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References

Brindley, G. W. & Méring, J. (1951). *Acta Cryst.* **4**, 441.

Diamond, R. (1956). Ph.D. Dissertation, Cambridge.

Robertson, J. M. (1951). *Proc. Roy. Soc.* A, **207**, 101.

Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.* p. 607.

Robertson, J. M. & White, J. G. (1947). *J. Chem. Soc.* p. 358.

Warren, B. E. (1941). *Phys. Rev.* **59**, 693.

Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 245.

Acta Cryst. (1957). **10**, 364

The Reduction of Oxide Films by Atomic Hydrogen

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The reactions of atomic hydrogen with thin films of oxides of copper, iron, lead and nickel were investigated, using electron diffraction to determine the crystalline state and composition of the film before and after the action of the atomic hydrogen.

No reduction was observed in the case of iron and nickel oxides, whilst complete reduction was observed with the copper and lead oxides investigated. The crystalline state of the metal after reduction was found to depend on the concentration of the atomic hydrogen, i.e. upon the speed of the reaction.

1. Introduction

The reactions of atomic hydrogen have been studied in detail by Bonhoeffer (1924), Kroepelin & Vogel (1936), and others. These and other previous workers in the field, however, had only optical methods available to identify the reaction products.

In the present experiments the use of electron diffraction has made possible a more critical analysis of the reaction products, and in particular has yielded information on the crystalline state of the products as well as that of the oxide being reduced.

2. Experimental details

The atomic hydrogen was produced by a condensed discharge between aluminium electrodes in the vessel in which the reduction was to take place. The reaction vessel was in the first instance a 6 in. diameter glass sphere with four ground joints, two holding the electrodes, one for the admission of the specimen, and one holding a glass screen which protected the specimen from sputtered aluminium.

In later experiments, however, the electron diffraction camera, in which approximately 60 kV. electrons were used, at camera lengths of 34·5 or 23 cm., was itself used as the reaction vessel to avoid transference of the reduction products through air to the electron diffraction camera with consequent risk of rapid reoxidation. The aluminium electrodes for the production of atomic hydrogen were held inside the camera on tungsten rods led in through glass seals. The electrodes were shielded to prevent the discharge going to the brass walls of the camera.

The hydrogen to be atomized was stored in contact with distilled water to ensure that it contained a certain amount of water vapour (that this was necessary for the production of atomic hydrogen by low and medium-power discharges was shown by Finch (1949)). It was admitted to the apparatus through a long narrow tube to limit its rate of entry, the pressure in the apparatus being kept at about 1 mm. of mercury by means of a rotary pump.

For some experiments hydrogen from a cylinder was purified by passage through the walls of a heated palladium tube before being let into the apparatus, and the apparatus was at the same time kept as dry as possible with phosphorus pentoxide.

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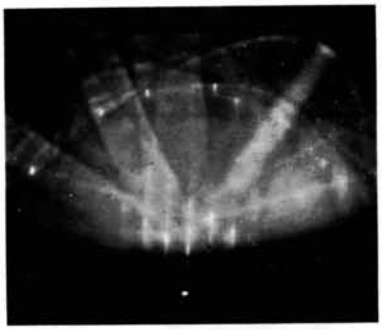
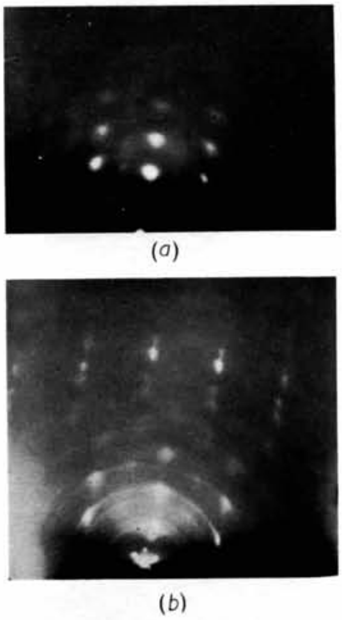


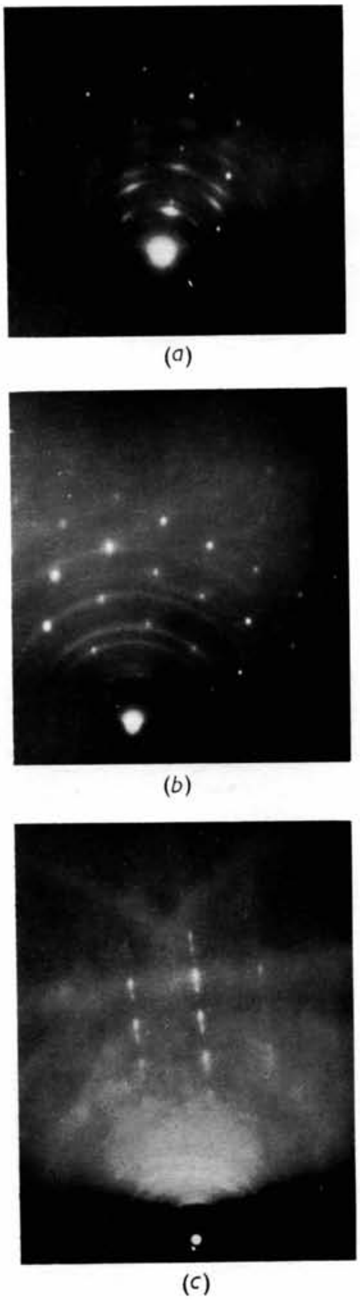
Fig. 1. Electropolished copper single crystal, approximately (111) face.



(a)

(b)

Fig. 3. (a) Thin film of cuprous oxide on the copper single crystal (111) face. Beam along $\langle 112 \rangle$. (b) Specimen shown in (a) after reduction by atomic hydrogen formed from purified hydrogen. Beam along $\langle 112 \rangle$.

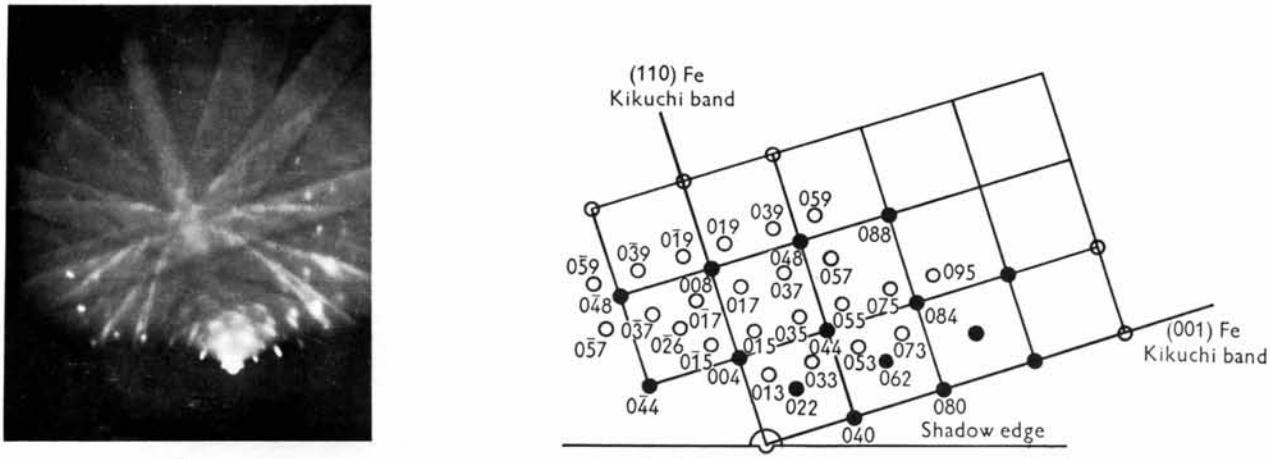


(a)

(b)

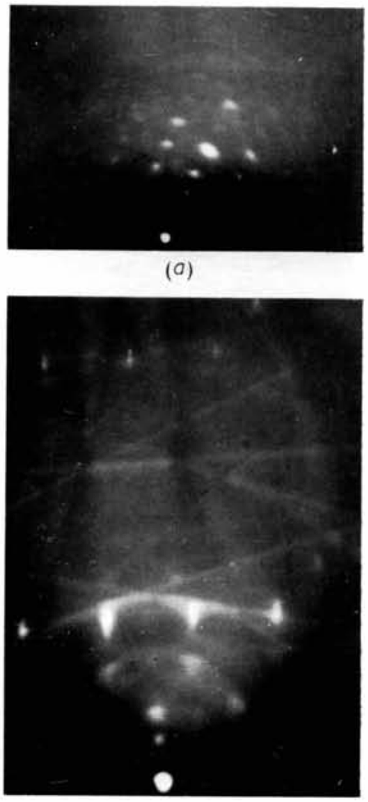
(c)

Fig. 2. (a) Thin film of cuprous oxide on the copper single crystal (111) face. Beam along $\langle 1\bar{1}0 \rangle$. (b) Specimen shown in (a) after reduction by atomic hydrogen formed from damp hydrogen. Beam along $\langle 1\bar{1}0 \rangle$. (c) Specimen as shown in (a) after reduction by atomic hydrogen formed from purified hydrogen. Beam along $\langle 112 \rangle$.



(a) b

Fig. 4. (*a*) Thin film of γFe_2O_3 or Fe_3O_4 on iron single crystal. Beam along $\langle 1\bar{1}0 \rangle$. (*b*) Main oxide spots in (*a*). Filled circles: main oxide spots; open circles: faint oxide spots.

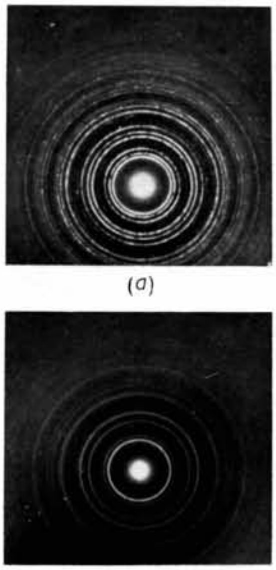


(a)

(b)

Fig. 5. (*a*) Film of γFe_2O_3 or Fe_3O_4 on iron single crystal. (*b*) Thin oxide film on iron single crystal.

Fig. 6. Thin film of nickel oxide on glass.



(a)

(b)

Fig. 7. (*a*) Thin film of orthorhombic PbO. (*b*) Specimen of (*a*) reduced to lead by atomic hydrogen.

The presence of atomic hydrogen was verified with the aid of a small spectrometer; it confirmed that the lines of the Balmer series of hydrogen were present in the discharge.

The reactions of atomic hydrogen were studied on surfaces initially at room temperature, though the specimens were heated by the action of the discharge.

3. Results

(i) *The formation and reduction of cuprous oxide*

The cuprous oxide films were formed on polycrystalline copper, and on a copper single crystal, by standing in air for 10 min. in a vessel kept at a given temperature, between 100° C. and 200° C. In addition, thin films of copper were oxidized by contact with distilled water for approximately 30 sec. at room temperature.

The polycrystalline copper and the copper single crystal were electropolished before each cycle of oxidation and reduction. A 60% solution of phosphoric acid in water was used, as described by Jacquet (1935). After such polishing, the single crystal yielded the electron diffraction pattern shown in Fig. 1. The face of the crystal giving the pattern is inclined at 7° to a (111) plane in the crystal, about the $\langle 1\bar{1}0\rangle$ direction. The clearness of the Kikuchi lines and the vertical elongation of the spots show that the crystal was highly perfect and that the surface was relatively smooth on the atomic scale.

In the first experiments, where damp hydrogen was used to produce the atomic hydrogen, both etched and unetched single crystal surfaces were used as substrate. With the former, the slight roughening caused by the light etching (1 sec. immersion in a 50% aqueous solution of nitric acid) resulted in the appearance in the electron diffraction pattern of diffraction spots due to the copper single crystal, in addition to the patterns of the oxide (they also appeared in addition to the ring pattern of the random polycrystalline copper caused by the reduction). This aided the determination of the chemical composition and the orientation of the oxide (and of the copper formed from it by reduction).

Fig. 2(*a*) shows the electron diffraction pattern of a cuprous oxide film formed on the single crystal on such a lightly etched surface at 160° C. The arcs in the pattern are due to Cu_2O, and their positions relative to the spots due to the copper show that the oxide was orientated with a (111) plane parallel to the surface (111) plane of the subtrate. Consideration of the relative intensities of the arcs on either side of the plane of incidence in the figure shows that the azimuthal orientation was of two kinds, with some spread about the mean. One type of orientation corresponds to parallelism of the axes of the copper and the Cu_2O (together with the 180°-rotated, or 'antiparallel' azimuthal orientation), i.e. with $\langle 1\bar{1}0\rangle$ Cu_2O parallel to the $\langle 1\bar{1}0\rangle$ copper in the copper (111) surface; and the other corresponds to orientations rotated through 90° from these orientations, i.e. with $\langle 112\rangle$ Cu_2O parallel to the $\langle 1\bar{1}0\rangle$ copper in the copper (111) surface.

The thickness of the oxide film, estimated from the uniform interference colours, was about 200 Å (Gwathmey & Young, 1951).

Exposure of this oxide for 10 min. to atomic hydrogen produced from damp hydrogen caused the crystal to regain its original colour, and to yield the electron diffraction pattern shown in Fig. 2(*b*). The rings in this pattern are due to copper crystals in random orientation. There was no sign of the oxide pattern, showing that complete reduction was achieved.

Exactly similar results were obtained with smooth unetched surfaces.

Cu_2O films formed on the unetched copper single crystal (111) face at 180° C. were exposed to atomic hydrogen formed from purified, and relatively dry, hydrogen. The electron diffraction patterns obtained from these oxides were the same as that shown in Fig. 2(*a*), except that the spots due to the copper substrate were absent. The reduction caused the crystal to regain its original colour, but yielded crystals of copper in the same orientation as those of the cuprous oxide (Fig. 2(*c*)), as well as unorientated crystals. Kikuchi lines can be seen, showing that the surface was very smooth, as it had been before oxidation.

Oxidation of the copper single crystal at 200° C. caused epitaxial growth of Cu_2O on the surface. Fig. 3(*a*) shows the electron diffraction pattern of the oxidized copper single crystal (111) face in $\langle 112\rangle$ azimuth. The Cu_2O had its (111) plane parallel to the (111) plane of the copper crystal, in the same way as the oxide shown in Fig. 2(*a*), but the spot intensities showed that there was a much stronger preference for the two azimuthal orientations such that $\langle 1\bar{1}0\rangle$ Cu_2O was parallel to $\langle 1\bar{1}0\rangle$ Cu in the copper (111) surface. There was only a small proportion of Cu_2O having azimuthal orientation with the $\langle 112\rangle$ Cu_2O parallel to the $\langle 1\bar{1}0\rangle$ Cu in the copper (111) substrate surface.

Reduction of this oxide for 10 min., using pure hydrogen to form the atomic hydrogen, caused the production of crystals of copper in exactly the same orientations as those of the cuprous oxide. This is illustrated in Fig. 3(*b*). The crystal is in the same azimuth as for Fig. 3(*a*), and the pattern is the same in the region near the undeflected beam, but on a larger scale to conform with the spacings characteristic of copper. The spots in the first-order circular Laue zone associated with the lattice row along the beam direction are in pairs, showing that both the parallel and antiparallel azimuthal positions of the crystals relative to the substrate had occurred. The rings also present show that some polycrystalline unorientated copper had been formed in addition.

Polycrystalline unorientated Cu_2O films, formed on the single crystal at slightly higher temperatures (and also formed on polycrystalline copper), were reduced to polycrystalline copper having no preferred orientation, both with atomic hydrogen produced from pure hydrogen and atomic hydrogen produced from damp hydrogen. Electron microscope examination of unorientated Cu_2O films formed by condensation of copper from the vapour in vacuum, followed by oxidation by contact with water, showed that the film was composed of grains with a mean diameter of about 1000 Å, but mean crystal size of about 250 Å, as calculated from the number of spots in a given diffraction ring. Reduction of this film led to very little change in grain size, or in crystal size.

An amorphous oxide film on the copper single crystal, formed by the action of air in a desiccator containing silica, was reduced to polycrystalline copper having no preferred orientation.

(ii) *The formation and attempted reduction of iron oxides*

Thin films of γFe_2O_3 or Fe_3O_4 (they have very similar electron diffraction patterns, and it was not possible to distinguish them from the patterns obtained in these experiments) were formed on an iron single crystal by heating the crystal for a few seconds in air over a non-luminous gas flame, and by immersing the crystal in concentrated nitric acid.

The iron crystal used as substrate had a surface inclined at 17° to a cube face, (001), about an axis near [110]. It was electropolished before each oxidation, using the acetic–perchloric acid bath described by Jacquet (1936).

The crystal was heated for 5 sec., and removed from the gas flame before any interference colours appeared, to produce the very thin oxide film giving the electron diffraction pattern shown in Fig. 4(*a*). The Kikuchi lines, and the spots due to the iron substrate, are strong, but additional spots show that an oxide layer only a few tens of Ångström units in mean thickness had been formed, and that this oxide was face-centred cubic γFe_2O_3 or Fe_3O_4.

The oxide spots are mainly in a centred square pattern, with some additional faint spots on the diagonals half-way between the square corners and the square centres. For clarity the oxide spot arrangement is shown diagrammatically in Fig. 4(*b*), and the spots have been indexed. The directions of the (110) and (001) Kikuchi bands due to the iron single-crystal substrate are also indicated. They show that the (001) plane of the oxide crystal is parallel to the iron (001) plane, and a [100] row of the oxide parallel to the $[1\bar{1}0]$ direction in the iron. The surface is not a cube face, however, and since this orientation is obtained it implies that it may also occur relative to the other cube faces ((010) and (100)), though this is not clearly established from the diffraction patterns. This is similar to the orientation found for FeO on iron single crystals by Mehl & McCandless (1937). The appearance of spots having indices not normally occurring in face-centred cubic γFe_2O_3 is probably due to an excess of oxygen in the lattice.

The distinctness of the iron Kikuchi lines in Fig. 4(*a*) shows that the iron surface was still relatively smooth, either beneath the oxide or in scarcely attacked regions between locally oxidized parts of the surface.

Exposure of this oxide to atomic hydrogen did not result in any observable reaction. The electron diffraction pattern was exactly the same after exposure as before, except for a slight diminution in intensity due to sputtered aluminium. The exposure could not be prolonged for more than 45 min., as after this time the diffraction pattern had been almost completely obscured by a thin layer of sputtered aluminium. Atomic hydrogen prepared from pure hydrogen yielded the same result as that prepared from damp hydrogen.

A thicker oxide film was made by heating the same single crystal of iron (after freshly resurfacing it by electropolishing) until yellow interference colours appeared. The film must therefore have been about 200 Å thick. The electron diffraction pattern obtained from it is shown in Fig. 5(*a*). The arcs form a centred rectangle pattern, the ratio of the sides of the rectangle being $\sqrt{10}$. In conjunction with the size of the rectangles, this shows that the surface was practically a single crystal of γFe_2O_3 or Fe_3O_4, the beam being approximately along the $\langle 310 \rangle$ direction. The film was sufficiently thick and continuous to prevent the appearance of the pattern due to the iron single-crystal substrate.

Exposure of this film to atomic hydrogen did not result in any observable reaction.

Another film of γFe_2O_3 or Fe_3O_4 was formed by immersion of the same single crystal (freshly electropolished) in concentrated nitric acid. The film, if continuous, must have been about 10 Å thick. The electron diffraction pattern is shown in Fig. 5(*b*). Those spots nearest the undeflected beam are due to the oxide; the other elongated spots and Kikuchi lines show that the iron single crystal was still very smooth.

Exposure of this film to atomic hydrogen again did not result in any observable reaction. Similarly, films of unorientated γFe_2O_3 (or Fe_3O_4) on polycrystalline, unorientated steel, films of polycrystalline αFe_2O_3, and a single crystal of haematite were not noticeably attacked by atomic hydrogen.

(iii) *The formation and attempted reduction of* NiO

As was found with the attempted reduction of the above iron oxides, no reduction of NiO was observed even after prolonged attack by atomic hydrogen. Two types of nickel oxide layer in particular were used. The electron diffraction pattern obtained from one of these oxides is shown in Fig. 6. This oxide was formed on glass by sublimation of nickel in vacuum, and subsequent heating in air to about 300° C. It showed mixed one-degree (111) and (100) orientations. The other type of oxide layer, showing only slight orientation, was formed by heating in air a polished and etched nickel sheet.

(iv) *The formation and reduction of lead oxide*

A thin film of lead oxide was lifted, by means of a nickel gauze, from the surface of molten lead of 'Analar' grade. It gave the transmission pattern shown in Fig. 7(*a*), the pattern after reduction being shown in Fig. 7(*b*). The oxide was identified as orthorhombic PbO from data in the A.S.T.M. file (1953). The pattern after reduction corresponds to lead. An amorphous, probably oxide, film on lead formed in air at room temperature was also reduced to the metal.

(v) *Other oxide films*

The action of atomic hydrogen on films of UO_2 on uranium, Cr_2O_3 on copper, and WO_2 on glass was studied, but no reduction was observed. On an oxidized single crystal of tin, however, the removal of the thin amorphous oxide layer formed by exposure to air in a desiccator was observed, the action of atomic hydrogen causing an increase in intensity of the spots and Kikuchi lines in the pattern obtained from the crystal. A thin film of tetragonal SnO supported on nickel gauze disappeared completely under the action of atomic hydrogen.

4. Discussion

(i) *The form of the reduction product*

From the oxides that were reduced, two different forms of reduction product were observed.

Small and disorientated crystals of copper were obtained by reduction of Cu_2O, using atomic hydrogen produced from damp hydrogen. The result was the same whether the initial Cu_2O crystals were disorientated or orientated. Atomic hydrogen is a very powerful reducing agent, so that in conditions favourable to its production in high concentration (such as those in experiments using damp hydrogen to produce atomic hydrogen) fast reaction would be expected with substances relatively easily reduced. The random-crystalline form of the result is analogous to that normally observed (e.g. Wilman, 1940) with fast heterogeneous reactions, particularly at fairly low temperatures (up to 200° C.).

Atomically smooth-surfaced crystals of copper with an orientation exactly similar to that of the cuprous oxide from which they were reduced were obtained by reduction by atomic hydrogen produced from purified hydrogen. In this case only a small proportion of hydrogen would be atomized owing to the absence of water vapour, thus the rate of reduction of the Cu_2O must have been much less than in the above case when moist hydrogen was used. The result is analogous to that obtained from slow heterogeneous reaction, particularly at an elevated temperature. The atoms of the metal released by the reduction in this case have mobility due to the elevated temperature, and can migrate over the surface so that crystal growth of the metallic reduction product occurs in a way similar to that in other heterogeneous reactions.

The reduction products in the case of these examples quoted thus seem to be in a form in general analogous to that found in other heterogeneous reactions, such as in the oxidation of a metal surface. In particular, the product can be epitaxially orientated, as in the case of the reduction of Cu_2O to copper, if the initial solid surface is atomically smooth and the rate of reduction is not too high.

(ii) *Reducibility of different oxides in atomic hydrogen*

Considerations of the free energy of formation of water from atomic hydrogen and oxygen, and of the formation of the oxides discussed, would lead one to expect reduction by atomic hydrogen to be likely in the case of Fe_2O_3 and NiO as well as PbO and Cu_2O at room temperature, especially as they are reduced by molecular hydrogen at relatively low temperatures (< 300° C. in these cases) (Mellor, 1923). An explanation of the non-reduction of the two first is suggested by the catalytic activity of the metals as regards the recombination of atomic hydrogen (Bonhoeffer, 1924). Both iron and nickel would be expected to be good catalysts, so that if only a very small amount of their oxides were reduced to metal (say a layer only one or two molecules thick, and therefore undetectable in these experiments) the layer of metal so formed could so catalyse the recombination of atomic hydrogen that no further reduction by atomic hydrogen in the concentration used in the experiments could take place. (It is also possible that the oxides act as catalysts for the recombination, though no indications of this have been found in the literature.)

If such a recombination of atomic hydrogen takes place on the surface this involves a heating-up of the surface regions, and such a heating of the specimens was indeed observed both in the case of materials which were reduced and also those not reduced. In the case of an oxidized iron surface a rough experimental estimate indicated that the temperature rose to at least 200° C.

The author wishes to express his grateful thanks to Dr H. Wilman for his constant interest in the work, and his many helpful suggestions. He is also indebted to Prof. G. I. Finch for the supervision in the earlier stage and for outlining the problem.

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References

A. S. T. M. (1953). *Index of X-ray Diffraction Data.* Philadelphia: American Society for Testing Materials.

Bonhoeffer, K. (1924). *Z. phys. Chem.* **113**, 199.

Finch, G. I. (1949). *Proc. Phys. Soc.* A, **62**, 465.

GWATHMEY, A. & YOUNG, W. (1951). *Rev. Métall.* **48**, 434.

JACQUET, P. (1935). *Nature, Lond.* **135**, 1076.

JACQUET, P. (1936). *Bull. Soc. Chim. Fr.* **3**, 705.

KROEPELIN, H. & VOGEL, E. (1936). *Z. anorg. Chem.* **229**, 1.

MEHL, R. & MCCANDLESS, E. (1937). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **125**, 531.

MELLOR, J. (1923). *A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* London: Longmans, Green.

WILMAN, H. (1940). *Proc. Phys. Soc.* **52**, 323.

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An X-ray and Physical Study of β-Naphthol

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Evidence is presented to show that the space group and unit-cell dimensions of β-naphthol are different from those previously reported. The space group is *Ia* and a unit cell of dimensions $a = 8{\cdot}185$, $b = 5{\cdot}950$, $c = 36{\cdot}29$ Å, $\beta = 119°\ 52'$ contains two sets of non-equivalent molecules.

1. Introduction

Crystallographic studies of β-naphthol have been described by several workers. The most recent and most detailed reports (Kitaijgorodskij, 1945, 1947) include a discussion of the position and orientation of the molecules and of hydrogen bonding between pairs of molecules.

In the course of an examination of some materials derived from β-naphthol one of us (Hargreaves, 1940) obtained X-ray data for β-naphthol which indicated a unit cell and space group different from those deduced by Kitaijgorodskij. We have now confirmed these results by more extensive measurements. The evidence and its bearing on the results obtained in other examinations of β-naphthol are discussed in this paper.

2. Previous examinations

Groth (1906–19, vol. 5, p. 374) has collected goniometric measurements on crystals of different habits and deduces

$$a:b:c = 1{\cdot}3662:1:2{\cdot}0300, \quad \beta = 119°\ 48'.$$

These values are based on very limited experimental data; none of the crystals examined had more than three forms of faces developed and in all only six interfacial angles were measured. The density is given as 1·217 g.cm.$^{-3}$ and the *C* cleavage is stated to be perfect.

X-ray data have been obtained from powder specimens by Bragg (1921), Bragg & Bragg (1924), Tanaka, Okuno & Tsuji (1931) and Neuhaus (1939), and from single-crystal specimens by Neuhaus (1939) and Kitaijgorodskij (1945, 1947). The later measurements are more reliable and only the results of Neuhaus and Kitaijgorodskij will be quoted—see Table 1.

Table 1. *Crystal data for β-naphthol*

	Neuhaus	Kitaijgorodskij	Hargreaves & Watson
a (Å)	8·14	8·09	8·185 ± 0·015
b (Å)	5·92	5·94	5·950 ± 0·003
c (Å)	18·2	17·80	36·29 ± 0·01
β	119° 48′*	119° 48′*	119° 52′ ± 7′
$d_{\text{obs.}}$ (g.cm.$^{-3}$)	1·245	1·23	1·252 ± 0·002
$d_{\text{calc.}}$ (g.cm.$^{-3}$)	1·249	1·29	1·249 ± 0·003
Z	4	4	8
Space group	—	$P2_1/a$	Ia

* The value of β adopted by Neuhaus and by Kitaijgorodskij is that given by Groth.

Both Neuhaus and Kitaijgorodskij took photographs with rotation or oscillation about each of the principal axes and deduced the axial lengths from layer-line spacings; but they experienced difficulty in obtaining reliable values of *c* by this method, and apparently for this reason both used measurements of $c \sin \beta$ to deduce the values of *c* given in Table 1.

3. Present examination

Most of the measurements have been made on material crystallized from carbon disulphide in the form of rhombic plates. X-ray oscillation photographs show that the crystals are monoclinic with the *b* axis lying in the plane of the plate and parallel to the shorter diagonal of the rhomb. The unit cell has been chosen so that the *a* axis is parallel to the longer diagonal of the rhomb and the *c* axis is inclined to *a* at an angle