

THE CRYSTAL STRUCTURE OF ARSENIC TRIIODIDE,  $\text{AsI}_3$ 

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## ABSTRACT

The crystal structure of arsenic triiodide has been investigated by means of Laue, powder, and oscillation photographs. It is shown to be a layer lattice. The underlying lattice is  $\Gamma_{\text{Th}}$  and the space group  $C_{3i}^2$ . The unit rhombohedron has dimensions  $r = 8.25\text{\AA}$  and  $\alpha = 51^\circ 20'$ ; there are two molecules to the unit cell. The coordinates of the atoms are arsenic  $\pm uuu$  where  $u = 60^\circ$ ; iodine  $\pm xyz, \pm zxy, \pm yzx$  where  $x = 152^\circ$ ,  $y = 28^\circ$ ,  $z = -90^\circ$ . Distances of closest approach of iodine are about  $4.28\text{\AA}$  and  $4.13\text{\AA}$  and of arsenic and iodine about  $2.97\text{\AA}$ . The iodine ions are in hexagonal close packing; each arsenic ion is surrounded by six iodine ions.

THE majority of compounds which have a simple chemical composition have already been examined by x-rays and their structure determined. But those substances which have the general formula  $AX_3$  are still to some extent unexamined because they are difficult to work with and prepare. They are frequently unstable, deliquescent, or occur only in the powdered state. However crystals of arsenic triiodide are easily prepared and although oxidized somewhat in air this is not sufficient to cause any real difficulty.

## MATERIAL

The crystals of arsenic triiodide used in the investigation were prepared by dissolving powdered arsenic triiodide in carbon disulphide and allowing the solution to evaporate slowly in a crystallization dish. The crystals so obtained were thick tablets of a beautiful ruby red colour.

## CRYSTALLOGRAPHIC AND PHYSICAL PROPERTIES

Arsenic triiodide belongs to the hexagonal system. Groth<sup>1</sup> gives  $a:c = 1:2.998$  corresponding to  $\alpha = 51^\circ 20'$ .

The angles on the crystal faces developed were measured on a Pye goniometer and referring to Groth two of the crystal faces were found to be 111, and 110. A stereographic projection showed a third face to lie at the intersection of two known zones and its indices were found to be 001. The crystals show good cleavage parallel to the 111 face. They are apt to twin and for this reason some of the crystals could not be used. The density of the arsenic triiodide crystals is  $4.39$ .<sup>2</sup>

## X-RAY INVESTIGATION

Laue photographs were taken with molybdenum radiation with the incident beam perpendicular to the basal plane. They showed a three-fold axis of symmetry. Oscillation photographs were obtained about the  $a$  axis. Because

<sup>1</sup> Groth, *Chemische Kristallographie* 1, 226.

<sup>2</sup> International Critical Tables, German *b* table No. 269 p. 110. Vol. 1.

of the large absorption the photographs so obtained were poor and not much information was derived from them. Molybdenum radiation was used. Several powder photographs were also taken using molybdenum radiation.

#### THE UNIT CELL

A measurement of values for the layer lines of rotation photographs about the  $a$  axis gave  $a_0 = 7.10\text{A}$ . Using the axial ratio  $1:2.998$   $c_0 = 21.30\text{A}$ .

H. Braekken,<sup>3</sup> who has been working on the structure of arsenic, antimony, and bismuth triiodides, and who evidently had better rotation photographs gives  $a_0 = 7.187 \pm 0.003\text{A}$  and  $c_0 = 21.394\text{A} \pm 0.010\text{A}$  for arsenic triiodide. These latter values were used in assigning indices to the lines of the powder photographs and new values of  $a_0$  and  $c_0$  then deduced from the powder photographic data.

Sodium chloride was used as a standard, the value of the angle of reflection,  $\theta$ , for each of the sodium chloride lines being known accurately. The distances between each sodium chloride line and adjacent arsenic iodide lines were then measured and the radius of the camera being known (20.39 cm) the difference between  $\theta$  for each arsenic iodide line and the nearest sodium chloride line was calculated. Thus a more accurate value of  $\theta$  for each arsenic iodide line was obtained than if the distance from the zero to each arsenic iodide line had been measured.

In order to index these lines, the value of  $\sin^2\theta$  for each line was compared with a list of theoretical values of  $\sin^2\theta$  for known planes.

For the hexagonal unit,

$$\sin^2\theta = K_1(h^2 + hk + k^2) + K_2l^2$$

where  $K_1 = \lambda^2/3a_0^2$ ,  $K_2 = \lambda^2/4c_0^2$  and  $h, k, l$  are the hexagonal indices of the plane.

Thus  $\sin^2\theta$  can be calculated for any plane. In this way planes were indexed as follows:

Exptl. $\sin^2$	Th. $\sin^2$	Plane hex.	rh.	Int. (estimated by eye)
0.00986	{0.00975	{1120	{101	8
	{0.01008	{0006	{222	
0.01210	0.01227	1123	210	10
0.01975	0.01983	1126	321	$6\frac{1}{2}$
0.02908	0.02925	3030	311	$7\frac{1}{2}$
0.03227	{0.03243	{1129	{432	
	{0.03177	{3033	{300	$5\frac{1}{2}$
0.03906	{0.03900	{2240	{202	
	{0.03933	{3036	{411	6
0.04160	{0.04152	{2243	{311	5
	{0.04032	{00012	{444	
0.04909	0.04908	2246	420	2
0.06128	0.06168	2249	531	1
0.07112	0.07077	4153	401	$2\frac{1}{2}$
0.07830	0.07833	4156	510	$\frac{1}{2}$

where two theoretical values are given the line may be due to reflection from one or both planes.

<sup>3</sup> H. Braekken, *Zeits. f. Krist.* **74**, 67 (1930).

To check the cell size the experimental values of  $\sin^2\theta$  for known planes were used in the above formula. With  $l=0$

$$\sin^2\theta = K_1(h^2 + hk + k^2)$$

Combining results so obtained for all such planes  $K_1$  was found to have the value 0.003267.

$$K_1 = \lambda^2/3a_0, \lambda = 0.7078\text{Å} \therefore a_0 = 7.150\text{Å}$$

Using other planes and knowing  $K_1$ ,  $K_2$  was found to equal 0.000276.  $K_2 = \lambda^2/4c_0^2: c_0 = 21.35\text{Å}$ .  $a_0:c_0 = 1:2.986$ . The Laue data check this giving  $a_0:c_0$  about 1:3.

#### THE LATTICE

The indices obtained from powder photographs are such that  $2H + K = 3n$  and  $L = 0, 3, 6, \dots$ . All the indices obtained from Laue photographs are such that  $h, k, l$  (rhombohedral indices) obtained from  $H, K, L$  (hexagonal indices) are all divisible by three. This shows that the lattice is rhombohedral,  $\Gamma_{rh}$  and not  $\Gamma_h$ .

#### NUMBER OF MOLECULES PER CELL

If  $V$  is the volume of the unit cell,  $D$  the density,  $M$  the molecular weight, and  $H$  the weight of the hydrogen atom, then  $Z$  the number of molecules in the cell

$$Z = VD/MH$$

$$V = r^3 \sin^2\alpha \sin\delta'$$

where  $r$  equals the edge of the rhomb,  $\alpha$  the rhombohedral angle, and  $\sin\delta'/2 = \sin\alpha/2/\sin\alpha$ .

The horizontal diagonal in the rhombohedral face is equal to the hexagonal  $a$  axis. The rhombohedral angle is  $51^\circ 20'$ .

$$r = 7.15/2 \sin 25^\circ 40' = 8.25\text{Å}$$

$$Z = (8.25)^3 \sin^2 51^\circ 20' \sin 67^\circ 23' \times 4.39/455.76 \times 1.649$$

$$= 1.86$$

i.e., there are two molecules per unit cell.

#### CLASS

The Laue photographs show that there is a three-fold axis. The possible classes to which the crystal might belong from this evidence are  $C_3$  and  $C_{3i}$  since in Laue photographs both these appear as  $C_{3i}$ .

#### SPACE GROUP

The only space groups in these classes which have  $\Gamma_{rh}$  as the fundamental lattice are  $C_3^4$  and  $C_{3i}^2$ .

$$C_3^4 = \left[ A \left( \frac{2\pi}{3} \right), \Gamma_{rh} \right] \text{ and } C_{3i}^2 = [C_3^4 I] \Gamma_{rh}.$$

## ARRANGEMENT OF THE ATOMS

The coordinates for the general positions in the space group  $C_3^4$  are, One equivalent position: (a)  $uuu$ . Three equivalent positions: (b)  $xyz, zxy, yzx$ . and for  $C_3^2$ , One equivalent position: (a)  $000$ ; (b)  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . Two equivalent positions; (c)  $uuu: \bar{u}\bar{u}\bar{u}$ . Three equivalent positions: (d)  $00\frac{1}{2}:\frac{1}{2}00:0\frac{1}{2}0$ ; (e)  $\frac{1}{2}\frac{1}{2}0:0\frac{1}{2}\frac{1}{2}:\frac{1}{2}0\frac{1}{2}$ . Six equivalent positions: (f)  $xyz:zxy:yzx:\bar{x}\bar{y}\bar{z}:\bar{z}\bar{x}\bar{y}:\bar{y}\bar{z}\bar{x}$ .

All the indices of planes identified in the powder diagrams are such that  $2H+K$  (hexagonal indices) is divisible by three and  $L=0, 3, 6, 9, \dots$ . From this it follows that the powder films can be indexed referred to a cell with axes  $a=7.150/\sqrt{3}=4.139\text{A}$  and  $c=21.35/3=7.12\text{A}$ .

The indices referred to this small cell are

Plane	Intensity
10.0	8
00.2	
10.1	10
10.2	$6\frac{1}{2}$
11.0	$7\frac{1}{2}$
10.3	$5\frac{1}{2}$
11.1	
20.0	6
11.2	
20.1	5
00.4	
20.2	2
20.3	1
21.1	$2\frac{1}{2}$
21.2	$\frac{1}{2}$

Absent planes;  $00.1:00.3:11.3$ .

This hexagonal cell however contains only  $2/3$  of a molecule of arsenic triiodide; that is  $2/3$  of an atom arsenic and two atoms iodine.

Consider first the two iodines alone besides which the arsenic can be neglected. Since  $(00.1)$ ,  $(00.3)$ , and  $(11.3)$  are absent the positions of the two iodines in the small cell must be  $(000)$  and  $(2/3, 1/3, 1/2)$ . The Laue diagrams definitely show that the correct hexagonal cell has dimensions  $a=7.15\text{A}$  and  $c=21.35\text{A}$ . If three of the small cells are placed on top of each other this gives the correct  $c$  axis; also if the new  $a$  axis is chosen  $30^\circ$  from the old one the new hexagonal cell is obtained.

The arsenic atoms were next considered. In the old small cell there were two-thirds of an atom only. To explain all the absences in the powder photographs the arsenic atoms must be arranged in vertical rows (parallel to  $c$ ) with a distance of  $c/3$  between them ( $c=21.35\text{A}$ ).

On each of these rows there can lie, however, only two arsenic atoms as there is only one arsenic per three iodine. Therefore in building up the large cell from three of the small cells two of the latter must contain each one atom

of arsenic and the third none. Braekken gives in his paper the following intensities for reflections from the basal plane.

	Large cell								
	00.3	00.6	00.9	00.12	00.15	00.18	00.21	00.24	00.27
	Small cell								
	00.1	00.2	00.3	00.4	00.5	00.6	00.7	00.8	00.9
$AsI_3$	0.	vs.	vw.	s.	w.	m.	0.	w.	vw.
$SbI_3$	w.	s.	m.	vs.	w.	m.	vw.	w.	m.
$BiI_3$	m.	m.	ms.	vs.	0.	vw.	mw.	ms.	

The reflection from 00.4 (small cell) is very strong for all compounds and remains practically unchanged from arsenic to bismuth. Consequently all atoms must cooperate for 00.4. The arsenic (antimony or bismuth) atoms must be displaced  $c'/4$  with respect to iodine ( $c'$  refers to the small cell). Further, arsenic must lie on a three fold axis: therefore their position in the cell is  $(1/3, 2/3, 1/4)$ .

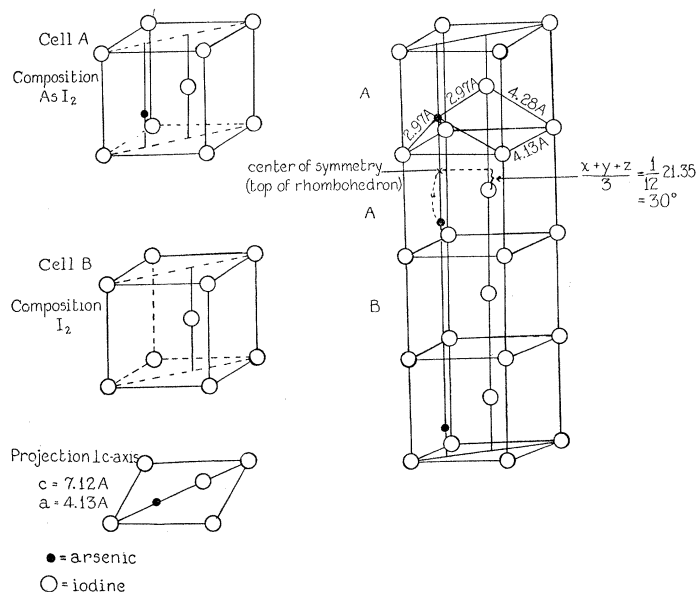


Fig. 1.

These arsenic positions are not very accurate because of the heavy iodine atoms. A somewhat different parameter, still on the three fold axis, is possible. Such a small displacement of the arsenic atoms is not incompatible with the intensities; the estimated intensities are however not accurate enough to prove whether any such displacement exists.

Fig. 1 shows the arrangement in the small and the large cells. Arsenic are separated in the vertical direction by distances  $7.12 \text{ \AA}$  or  $2 \times 7.12 \text{ \AA}$ .

By placing one cell  $B$  on the top of two cells  $A$  and by choosing new  $a$  axes  $30^\circ$  from the old axes a cell of the correct dimensions is obtained and the atoms in the cell possess the symmetry of the space group  $C_{3i}^2$ . This arrangement explains the absent planes in the powder data and also the intensities of the different orders of reflection from the basal plane.

The coordinates of the atoms can be referred to the unit rhombohedron. The top of the rhombohedron has coordinates (000) and is the center of symmetry. The arsenic atoms have coordinates  $uuu \bar{u}\bar{u}\bar{u}$  where  $u$  is their distance

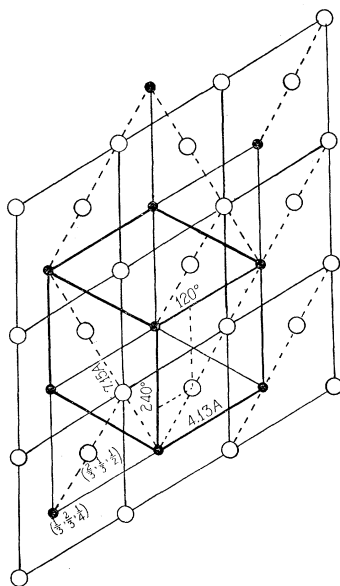


Fig. 2.

along the  $c$  axis. This distance is seen from Fig. 1 to be  $1/6$  the length of the  $c$  axis i.e.,  $u = 60^\circ$ .

The iodine atoms have coordinates  $\pm xyz: \pm zxy: \pm yzx$ . They are seen to lie in a plane displaced  $1/12$  the length of the  $c$  axis along the diagonal, i.e.,  $x+y+z/3 = 30^\circ$ .

Fig. 2 shows a projection of the structure perpendicular to the  $c$  axis from which it is seen that  $y-z = 120^\circ$  and  $x-z = 240^\circ$ . Combining these three equations:  $x = 150^\circ$ ,  $y = 30^\circ$ ,  $z = -90^\circ$ . The distance between two iodines in the same plane is the side of the small cell or  $4.13^\circ$ .

Two iodines in different planes are separated by a vertical distance of  $60^\circ$  or  $3.56\text{A}$ . The horizontal separation is  $1/3$  the diagonal of the small cell or  $2.38\text{A}$ .

Therefore the distance between two iodines in different planes

$$\begin{aligned} &= ((2.38)^2 + (3.56)^2)^{1/2} \\ &= 4.28\text{A}. \end{aligned}$$

Arsenic and iodine are separated by a horizontal distance of  $1/3$  the diagonal of the small cell or 2.38A and a vertical distance of  $30^\circ$  or 1.78A.

Therefore the distance between arsenic and iodine

$$= ((2.38)^2 + (1.78)^2)^{1/2}$$

$$= 2.97A.$$

These are all reasonable interionic distances as arsenic is considered to have an ionic radius of about 0.9A and iodine an ionic radius of a little more than 2A. The only data, other than the general absences in the powder films, by means of which to test this structure were the Laue data.

The Laue spots were indexed in the usual way. The axial ratio obtained

TABLE I.

Plane	Observed intensity	Calculated int.
6I1	6	$2F_{As} + 2.94F_I$ 143
6I1	5	$2F_{As} + 2.94F_I$ 143
5I1	0	$F_{As} - .62F_I$ 1
5I1	4	$F_{As} + .62F_I$ 42
522	3	$F_{As} + .26F_I$ 32
522	<1	$F_{As} - .26F_I$ 12
322	12	$-2F_{As} + 5.16F_I$ 164
322	15	$-2F_{As} - 5.16F_I$ 260
40I	10	$-2F_{As} + 5.16F_I$ 168
4I0	15	$-2F_{As} - 5.16F_I$ 268
30I	9	$-F_{As} - .3F_I$ 40
3I0	7	$-F_{As} - .3F_I$ 40
I02	5	$F_{As} + .3F_I$ 39
I20	2	$F_{As} - .3F_I$ 13
205	1	$-2F_{As} + 5.12F_I$ 158
250	3	$-2F_{As} - 5.12F_I$ 252
I03	4	$-F_{As} - .3F_I$ 34
I30	4	$-F_{As} - .3F_I$ 34
I04	10	$-2F_{As} - 5.16F_I$ 228
140	7	$-2F_{As} + 5.16F_I$ 144
I06	0	$F_{As} - .58F_I$ 0
I60	4	$F_{As} + .58F_I$ 48
I07	3	$2F_{As} + 2.94F_I$ 172
I70	3	$2F_{As} + 2.94F_I$ 172
02I	8	$F_{As} + .3F_I$ 40
0I2	5	$F_{As} - .3F_I$ 14
052	2	$-2F_{As} + 5.12F_I$ 166
025	4	$-2F_{As} - 5.12F_I$ 266
03I	5	$-F_{As} - .3F_I$ 35
0I3	7	$-F_{As} - .3F_I$ 35
04I	13	$-2F_{As} - 5.16F_I$ 235
0I4	9	$-2F_{As} + 5.16F_I$ 147
05I	0	$-F_{As} - .26F_I$ 12
0I5	1	$-F_{As} - .26F_I$ 12
06I	0	$F_{As} - .58F_I$ 0
0I6	4	$F_{As} + .58F_I$ 42
07I	3	$2F_{As} + 2.94F_I$ 134
0I7	3	$2F_{As} + 2.94F_I$ 134
343	2	$-F_{As} + .46F_I$ 4
334	2	$-F_{As} + .46F_I$ 4
232	5	$-2F_{As} + 5.16F_I$ 141
223	8	$-2F_{As} - 5.16F_I$ 221
I2I	3	$-F_{As} + .08F_I$ 22
I12	0	$-F_{As} + .84F_I$ 16

from the Laue photographs was about 1:3 checking the more accurate value of the powder photographs.

Because of the high absorption of the crystal the only comparison of intensities which can be definitely relied upon are those of planes having the same  $\sin \theta$  and the same  $n\lambda$ . Pairs of spots having the same  $\sin \theta$  and  $n\lambda$  were collected. The theoretical intensities for these planes were computed using the above structure: if the structure is correct the calculated and observed intensities for each pair of planes will be in the same proportion. This was found not to be the case. Slight variations in the orientation of iodine triangles in a plane perpendicular to the  $c$  axis were tested. These variations will not affect the general absences in the powder films or the intensities of the different orders from the basal plane which are known to check with the experimental data.

The only parameters which gave agreement with the observed Laue data were  $x = 152^\circ$ ,  $y = 28^\circ$ ,  $z = -90^\circ$ . Many other slight variations were tested but none found to agree with observed results so well as these values of the parameters. Table I shows the calculated and observed intensities for the Laue pairs.

To obtain numerical values of the calculated intensities Thomas' method of finding atomic  $F$  values was used.<sup>4</sup> He has deduced that for the heavier atoms

$$F = F_0 N / 55$$

where  $F$  = atomic  $F$  value of the atom considered

$N$  = atomic number of the atom considered

$F_0$  = atomic  $F$  value of caesium, at a point on the  $\sin \theta/\lambda$  scale given by  $\sin \theta/\lambda$  for atom  $N/\sin \theta/\lambda$  for Cs =  $(N/55)^{1/3}$ .

Knowing the variation of the  $F$  value of caesium with  $\sin \theta/\lambda$ , curves were plotted showing the same relation in the cases of arsenic and iodine. Using these graphs the  $F$  value for arsenic and iodine is known for any value of  $\sin \theta/\lambda$  and therefore the value to be used in calculating the intensity due to reflection from any particular plane.

Groups of plane were now collected with values of  $\sin \theta/\lambda$  and  $n\lambda$  which did not differ greatly and the theoretical intensity calculated for planes in these groups. The calculated and observed intensities of planes in each group did not check nearly so well as did the pairs of planes. The only explanation seems to be that even a slight variation in  $\sin \theta/\lambda$  and  $n\lambda$  must cause too large a change in absorption for such planes to be any longer comparable. The structure here proposed is a very reasonable one and it seems doubtful that any structure which is not correct would fit the Laue pairs so well.

#### DISCUSSION OF THE STRUCTURE

The crystal structure of arsenic triiodide has been investigated by means of Laue, powder, and oscillation photographs. It is shown to be a layer lattice. The underlying lattice is  $\Gamma_{rh}$  and the space group  $C_{3i}^2$ . Braekken in his paper

<sup>4</sup> Thomas, Zeits. f. Krist. 69, 137 (1928-9).



concluded that the lattice was hexagonal but agreed later that the lattice was rhombohedral. The incorrect fundamental lattice also led him to predict an incorrect space group although his structure is essentially the same as that given here.

The unit rhombohedron has dimensions  $r=8.25\text{\AA}$  and  $\alpha=51^\circ 20'$ ; there are two molecules to the unit cell.

The coordinates of the atoms are: Arsenic  $\pm uuu$  where  $u=60^\circ$ . Iodine  $\pm xyz$ ,  $\pm zxy$ ,  $\pm yzx$  where  $x=152^\circ$ ,  $y=28^\circ$ ,  $z=-90^\circ$ . Distances of closest approach of iodine are about 4.28 $\text{\AA}$  and 4.13 $\text{\AA}$  and of arsenic and iodine about 2.97 $\text{\AA}$ . The iodine ions are in hexagonal close packing; each arsenic ion is surrounded by six iodine ions.

The arsenic positions are not very accurate because of the heavy iodine atoms. The arsenic atoms may be slightly displaced away from the center of the iodine octahedron in the direction of one face. Such a displacement is not only possible, but rather probable, because arsenic occurs in the form of trivalent arsenic and thus possesses two electrons more than a complete 18 shell. Such a displacement is not incompatible with the intensities though rather difficult to predict.

The writer wishes to express her appreciation to Professor W. H. Zacharia- sen for his assistance throughout the duration of the work and to Dr. P. M. Harris who suggested the problem.