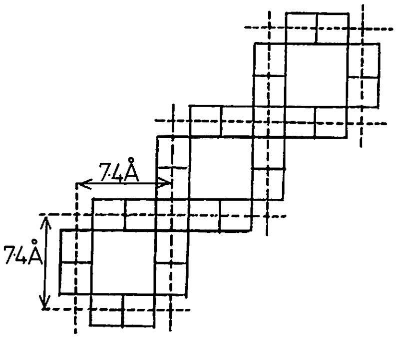

Fig. 1. Schematic diagram of the β-FeOOH structure. Each small square represents one Fe/O_6 octahedron.

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evidence for the presence of internal pores in the crystals. The precipitated β-FeOOH was embedded and sectioned to achieve required orientations and full structural information.

2. Experimental

β-FeOOH was prepared by the room-temperature hydrolysis of a 0·01*M* $FeCl_3.6H_2O$ solution. The yellow-brown precipitate was washed three times with deionized water, dried in air at 40 °C and ground lightly between glass slides.

Ultrasonic dispersion was carried out in a Kerry 100S ultrasonic generator (60 kHz).

Ultrathin sections ~500 Å thick were prepared by embedding the washed and dried crystals in Scandiplast metallurgical embedding resin, followed by sectioning on an LKBIII ultramicrotome fitted with a diamond knife. The thin sections were mounted on uncoated 400 mesh grids.

All samples were examined on a JEM 100C electron microscope, fitted with a high-resolution objective pole-piece (spherical-aberration constant $C_s = 0{\cdot}7$ mm) at magnifications of 150 000–300 000×. To minimize the effects of thermal drift and irradiation damage, Ilford Industrial G X-ray film was used, with exposure times of less than 1 s.

The low value of the spherical aberration caused the Scherzer focus to be 500–600 Å underfocus. At this value the constant-contrast transfer envelope extended down to 3 Å; thus all periodicities in excess of 3 Å could be imaged without contrast reversal. For thin sections the image at the Scherzer focus would represent the specimen for all periodicities above 3 Å.

3. Results and discussion

On examination in the electron microscope the yellow-brown crystals of β-FeOOH were found to have the characteristic cigar shape as shown in Fig. 2. When exposure to the electron beam was kept to a minimum no regular intensity variations, compatible with the proposed hollow-rod structure, were observed. At high magnifications, as shown in Fig. 3, it could be seen that the β-FeOOH was crystallographically homogeneous.

After a short period of irradiation, however, striations developed, as shown in Fig. 4. These striations were too irregular to be consistent with the crystallographic rod structure and, in any case, the striations appeared only as decomposition to γ-Fe_2O_3 progressed, as shown by selected-area diffraction. Watson *et al.* (1962) dehydrated the β-FeOOH crystals in alcohol, thereby removing or replacing at least some of the H_2O and Cl^- in the small 5 Å tunnels running parallel to the *c* axis. This removal would hasten the

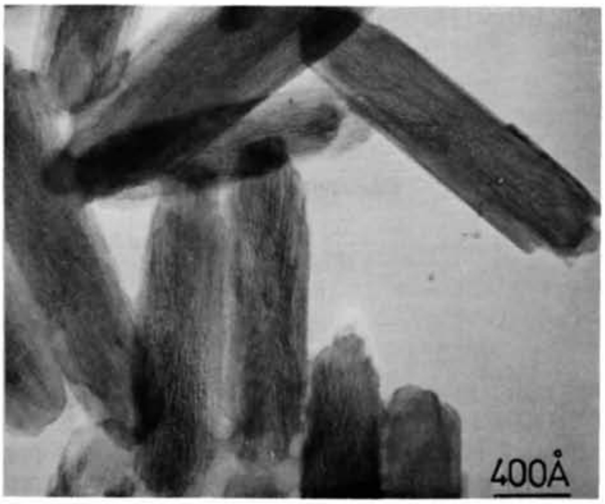

Fig. 2. Cigar-shaped β-FeOOH crystals.

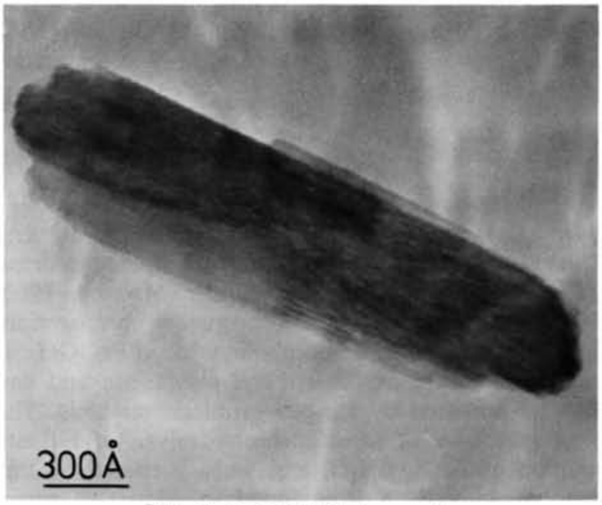

Fig. 3. β-FeOOH single crystal.

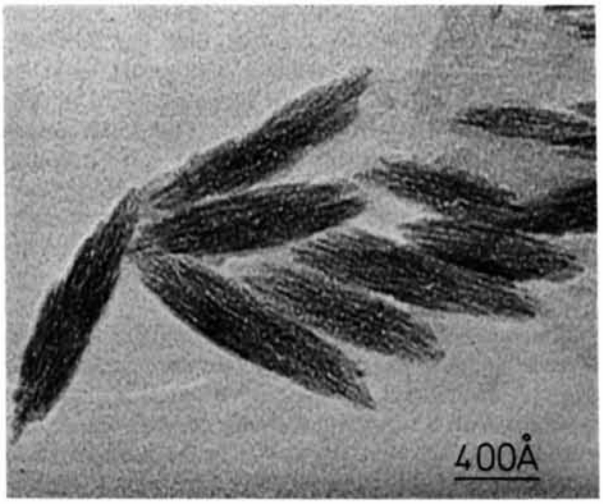

Fig. 4. Irradiated β-FeOOH crystals, showing striations.

decomposition to γ-Fe_2O_3 since the presence of anions in these tunnels is essential to stabilize the structure. This may account, in part, for the large number of striations observed by Watson *et al.* (1962).

Since our studies of the intact crystals provided no evidence for the hollow-rod structure, ultrasonic dispersion was used to break up the crystals, in order to manifest any inherent rod structure. After treatment for 30 s considerable fragmentation was observed (Fig. 5) and in almost all cases cleavage appeared to be parallel to the *c* axis. There was no preponderance of fragments 60 Å wide, as would have been expected from a crystal consisting of 60 Å rods, and none of the resultant particles appeared to be tubular. The present studies thus indicate that β-FeOOH consists of a continuous homogeneous crystalline array, and not of stacked rods.

To ascertain the presence or absence of 30 Å pores as postulated by Watson *et al.* (1962) and Gallagher (1970), thin sections of β-FeOOH crystals were examined. A typical section is shown in Fig. 6, and it can be seen that the crystals lie randomly in many different orientations.

When the cutting angle was at 90° to the *c* axis, a good cross section could be obtained (as shown in Fig. 7), the 7·4 Å (110), 5·2 Å (200), and 3·3 Å (310) lattice fringes all being well resolved. By comparison with Fig. 1, it can be seen that the (110) planes delineate the 5 Å hollandite tunnels.

The cross sections were predominantly square as would be expected at this temperature (Mackay, 1962*a*) but many stepped edges were seen. In almost all cases, the crystal edges were bounded by the (200) planes.

Fig. 8 shows a cross section on which the size of the proposed pore has been indicated. It can be clearly seen that no pore of this size was present in the crystal.

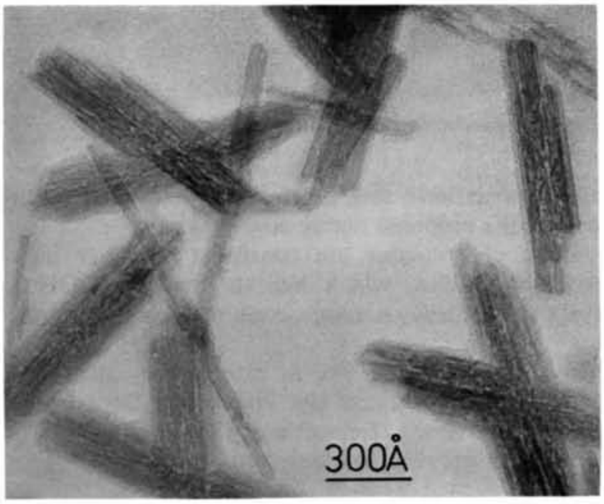

Fig. 5. β-FeOOH crystals after ultrasonic treatment.

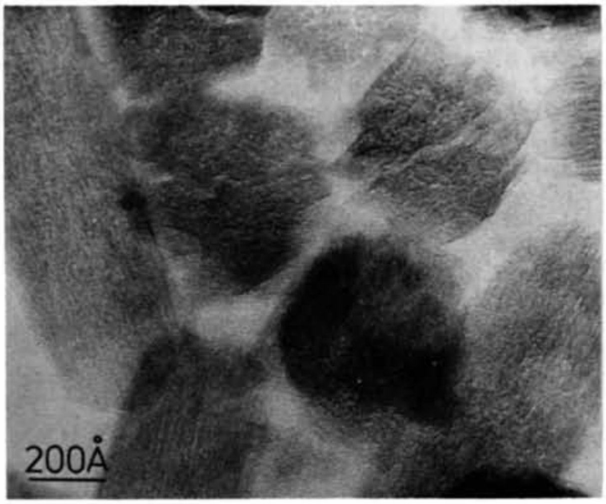

Fig. 6. Typical thin section of β-FeOOH crystals.

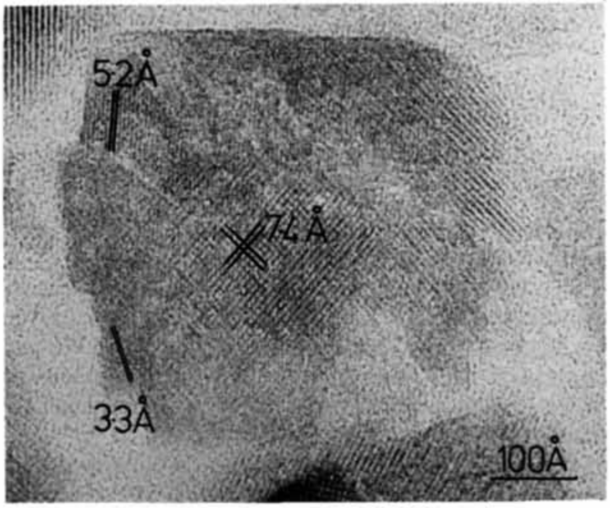

Fig. 7. Cross section of β-FeOOH crystal.

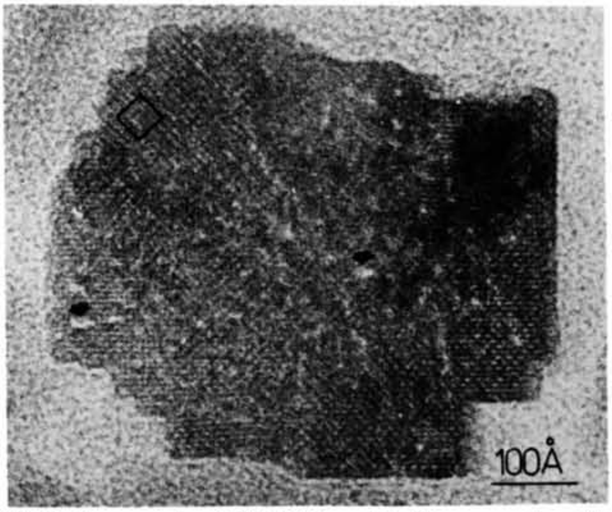

Fig. 8. Cross section of β-FeOOH crystal. The square shows the size of the proposed pore.

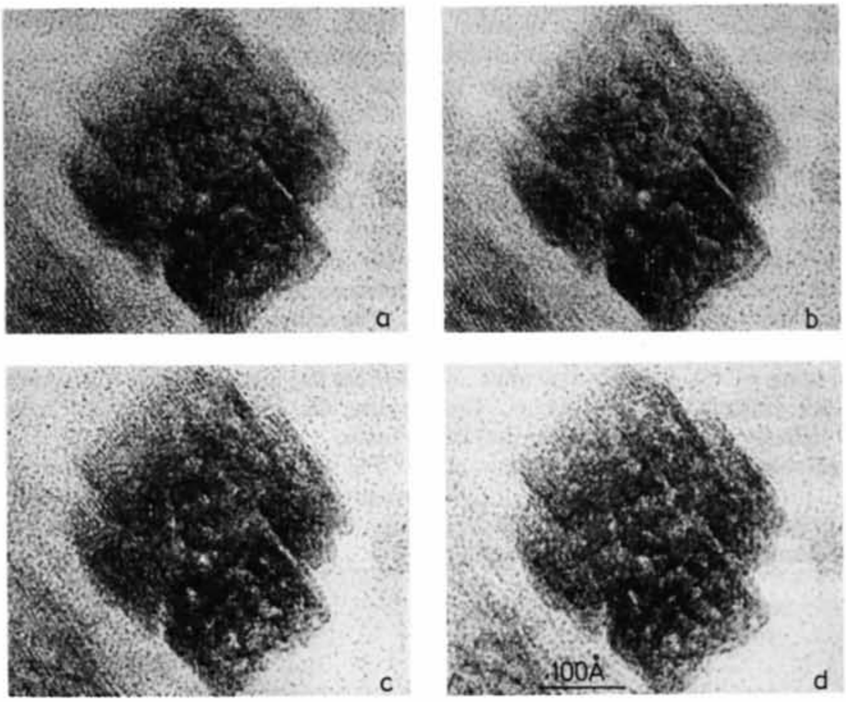

Fig. 9. Series of micrographs, taken at intervals of 1 min, showing development of 'mottling' on irradiation.

Some small crystal imperfections were visible (arrowed) but these were probably due to radiation damage.

The cross sections shown in Fig. 9(*a*)–(*d*) illustrate the effect of progressively increasing the exposure to the electron beam. The small areas of damage became larger and more numerous as irradiation proceeded whilst selected-area electron diffraction showed that dehydration to γ-Fe_2O_3 occurred simultaneously.

The pattern of 'mottling' in Fig. 9(*d*) was very similar to that observed by Watson *et al.* (1962) and interpreted by them as being indicative of a porous structure. We have found that such mottling developed only on irradiation and was not present in an undamaged crystal.

4. Conclusions

This investigation of β-FeOOH shows that the crystals do not consist of arrays of hollow rods as postulated by earlier workers and that the microscopic evidence for the previously proposed structure resulted from irradiation damage in the electron microscope.

Gallagher's (1970) studies on the porous nature of β-FeOOH using nitrogen adsorption data have recently been repeated and reassessed by Paterson & Tait (1977) who concluded that the apparent porosity was due to adsorption in the interstices between the crystals, rather than within the crystals. Their measured surface areas were also much lower than those calculated for the proposed highly porous system.

These observations are consistent with our high-resolution studies, which indicate that β-FeOOH is crystallographically homogeneous, with no 30 Å pores.

The authors would like to express their thanks to Mr Ian Montgomery of the Physiology Department, Glasgow University, for sectioning the crystals, and to the SRC for provision of equipment.

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