

XLII. *The Crystalline Structure of Copper.* By W. LAWRENCE BRAGG, B.A., *Allen Scholar of the University of Cambridge* *.

THE copper crystals used in this investigation were some natural specimens, for which I am indebted to Mr. Hutchinson, of the Mineralogical Laboratory at Cambridge. In their natural state these specimens are obviously rough crystals, and have some faces of large dimensions (1 cm. each way), but these faces are very much warped and distorted. An attempt was made to obtain an X-ray reflexion from various natural faces of such crystals, but it was not successful. Apparently the outer surface of the crystal has been so battered and distorted that little regular crystalline arrangement is left. Any attempt to grind crystal faces artificially also destroys the crystalline character of the surface and so prevents the reflexion of X rays from the face.

It was observed, however, that when the crystal was placed in nitric acid until the surface was eaten away to an extent of perhaps $\frac{1}{4}$ millimetre, the faces were etched deeply into numerous parallel facets, which all reflected the light simultaneously in the usual way. This suggested that, internally the crystal structure was perfect, and showed further that in some cases the whole specimen was composed of a single crystal. Moreover, in this case the surface layers are not pulled about, and so are capable of reflecting the X rays falling on them. This method of obtaining a crystal surface was suggested by some previous experiments on natural zinc oxide, zincite. Zincite occurs very rarely as crystals, and the specimens used had merely a platy structure. However, by partly dissolving a block of the mineral in hydrochloric acid, the etched mass showed indications of crystalline structure sufficient to serve as a guide in the preparation of various faces. The faces reflected the X rays and led to the determination of the arrangement of zinc and oxygen atoms.

Copper crystallizes in the cubic system, holohedral class. The natural crystals of copper used in the experiments were mostly of one type, being composed of two individuals twinned about the plane (111). The faces of the simplest crystals approximated to those of the rhombic dodecahedron {110}. The face first investigated was that parallel to the twin plane (111) of the best of the crystals. The crystal appeared like two triangular pyramids joined base to base, and the apex of one pyramid was ground down on a carborundum wheel until a triangular face (111) was formed.

* Communicated by the Author.

This was roughly polished, treated with nitric acid to dissolve away the outer layers, and then mounted in the usual way in the X-ray spectrometer*.

By assuming various arrangements for the copper atoms, we can calculate the spacings of various planes of the crystal, starting from the density of copper, 8.96, as a basis. For instance, if the copper atoms are arranged at the corners of cubes, so as to form a simple cubic lattice, we have the relation

$$(d_{(100)})^3 \cdot 8.96 = 63.57 \cdot 1.64 \cdot 10^{-24},$$

since we know that

1. Mass of a copper atom = $63.57 \cdot (\text{Mass of a hydrogen atom})$
 $= 63.57 \cdot 1.64 \cdot 10^{-24}$ gram,
2. The unit cube of the structure contains one copper atom.

This gives the relation

$$d_{(100)} = 2.26 \cdot 10^{-8} \text{ cm.}$$

The X rays from an anticathode of palladium, such as was used for the purposes of this experiment, have a wave-length of $.576 \cdot 10^{-8}$ cm. This is reflected from the planes $d_{(100)}$ at an angle given by the equation

$$\lambda = 2 \cdot d_{(100)} \cdot \sin \theta.$$

Substituting the above values for λ and $d_{(100)}$, we find that $\theta = 7^\circ 20'$.

Suppose, on the other hand, that the copper atoms were on a face-centred cubic lattice. This lattice has a point at each corner of a set of cubes, and one at the centre of each cube face. The volume $(d_{(100)})^3$ now contains only one-half a copper atom. From this it can be calculated that $d_{(100)} = 1.80 \cdot 10^{-8}$ cm. So for the other faces; the results are summarized below.

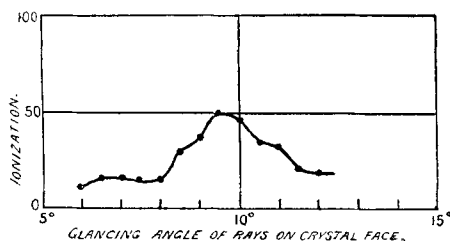
	Spacing of planes.	Glancing angle of reflexion, Pd rays.
Face-centred lattice :		
	$d_{(100)} = 1.80 \cdot 10^{-8} \text{ cm.}$	$\theta_{(100)} = 9^\circ 13'$
	$d_{(110)} = 1.27 \cdot 10^{-8} \text{ cm.}$	$\theta_{(110)} = 13^\circ 2'$
	$d_{(111)} = 2.08 \cdot 10^{-8} \text{ cm.}$	$\theta_{(111)} = 8^\circ 0'$
Simple cubic lattice :		
	$d_{(100)} = 2.26 \cdot 10^{-8} \text{ cm.}$	$\theta_{(100)} = 7^\circ 20'$
	$d_{(110)} = 1.59 \cdot 10^{-8} \text{ cm.}$	$\theta_{(110)} = 10^\circ 22'$
	$d_{(111)} = 1.30 \cdot 10^{-8} \text{ cm.}$	$\theta_{(111)} = 12^\circ 50'$

* For a description of the instrument and its manipulation, see Proc. Roy. Soc. A. vol. lxxxviii. p. 428, and A. vol. lxxxix. p. 468.

The face (111) of the copper crystal, prepared as described above, was first investigated. The chamber was set at $25^{\circ} 40'$ ($= 2 \times 12^{\circ} 50'$). The crystal face, being adjusted so that the rays fell on it at a small glancing angle, was turned so that this angle assumed in turn a series of values between 6° and 20° , in order to find if, in some position, it reflected the X rays. This had to be done because the true orientation of the plane (111) in the crystal was not known with any exactness. At none of these angles was there a reflexion into the chamber, the simple cubic arrangement of the copper atoms being therefore ruled out.

On setting the ionization chamber at 16° , however, a marked effect was found. Fig. 1 shows the current in the chamber for a series of angles at which the crystal was set.

Fig. 1.

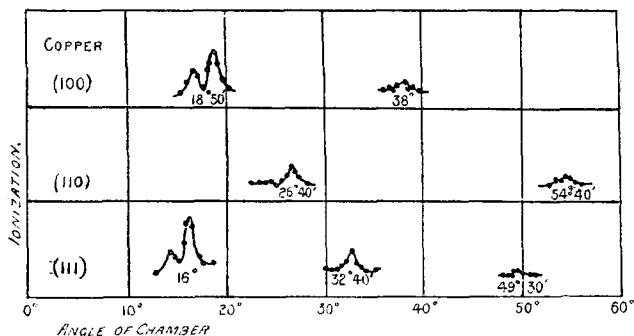


Between 8° and $11^{\circ} 30'$ there is a marked increase in the ionization current, which rises to a maximum at $9^{\circ} 30'$. Now if the crystal were perfect, the range of angles at which it reflected the X rays would be limited to some $30'$ at most. The fact that the crystal reflects over such a wide range of angles shows that its planes are distorted to an extent of several degrees, instead of being strictly parallel. As the crystal is turned round, one set of planes after another comes into the reflecting position and causes an ionization current in the chamber. From the curve we deduce that when the crystal is set at $9^{\circ} 30'$ the area of its face so oriented as to reflect is larger than at any other angle.

A series of readings are now taken with the chamber at various angles " θ ," and the crystal in each case at the angle " $\frac{\theta}{2} + 1^{\circ} 30'$," in order always to make use of this larger reflecting area. The results are shown in the curve for the face

(111) of fig. 2. Here we have two peaks close together in the curve, representing the two lines in the spectrum of palladium. The curve shows a decided first- and second-order spectrum, and even perhaps a third, though this last is-

Fig. 2.



somewhat doubtful. It must be noted that the range of angles, over which the ionization chamber may be set so as to receive the reflected beam, is confined to 1° , though the crystal structure is so imperfect. If the crystal were perfect it would be scarcely smaller, and the reason for this is clear. Although there are a number of settings for the crystal which enable a set of planes somewhere on its distorted face to receive the incident X rays at a glancing angle of 8° and so to reflect them, the reflected rays all converge and are received by the chamber when set exactly at 16° *. Therefore, when the chamber and crystal are moved simultaneously, the reflexion is only found when the chamber is in the neighbourhood of 16° .

Fig. 2 also shows the curves for faces (110) and (100) of copper. The angles at which the spectra are found are as follows:—

$$\theta_{(100)} = 9^\circ 24' \quad \sin \theta_{(100)} = \cdot 163. \quad \text{Calculated angle } 9^\circ 13'$$

$$\theta_{(110)} = 13^\circ 18' \quad \sin \theta_{(110)} = \cdot 230. \quad \text{,, ,, } 13^\circ 2'$$

$$\theta_{(111)} = 8^\circ 0' \quad \sin \theta_{(111)} = \cdot 139. \quad \text{,, ,, } 8^\circ 0'$$

$$\sin \theta_{(100)} : \sin \theta_{(110)} : \sin \theta_{(111)} = 1 : 1.41 : .85 = 1 : \sqrt{2} : \sqrt{\frac{3}{2}}.$$

This relation between the angles of reflexion from the

* Cf. W. H. Bragg, *Phil. Mag.* May 1914, p. 887.

three principal faces of the crystal is that which would exist for a face-centred cubic lattice. In such a lattice

$$d_{(100)}:d_{(110)}:d_{(111)} = 1:\frac{1}{\sqrt{2}}:\frac{2}{\sqrt{3}}.$$

We have already seen that the absolute values of the angles at which reflexion occurs are those to be expected if the copper atoms lie on a face-centred lattice. It is further to be observed that the 1st, 2nd, and 3rd order peaks reflected from the faces of the crystals are in every case quite normal, the first order being greater than the second, and that greater than the third. This, as has been shown in former papers (Proc. Roy. Soc. A. vol. lxxxix. p. 472) implies a regular arrangement of reflecting planes, equally spaced and identical in nature. Lastly, as a check, a search was made for spectra at half the angles at which the first spectra of fig. 2 occur, in the case of the planes (100) and (110). This search gave a negative result. Taking all this into consideration, there can be little doubt that *the atoms of a copper crystal are arranged on a face-centred cubic lattice.*

The results are interesting in that they show that considerable accuracy of measurement can be obtained with the X-ray spectrometer, even when the crystal itself is highly irregular. If the cubic symmetry of the copper crystal had not rendered this unnecessary, it would have been possible to measure the axial ratio of the crystal within 1 per cent. of the truth, although the faces of the crystal were distorted by many degrees. Since the crystal is so irregular, only a fraction of its surface reflects at any one angle, and therefore the electroscope had to be very sensitive when measuring the small ionization current. This explains the very obvious irregularities of the curves in fig. 2. The dots in this figure represent a set of readings. All these curves were repeated several times, some with different crystal faces. Some curves were more irregular than others, but all agreed closely in the positions of the spectra.

I wish to take this opportunity of again thanking Mr. Hutchinson for his kind help, both in supplying material and in aiding with his advice the preparation of the various crystal faces. I wish to thank Professor Sir J. J. Thomson for his kind interest in the experiments. I am indebted to the Institut International de Physique Solvay for a grant with the aid of which the apparatus used in these experiments was purchased.

Summary.

It was found possible, by treating with acid prepared surfaces of a natural crystal of copper, to obtain crystal faces which could be used as reflectors in the X-ray spectrometer.

The results of the investigations, thus rendered feasible, showed that in a copper crystal the atoms are arranged on a face-centred cubic lattice. This is the close-packed lattice, to which attention has been drawn by Pope and Barlow. The crystal structure is the most simple of any as yet analysed.

The Cavendish Laboratory,
July 16th, 1914.

XLIII. *On the Absorption Spectrum of Zinc Vapour.* By
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Toronto* *.

[Plate VI.]

IN a paper by Wood and Guthrie† on the absorption spectra of certain metallic vapours, the statement is made that with zinc vapour they found no trace of any absorption in the range of the spectrum investigated by them. This region began at about $\lambda 5200$ and, from indications in the paper, did not extend beyond $\lambda 2150$.

In view of the prediction made by Paschen‡ and subsequently confirmed by Wolff§, that the emission spectrum of zinc should include a series of single lines with the first member of the series at $\lambda 2139\cdot33$, it seemed to the writer desirable to look for absorption by zinc vapour in the region below $\lambda 2150$.

With the object of investigating this point, some pure zinc was placed in a clear fused quartz tube 2 cm. in diameter, which was then highly exhausted and sealed up. This tube was placed before the slit of a quartz spectrograph and heated with a Bunsen burner. When the spark between zinc terminals in air was used as the source of light, it was found that the vapour evolved when the zinc was melted and raised to a red heat was sufficient to completely cut out the line $\lambda 2139\cdot33$. With this moderate heating the absorption band was sharply edged and quite narrow. With stronger heating,

* Communicated by the Author.

† Wood and Guthrie, *Astrophys. Jl.* vol. xxix. no. 1, 1909, p. 211.

‡ Paschen, *Ann. der Phys.* 1909, vol. xxx. p. 746, and 1911, vol. xxxv. p. 860.

§ Wolff, *Ann. der Phys.* 1913, vol. xlii. p. 825.