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CRYSTALLINE STRUCTURE OF ANTIMONY AND BISMUTH.

By A. Ogg.

(With two Text-figures.)

ANTIMONY.

Antimony crystallises in the dihexagonal alternating (calcite) class of hexagonal crystals. The crystalline symmetry is that of a rhombohedron, the three edges which meet in the trigonal axis being the axes of the crystal. The angle between any two of these edges is $86^{\circ}58'$. From the geometry of the rhomb it is easy to find that the angle between the planes (111) and (110) is $37^{\circ}23'$ and that between the planes (100) and (111) is $56^{\circ}48'$.

If we take the sides of the rhomb to be a and suppose that an atom is placed at each of the corners of the rhomb, then the distances between the planes of atoms are—

$$d_{100} = \cdot 9973a \quad (1)$$

$$d_{111} = \cdot 6071a \quad (2)$$

$$d_{110} = \cdot 7236a \quad (3)$$

$$d_{\bar{1}\bar{1}0} = \cdot 6881a \quad (4)$$

By means of an X-ray spectrometer, the bulb having a palladium anti-cathode, the glancing angles of the first order spectra were experimentally found to be—

(100)	(111)	(110)
$5^{\circ}30'$	$4^{\circ}30'$	$7^{\circ}30'$

Applying the formula $n\lambda = 2d \sin \theta$, where n is the order of the spectrum, $\lambda = 0.584 \times 10^{-8}$ cm., and θ the observed glancing angle, we find—

$$d_{111} = 3.72 \times 10^{-8} \text{ cm.} \quad (5)$$

$$d_{100} = 3.05 \times 10^{-8} \text{ „} \quad (6)$$

$$d_{110} = 2.24 \times 10^{-8} \text{ „} \quad (7)$$

From (2) and (5) we find $a = 6.12 \times 10^{-8}$ cm.

$$\text{„ (1) „ (6) „ „ } a = 3.06 \times 10^{-8} \text{ „}$$

$$\text{„ (3) „ (7) „ „ } a = 3.09 \times 10^{-8} \text{ „}$$

It is evident from the calculated values of a that the spacings between the (100) planes and also those between the (110) planes are half what we

have supposed them to be by placing atoms merely at the corners of the rhomb. If we take a face-centred lattice—

$$\text{then } d_{111} = \cdot 6071a \text{ as before (8)}$$

$$\text{but } d_{100} = \cdot 499a \quad (9)$$

$$\text{and } d_{110} = \cdot 367a \quad (10)$$

$$\text{hence from (5) and (8) } a = 6 \cdot 12 \times 10^{-8} \text{ cm.}$$

$$(6) \text{ ,, (9) } a = 6 \cdot 18 \times 10^{-8} \text{ ,,}$$

$$(7) \text{ ,, (10) } a = 6 \cdot 12 \times 10^{-8} \text{ ,,}$$

$$\text{mean value of } a = 6 \cdot 14 \times 10^{-8} \text{ ,,}$$

Taking the density of antimony as 6.70 grms./cm.³ the mass of the rhomb is equal to—

$$\begin{aligned} & 6 \cdot 70 \times 6 \cdot 14^3 \times 0 \cdot 9973^2 \times 10^{-24} \\ & = 1545 \times 10^{-24} \text{ gm.} \end{aligned}$$

Since the atomic weight of antimony = 120.2, and the mass of the hydrogen atom = $1 \cdot 64 \times 10^{-24}$ gm., then $n \times 120 \cdot 2 \times 1 \cdot 64 \times 10^{-24} = 1545 \times 10^{-24}$ gm., where n is the number of atoms per unit rhomb. This gives $n = 7 \cdot 85$.

It is clear, then, that there are 8 atoms per unit rhomb.

Let us take 8 atoms per unit rhomb, find the mass of the rhomb, hence its volume and then find a . We find $a = 6 \cdot 20 \times 10^{-8}$ cm.

Assuming a face-centred lattice we find then—

$$d_{100} = 3 \cdot 09 \times 10^{-8} \text{ cm.}$$

$$d_{111} = 3 \cdot 76 \times 10^{-8} \text{ ,,}$$

$$d_{110} = 2 \cdot 24 \times 10^{-8} \text{ ,,}$$

$$d_{110} = 2 \cdot 13 \times 10^{-8} \text{ ,,}$$

We can now calculate the glancing angles for the spectra from the different faces.

	Planes.		
	(100)	(111)	(110)
Observed angle	5° 30'	4° 30'	7° 30'
Calculated	5° 25'	4° 27'	7° 32'

Arrangement and Spacings of the Atoms.

(a) (111) planes:

We conclude that the underlying structure is the face-centred lattice, but a face-centred lattice gives only 4 atoms per unit rhomb. To determine the positions of the other 4 atoms we must investigate the relative intensities of the spectra from different faces. The observed intensities of the spectra of five orders from the (111) planes were—30 : 100 : 33 : 4 : 12.

The first order being weaker than the second shows that there is a plane of atoms dividing the distance ($3 \cdot 76 \times 10^{-8}$ cm.) between the (111) planes. Let β be the phase difference between the two sets of planes, and taking the

$$\frac{30}{100} = \frac{100}{34} \frac{1 + \cos \beta}{1 + \cos 2\beta},$$

The distance between one set of (111) planes would be divided by another set of (111) planes in the ratio of 0.412 : 0.588.

The calculated ratios of the intensities for this spacing are 30 : 100 : 31 : 5 : 15, which is in close agreement with the observed ratios.

FIG. 1.—Spacings of planes in Ångström units (10^{-8} cm.).

The spectra could be explained by a structure similar to that of the diamond but distorted along the trigonal axis,[†] one set of (111) planes dividing the distance between those belonging to the other in the ratio of about 3 : 2 instead of 3 : 1 as in the diamond.

(b) (100) planes :

To settle whether a structure similar to that of the diamond will fit the observed facts we must examine what this ratio would give for the spectra

* James and Tunstall, 'Phil. Mag.,' S. 6, vol. 40, No. 236.

† Sir W. H. Bragg and Prof. W. L. Bragg arrived at this conclusion in 1914: 'X ray and Crystal Structure,' p. 227.

from the (100) planes. We find at once that it will not explain the (100) spectra.

The observed (100) spectra are nearly normal, and there can be only a small difference of phase between the two sets of planes. James and Tunstall* have shown that this can be accomplished in the following way. Divide the unit face-centred rhomb into eight equal rhombohedral cells. Place an atom at each of the unoccupied corners of the small cells and then

FIG. 2.

push each atom along the diagonal by an amount equal to 0.074 of the length of a diagonal of one of the small cells.

The spacings we have determined for the (111) planes would make this amount to be 0.059 instead of 0.074.

The spacing for the (100) planes would be 0.059 : 0.941. The two sets of planes differ in phase by about 21° , and would give a nearly normal set of spectra in agreement with observation.

(c) (110) planes :

We must now examine whether such an arrangement would suit the spectra from the (110) planes. The planes would contain an equal number of atoms, and the spacings are 0.118 : 0.862.

* James and Tunstall, *loc. cit.*

The intensities of the first three orders were observed to be 100 : 17 : 0, while calculation gives 100 : 20 : 3.

(d) $(1\bar{1}0)$ and $(11\bar{1})$ planes :

James and Tunstall examined the spectra from these planes and found that they agreed with this arrangement.

The spacings of the planes have been determined by the relative intensities of the spectra from the (111) planes ; hence the determinations of these intensities are of importance. The ratios were found to be 30 : 100 : 33 : 4 : 12, while James and Tunstall found 60 : 100 : 48 : 0 : 15, giving a phase difference of 140° between the two sets of planes. We found a phase difference of 148° .

The spacings of the planes are given in Fig. 1. Fig. 2 shows the arrangement of the atoms on one of the eight small cells into which the rhombohedron can be divided.

The shortest distance between atomic centres is 2.92×10^{-8} cm.

BISMUTH.

Bismuth, like antimony, crystallises in the dihexagonal alternating system (calcite class). The three edges of the rhombohedron meet in the trigonal axis and the angle between any two of the edges is $87^\circ 34'$. The angle between the faces (100) and (111) is $56^\circ 24'$.

Again using an X-ray bulb with a palladium anticathode the glancing angles for the first order spectra were—

(111)	(100)
$4^\circ 18'$	$5^\circ 8'$

Taking the density of bismuth 9.80 grm./cm.³ we find that the unit rhomb contains 8 atoms and that the length of the side of unit rhomb is 6.52×10^{-8} cm.

Assuming the structure of crystalline bismuth to be similar to that of antimony we find the spacings of one set of planes to be—

	Planes.				
	(100)	(110)	(111)	$(1\bar{1}0)$	$(11\bar{1})$
Spacings	3.25	2.35	3.92	2.25	3.69

The spacings are given in Ångström units (10^{-8} cm.) The relative positions of the two sets of planes have not been accurately determined. The intensities of the spectra from the (111) face showed much the same order as those from the corresponding face of antimony but were much fainter.

Experiments are in progress for the measurement of these intensities whereby the second set of planes may be fixed.

UNIVERSITY OF CAPE TOWN,
February, 1921.

G. A. BOULENGER and J. H. POWER.—Map showing the distribution of the genus *Agama*. (Left over from the paper on the subject published in Vol. IX, Part 3.)