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Crystal Structures of Six New Polytypes of Cadmium Iodide

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Crystal structures of six new polytypes, $8H_3$, $14H_2$, $16H_1$, $16H_2$, $16H_3$ and $20H_3$, of cadmium iodide have been determined. The structures are represented as (1232), $(1122)_2 11$, (22 22 11 11 11 11), (22 22 211211), (2221221211) and $22(11)_8$ in Zhdanov symbols and they all belong to the space group $P3m1$. The formation of these polytypes are discussed in terms of the stacking faults which occur during the growth of crystals.

Introduction

In recent years cadmium iodide has emerged as a strongly polytypic compound. The total number, nearly 160, of its known polytypes exceeds that for any other compound (Trigunayat & Chadha, 1971). The *c*-dimensions of polytypes range from 6·84 to 738·72 Å and the crystal structures of 26 of them have been determined so far. The origin of polytypism in this and other related compounds, *viz.* lead iodide and cadmium bromide, is not yet fully clear but recent investigations have demonstrated that the phenomenon is strongly influenced by the edge dislocations generated during crystal growth (Agrawal & Trigunayat, 1969; Agrawal, Chadha & Trigunayat, 1970). In the present investigation, which has been mainly concerned with the study of phase transformations with temperature in polytypic structures, several new polytypes of cadmium iodide have been discovered, of which it has become possible to work out the complete crystal structures of six polytypes. This paper reports these new structures and discusses their modes of formation during crystal growth.

Experimental methods

The crystals were grown from solution (Mitchell, 1956) at room temperature in a crystallizing dish. Since they were extremely soft, great care was exercised in removing them from the solution onto a glass slide, where they were examined for perfection under a polarizing microscope before being mounted on the X-ray camera. For structure determination, the calculated intensities were compared with the observed ones for $10.l$ reflexions (Mitchell, 1956), recorded on oscillation photographs [Fig. 1(*a*) to (*f*)]. The range of oscillation 15°, was such that the angle between the incident X-ray beam and the *c* axis varied between 25 and 40°. It was so chosen to obtain a large number of $10.l$ spots in a continuous succession on the X-ray films (Chadha & Trigunayat, 1967). The Weissenberg photographs were also taken and had the same intensity sequences of spots as on the oscillation photographs. Hence they have not been reproduced.

Structure determination

In the structure determination of cadmium iodide polytypes there are 2^{n-1} possible structures to be considered where n is the total number of layers in a unit cell. However, the empirical fact of Zhdanov numbers 1, 2 and 3 alone occurring in the zigzag sequences of the known cadmium iodide structures, coupled with the frequent observation that the intensity sequences of the diffraction spots of the polytypes simulate that of a small-period type, helps to reduce the possibilities to a sensible proportion. The following formulae have been employed for intensity calculations.

$$I \propto A^2 + B^2 ,$$

where,

$$A = [\sum_{zA,\alpha} f_{\mathrm{I,Cd}} \cos 2\pi lz + \sum_{zB,\beta} f_{\mathrm{I,Cd}} \cos 2\pi(lz - \tfrac{1}{3}) + \sum_{zC,\gamma} f_{\mathrm{I,Cd}} \cos 2\pi(lz + \tfrac{1}{3})]$$

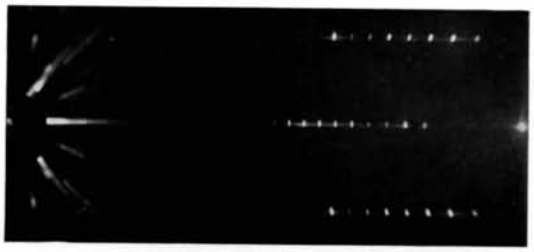
and

$$B = [\sum_{zA,\alpha} f_{\mathrm{I,Cd}} \sin 2\pi lz + \sum_{zB,\beta} f_{\mathrm{I,Cd}} \sin 2\pi(lz - \tfrac{1}{3}) + \sum_{zC,\beta} f_{\mathrm{I,Cd}} \sin 2\pi(lz + \tfrac{1}{3})]$$

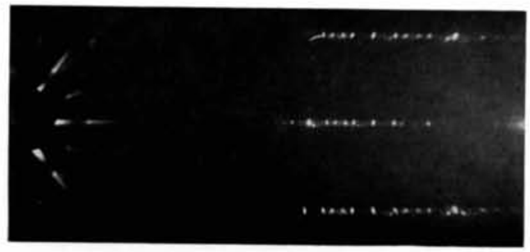
where $\sum_{zA,\alpha}$ denotes the summation over the z coordinates of the I atoms at A sites and Cd atoms at α sites; similarly for $\sum_{zB,\beta}$ and $\sum_{zC,\gamma}$ respectively. z represents the z coordinates of ions on the three vertical symmetry axes A, B and C passing through $(0, 0, z)$, $(\frac{2}{3}, \frac{1}{3}, z)$ and $(\frac{1}{3}, \frac{2}{3}, z)$ respectively. Roman letters represent the iodine ions and Greek letters the Cd ions. The intensities obtained by employing the expression $I \propto A^2 + B^2$ are multiplied by the Lorentz–polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$, where θ is the Bragg angle.

The detailed atomic structures worked out for the six polytypes, $8H_3$, $14H_2$, $16H_1$, $16H_2$, $16H_3$ and $20H_3$ are described below.*

* The polytype notation follows the pattern recently suggested in review article on polytypism (Trigunayat & Chadha, 1971).



(*a*)



(*b*)

(*c*)

(*d*)

(*e*)

(*f*)

Fig. 1. 15° *a*-axis oscillation photographs of the polytypes (*a*) $8H$, (*b*) $14H_2$, (*c*) $16H_1$, (*d*) $16H_2$, (*e*) $16H_3$ and (*f*) $20H_3$; 3 cm camera; Cu $K\alpha$ radiation. The strongest spot on the zero-layer line in each case has the index $10\,.\,n/2$, where n is the number of layers in the unit cell of the polytype.

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Polytype $8H_3$
Space group $P3m1$
Zhdanov symbol 1232
ABC sequence
$(A\gamma B)$ $(A\beta C)$ $(A\gamma B)$ $(C\alpha B)$
$a=b=4{\cdot}24$, $c=27{\cdot}34$ Å
Atomic coordinates
3 iodine atoms at $00z_1$
$z_1=0, 4z, 8z$
3 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 10z, 14z$
2 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=6z, 12z$
1 cadmium atom at $00z_4$
$z_4=13z$
1 cadmium atom at $\frac{2}{3}\frac{1}{3}z_5$
$z_5=5z$
2 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_6$
$z_6=z, 9z$
where $z=\frac{1}{16}$.

Polytype $14H_2$
Space group $P3m1$
Zhdanov symbol $(1122)_2 11$
ABC sequence
$(A\gamma B)$ $(A\gamma B)$ $(C\alpha B)$ $(A\gamma B)$ $(A\gamma B)$ $(C\alpha B)$ $(A\gamma B)$
$a=b=4{\cdot}24$, $c=47{\cdot}845$ Å
Atomic coordinates
5 iodine atoms at $00z_1$
$z_1=0, 4z, 12z, 16z, 24z$
7 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 22z, 26z$
2 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=8z, 20z$
2 cadmium atoms at $00z_4$
$z_4=9z, 21z$
5 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z, 5z, 13z, 17z, 25z$
where $z=\frac{1}{28}$.

Polytype $16H_1$
Space group $P3m1$
Zhdanov symbol 222211111111
ABC sequence
$(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)(A\gamma B)(A\gamma B)(A\gamma B)$
$a=b=4{\cdot}24$, $c=54{\cdot}68$ Å
Atomic coordinates
6 iodide atoms at $00z_1$
$z_1=0, 8z, 16z, 20z, 24z, 28z$
8 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z$
2 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z, 12z$
2 cadmium atoms at $00z_4$
$z_4=5z, 13z$
6 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z, 9z, 17z, 21z, 25z, 29z$
where $z=\frac{1}{32}$.

Polytype $16H_2$
Space group $P3m1$
Zhdanov symbol 2222211211
ABC sequence
$(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(C\alpha B)(A\gamma B)$
$a=b=4{\cdot}24$, $c=54{\cdot}68$ Å
Atomic coordinates
4 iodine atoms at $00z_1$
$z_1=0, 8z, 16z, 28z$
8 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z$
4 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z, 12z, 20z, 24z$
4 cadmium atoms at $00z_4$
$z_4=5z, 13z, 21z, 25z$
4 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z, 9z, 17z, 29z$
where $z=\frac{1}{32}$.

Polytype $16H_3$
Space group $P3m1$
Zhdanov symbol 2221221211
ABC sequence
$(A\gamma B)$ $(C\alpha B)$ $(A\gamma B)$ $(C\alpha B)(C\beta A)(C\alpha B)(C\alpha B)(A\gamma B)$
$a=b=4{\cdot}24$, $c=54{\cdot}68$ Å

Table 1. *Observed and calculated relative intensities for* 10.*l reflexions of polytype* $8H_3$

l	Observed intensity*	Calculated intensity	*l*	Observed intensity*	Calculated intensity	Further observed relation between intensities
0	*a*†	1	9	*w*	203	
1	*a*†	133	10	*vs*	1625	
2	*a*	40	11	*a*	12	4>3>7
3	*vs*	1307	12	*s*	1280	12>6
4	*vs*	1643	13	‡	107	
5	*vvs*	2018	14	‡	85	
6	*s*	938	15	‡	34	
7	*vs*	1198	16	‡	0	
8	*w*	206				

* The observed intensities were actually taken from the series 10.2*n* to 10.4*n*, which have a similar sequence to the series 10.0 to 10.2*n* ($n=8$).
† As can be seen in the Fig. 1(*a*), the absorption is abnormally high for these reflexions because of the plate-like shape of the crystal.
‡ Not recorded on the X-ray film in the chosen range of oscillation.

Atomic coordinates
4 iodine atoms at $00z_1$
$z_1=0,\ 8z,\ 18z,\ 28z$
7 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z,\ 6z,\ 10z,\ 14z,\ 22z,\ 26z,\ 30z$
5 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z,\ 12z,\ 16z,\ 20z,\ 24z$
4 cadmium atoms at $00z_4$
$z_4=5z,\ 13z,\ 21z,\ 25z$
1 cadmium atom at $\frac{2}{3}\frac{1}{3}z_5$
$z_5=17z$
3 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_6$
$z_6=z,\ 9z,\ 29z$
where $z=\frac{1}{32}$.

Polytype $20H_3$

Space group $P3m1$
Zhdanov symbol $22(11)_8$

ABC sequence
$(A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (A\gamma B)\ (A\gamma B)\ (A\gamma B)\ (A\gamma B)$
$(A\gamma B)\ (A\gamma B)\ (A\gamma B)$
$a=b=4{\cdot}24,\ c=68{\cdot}35$ Å
Atomic coordinates
9 iodine atoms at $00z_1$
$z_1=0,\ 8z,\ 12z,\ 16z,\ 20z,\ 24z,\ 28z,\ 32z,\ 36z$
10 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z,\ 6z,\ 10z,\ 14z,\ 18z,\ 22z,\ 26z,\ 30z,\ 34z,\ 38z$
1 iodine atom at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z$
1 cadmium atom at $00z_4$
$z_4=5z$
9 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z,\ 9z,\ 13z,\ 17z,\ 21z,\ 25z,\ 29z,\ 33z,\ 37z$
where $z=\frac{1}{40}$.

The observed and calculated values of the intensities for the six polytypes have been listed in Tables 1 to 6.

Table 2. *Observed and calculated relative intensities for* $10.l$ *reflexions of polytype* $14H_2$

l	Observed intensity*	Calculated intensity	l	Observed intensity*	Calculated intensity	Further observed relation between intensities
0	*a*†	1	15	*w*	51	
1	*a*†	0	16	*mw*	87	
2	*a*†	10	17	*vw*	36	
3	*a*†	10	18	*vw*	31	12 > 9
4	*vvw*	17	19	*w*	53	13 > 5 ≃ 11 ≃ 15 ≃ 19
5	*w*	53	20	*a*	3	17 > 18
6	*a*	4	21	*vvs*	358	
7	*vs*	313	22	‡	1	
8	*a*	6	23	‡	15	
9	*ms*	106	24	‡	5	
10	*w*	54	25	‡	3	
11	*w*	55	26	‡	2	
12	*ms*	116	27	‡	0	
13	*w*	68	28	‡	0	
14	*s*	206				

* As in Table 1 ($n=14$).
† and ‡ See Table 1.

Table 3. *Observed and calculated relative intensities for* $10.l$ *reflexions of polytype* $16H_1$

l	Observed intensity*	Calculated intensity	l	Observed intensity	Calculated intensity	Further observed relation between intensities
0	*a*†	1	17	*w*	41	
1	*a*†	1	18	*a*	0	
2	*a*†	0	19	*a*	33	
3	*vvw*	7	20	(*mw*)	58	
4	(*vvw*)§	23	21	*vw*	25	
5	*vvw*	17	22	*a*	0	
6	*a*	0	23	*a*	16	7 > 9 > 11 ≃ 13
7	*vw*	29	24	(*vvs*)	342	13 ≃ 15
8	(*vs*)	250	25	‡	10	15 > 17
9	*w*	39	26	‡	0	
10	*a*	0	27	‡	4	
11	*w*	46	28	‡	6	
12	(*vs*)	95	29	‡	1	
13	*w*	48	30	‡	0	
14	*a*	0	31	‡	0	
15	*w*	46	32	‡	0	
16	(*s*)	206				

* As in Table 1 ($n=16$).
† and ‡ See Table 1.
§ The reflexions in parentheses could not be well-resolved owing to their overlapping with the $4H$ spots.

Discussion

Polytype $8H_3$

Two other 8-layered polytypes have been reported earlier (Mitchell, 1956; Chadha & Trigunayat, 1967). So the new type has been designated as $8H_3$ [Fig. 1(*a*)]. Its crystal structure, (2123) is similar to that of polytype $12H_1$ (222123), reported by Mitchell (1956), pointing to the possible existence of a new structure series $(22)_n$ 2123 of CdI_2 polytypes. For the formation of the type $12H_1$ Mitchell postulated a cooperation between two near screw dislocations during its growth. However, he did not attempt to observe the dislocations through an optical microscope or otherwise. No growth spiral, which should necessarily be associated with a screw dislocation, has been observed by us in the microscopic examination of the polytype $8H_3$, thus ruling out the possibility of its growth by the screw dislocation mechanism. Its growth can best be understood on the basis of layer transposition mechanism, proposed by Jagodzinski (1954). By introducing suitable stacking faults in the $4H$ structure $(A\gamma B)$ $(C\alpha B)$, which, on account of its great relative abundance of occurrence, may be regarded as the prototype of all cadmium iodide polytypes, the structure of $8H_3$ may be obtained as follows:

$$(A\gamma B)\,(C\alpha B)\,(A\gamma B)\,(C\alpha B)$$
$$\downarrow$$
$$(A\beta C)\,(B\alpha C)\,(A\beta C)$$
$$\downarrow$$
$$(A\gamma B)\,(C\alpha B)$$

Final sequence: $(A\gamma B)\,(A\beta C)\,(A\gamma B)\,(C\alpha B) \rightarrow (1232)$.

It will be seen in the Fig. 1(*a*) that a faint streak runs through the diffraction spots on the first layer line, thus indicating the creation of random stacking faults, too, during the growth of polytype. The stacking

Table 4. *Observed and calculated relative intensities for* $10.l$ *reflexions of polytype* $16H_2$

l	Observed intensity*	Calculated intensity	l	Observed intensity*	Calculated intensity	Further observed relation between intensities
0	*a*†	1	17	*vvw*	21	
1	*a*†	0	18	*vw*	65	
2	*a*†	5	19	*mw*	100	
3	*a*†	21	20	*mw*	102	
4	*vw*	41	21	*vw*	74	
5	*vw*	52	22	*vvw*	36	
6	*vw*	40	23	*a*	8	13 > 14
7	*vvw*	14	24	*vs*	338	19 ≃ 20
8	*vvs*	875	25	‡	5	18 > 15 > 6
9	*vvw*	20	26	‡	12	4 ≃ 6
10	*vw*	75	27	‡	14	22 > 9 > 7
11	*w*	138	28	‡	10	9 ≃ 15 ≃ 17
12	*ms*	167	29	‡	5	
13	*w*	145	30	‡	1	
14	*w*	84	31	‡	0	
15	*vvw*	23	32	‡	0	
16	*s*	206				

* As in Table 1 ($n=16$).
† and ‡ See Table 1.

Table 5. *Observed and calculated relative intensities for* $10.l$ *reflexions of polytype* $16H_3$

l	Observed intensity*	Calculated intensity	l	Observed intensity*	Calculated intensity	Further observed relation between intensities
0	*a*†	1	17	*ms*	195	
1	*vvw*	15	18	*a*	0	
2	*vvw*	24	19	*vs*	499	
3	*vvw*	12	20	*w*	82	
4	*w*	48	21	*vw*	66	
5	*ms*	249	22	*mw*	146	12 > 11 ≃ 14
6	*vvw*	11	23	*ms*	240	23 > 16 > 15 > 17
7	*w*	75	24	*vs*	466	16 ≃ 10
8	*vvs*	1921	25	‡	145	26 ≃ 25
9	*w*	87	26	‡	30	
10	*ms*	207	27	‡	35	
11	*s*	319	28	‡	1	
12	*s*	378	29	‡	23	
13	*ms*	199	30	‡	0	
14	*s*	306	31	‡	1	
15	*ms*	201	32	‡	0	
16	*ms*	206				

* As in Table 1 ($n=16$).
† and ‡ See Table 1.

faults are presumably brought about by slip between the atomic layers.

Polytype $14H_2$

Three polytypes of 14 layers each have been reported earlier (Trigunayat & Chadha, 1971). The complete structure of only one of them, designated as $14H_1$, has been worked out (Mitchell, 1956). It is represented as $(22)_3 11$ and belongs to the structure series $(22)_n 11$ of the cadmium iodide polytypes. The present polytype, designated as $14H_2$, has the crystal structure as $(1122)_2 11$. Mitchell attempted to account for the formation of $14H_1$ on the basis of screw dislocation mechanism, since it could be generated by spiral growth around a single screw dislocation of appropriate Burgers vector created in the basic $4H$ structure. However, an optical microscopic and interferometric examination of the crystal showed that no growth spirals existed on the surface of the present polytype $14H_2$. Like the preceding case of the polytype $8H_3$, the formation of this polytype may also be visualized in terms of the layer transposition mechanism as follows:

$$(C\alpha B)\ (A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)$$
$$\downarrow$$
$$(A\beta C)\ (B\alpha C)\ (A\beta C)\ (B\alpha C)\ (A\beta C)$$
$$\downarrow$$
$$(A\gamma B)\ (A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)$$
$$\downarrow$$
$$(C\beta A)\ (B\gamma A)\ (C\beta A)\ (B\gamma A)$$
$$\downarrow$$
$$(C\alpha B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)$$
$$\downarrow$$
$$(A\beta C)$$
$$\downarrow$$
$$(A\gamma B)$$

Final sequence: $(C\alpha B)\ (A\gamma B)\ (A\gamma B)\ (C\alpha B)\ (C\alpha B)\ (A\gamma B)\ (A\gamma B) \rightarrow (1122)_2 11$.

In contrast to the growth of the polytype $8H_3$, which involved slips between the sandwiches alone, here the slip occurs inside the sandwiches also. Since the layers of iodine and cadmium are held together by strong ionic bonds within a sandwich, such a slip may appear *prima facie* to be highly improbable. It could really be so if the slip had to occur after the completion of crystal growth. But we are visualizing the slip here when the crystal is actually growing in the solution. Then, as the ionic layers are laid down one after another, it is quite possible that a stacking fault causes the cadmium ions to move into a position other than the normal ones, *e.g.* they may deposit into γ position instead of the normal β positions over an A layer of iodine ions, thus eventually giving rise to a sandwich $(A\gamma B)$ instead of the normal arrangement $(A\beta C)$. It is necessary that the fault occurs in the initial stages of deposition of the cadmium ions. Once the mistake has been made over a part of the layer, it will perpetuate over the rest of the layer by the sequential force of the crystal structure, because with the underlying iodine layer being in the A position both β and γ positions have equal probability of occupation by the cadmium ions.

There are alternative ways of obtaining the $14H_2$ structure from the parent $4H$ structure by the introduction of suitable layer transpositions, but we have chosen the above scheme for its formation because it involves the least number of transpositions within the sandwiches. A slip between two neighbouring sandwiches is more likely because the sandwiches are held together by weak van der Waals forces of attraction.

It is seen in Fig. 1(*b*) that a few weak spots, with half the spacing of the $14H$ spots, occupying a slightly lower position are also present, indicating the existence of a 28-layered polytype in the crystal. Also one can notice some weak irregularly spaced spots belonging to an unidentified polytype. Since all these spots are present in the region of reflexion on the X-ray photograph, where the spots arise from surface reflexion alone, it is obvious that three polytypes, $14H$, $28H$ and the unidentified one, are intergrown on the same crystal face. This is an example of parallel growth of crystals (Jeffery & Murty, 1962).

Polytypes $16H_1$, $16H_2$ *and* $16H_3$

Four CdI_2 polytypes of sixteen layers each have been reported by four different workers (Trigunayat & Chadha, 1971), but the crystal structure of none of them has been worked out. Consequently, the three 16-layered polytypes encountered in the present study have been designated as $16H_1$, $16H_2$, and $16H_3$ respectively. These have their respective crystal structures as (222211111111), (2222211211) and (2221221211) in their Zhdanov symbols. Each one of them can be derived from the basic $4H$ structure by introducing stacking faults in the same way as for the preceding $8H_3$ and $14H_2$ structures with the restriction that the number of faults within the sandwiches are kept to a minimum.

Polytype $20H_3$

Nineteen cadmium iodide polytypes of twenty layers each have been reported earlier by six different workers (Trigunayat & Chadha, 1971). Out of these the crystal structures of two have been worked out. The present polytype has been designated therefore as $20H_3$. It has the structure $22(11)_8$ in the Zhdanov symbol. The dominance of (11) units in the structure indicates that it was most probably generated from the $2H$ structure, represented as (11), which is the most common polytype of cadmium iodide after $4H$. Only two faults are enough to obtain the requisite structure as follows.

$$(A\gamma B)\ (A\gamma B)\ (A\gamma B)\ \ldots\ldots\ldots\ (A\gamma B)$$
$$\downarrow$$
$$(C\beta A)\ (C\beta A)\ \ldots\ldots\ldots\ (C\beta A)$$
$$\downarrow$$
$$(C\alpha B)\ (A\gamma B)\ \ldots\ldots\ldots\ (A\gamma B)\,.$$

Final sequence: $(A\gamma B)\ (C\alpha B)\ (A\gamma B)_8 \rightarrow 22(11)_8$.

Table 6. *Observed and calculated relative intensities for* 10.*l reflexions of polytype* $20H_3$

l	Observed intensity*	Calculated intensity	l	Observed intensity*	Calculated intensity	Further observed relation between intensities
0	*a*†	1	21	*mw*	8	
1	*a*†	0	22	*w*	7	
2	*a*†	0	23	*vw*	6	
3	*a*†	0	24	*a*	6	
4	*a*	1	25	*a*	5	
5	*a*	2	26	*a*	4	15≃16≃17≃18
6	*a*	3	27	*a*	4	12≃13≃14≃19≃21
7	*vvw*	4	28	*a*	3	15 > 14
8	*vvw*	4	29	*a*	3	21 > 22 > 23
9	*vvw*	5	30	(*s*)	274	
10	(*vs*)§	100	31	‡	2	
11	*w*	7	32	‡	1	
12	*mw*	8	33	‡	1	
13	*mw*	8	34	‡	0	
14	*mw*	8	35	‡	0	
15	*ms*	9	36	‡	0	
16	*ms*	9	37	‡	0	
17	*ms*	9	38	‡	0	
18	*ms*	9	39	‡	0	
19	*mw*	8	40	‡	0	
20	(*vs*)	206				

* As in Table 1(n=20).
† and ‡ See Table 1.
§ The reflexions in parentheses could not be well-resolved owing to their overlapping with the 2*H* spots.

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The Crystal and Molecular Structure of Bismuth Trichloride

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The crystal structure of bismuth trichloride has been determined. Three-dimensional data were collected on a four-circle diffractometer using Mo $K\alpha$ radiation. The space group is $Pn2_1a$ with orthorhombic cell a=7·641 (2), b=9·172 (7), c=6·291 (2) Å. The final residual for the 935 observations is 4·43 %. The molecular structure consists of a bismuth atom closely associated with three chlorine atoms in the shape of distorted trigonal pyramid and with five other chlorine atoms at bridging distances. The geometry of this eightfold coordination is best described as a trigonal prism with six chlorine atoms at its corners, and with two more chlorine atoms in face-bridging positions. The three close Bi–Cl distances are 2·468, 2·513 and 2·518 Å; distances to the bridging chlorines range from 3·216 to 3·450 Å.

Introduction

Examination of the gas-phase Raman spectra of some Group VA trihalides (Denchik, Nyburg, Ozin & Szymański, 1971) revealed significant differences between the spectra of antimony and bismuth trichloride. The spectrum of the latter shows modes that were interpreted as being due to strong chlorine bridging. The