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Crystal Structures of Four New Polytypes of Cadmium Iodide

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Crystal structures of four new polytypes of cadmium iodide, two rhombohedral and two hexagonal, have been determined. The structures of the rhombohedral polytypes, *viz.* 24*R* and 36*R*, have been found to be $(2213)_3$ and $(22112121)_3$, in Zhdanov notation. The two hexagonal polytypes, *viz.* $18H_g$ and $30H_d$, have been found to possess the structures $(22)(11)_7$ and $(2211)_4 1122$ respectively. All four polytypes were found to have grown in syntactic coalescence with other polytypes, showing a transformation of structure during growth. The polytype $30H_d$ is the largest hexagonal cadmium iodide polytype for which the atomic structure is known. The growth of these polytypes is discussed.

Introduction

Hitherto, over 80 cadmium iodide polytypes have been reported with cell heights ranging from 6·84 (2*H*) to 218·88 Å (64*H*). Of these, the crystal structures of only 20 polytypes, 17 hexagonal and 3 rhombohedral, have been determined(Mitchell, 1956; Srivastava & Verma, 1962, 1964, 1965; Chadha & Trigunayat, 1967*a*,*b*; 1968; Agrawal & Trigunayat, 1968). During the course of a study of one-dimensional disorder in cadmium iodide crystals, 46 hexagonal and 7 rhombohedral polytypes have been discovered (Jain, 1968), from which it has been possible to work out the complete crystal structures of two rhombohedral and two hexagonal polytypes, *viz.* 24*R*, 36*R*, $18H_g$ and $30H_d$. The crystals show significant structure-transformations during growth and provide information regarding the origin of polytypism in crystals.

Experimental

c and *a* axis oscillation photographs of cadmium iodide crystals were used for the identification of the polytypes. In the case of the *c* axis photographs the identity of the polytype could be established by direct measurement of the *c* parameter, which could also be calculated from the *a* and *b* dimensions, which are the same for all polytypes, from the *a* axis photographs (Trigunayat, 1959). The *c* axis oscillation photographs were taken over a 15° range (from the position where the *a* axis made an angle of 31·5° with the incident X-ray beam to the position (31·5+15)=46·5°). This range of oscillation was found to be the most suitable for all cadmium iodide polytypes as it includes all the reflexions from 10.0 to 10.*X* for an *X*H polytype. In the case of the *a*-axis photographs, the usual range of oscillation, *viz.* 25 to 40°, which covers the surface reflexion spots (Chadha & Trigunayat, 1967*a*), was chosen. In the structures determinations the intensities of the reflexions were compared on both the oscillation and Weissenberg photographs, because the crystals were too thick to give transmission diffraction spots. As has already been shown by Ramsdell (1944) and Mitchell (1955), it is sufficient to compare the observed and calculated intensities of only the 10.*l* or 01.*l* reflexions in order to determine a crystal structure. Zero-layer *a* axis Weissenberg photographs were therefore used for the structure determination.

The crystals used in the present study were grown from solution by a method already described (Jain & Trigunayat, 1968*a*).

Structures of polytypes

Polytype 24*R*

This new modification was discovered in a well-developed crystal which displayed no growth spiral on its (0001) basal plane. It was found to have grown in syntactic coalescence with a hexagonal polytype based on the 2*H*-phase. The latter could not be identified as its diffraction spots were very close together, accompanied by considerable disorder. The identification of the polytype 24*R* was achieved from its *c*-axis oscillation photograph (Fig. 1). The photograph shows unsymmetrical spots about the zero-layer line, as expected for a rhombohedral lattice. Fig. 2 is an *a* axis normal-beam Weissenberg photograph taken for the structure determination. The large *c* dimension of 24*R* greatly increases the number of possible atomic arrangements in the unit cell, thus rendering the task of postulating the correct structure a very tedious one. However, the intensity sequence of 10.*l* spots was found to be very similar to that of a type investigated earlier, 12*R* (Agrawal & Trigunayat, 1968). Using the structure of 12*R* and adding one more (22) unit, which is the structure of the common type 4*H*, the arrangement $(2213)_3$ is obtained. The 10.*l* intensities for this arrangement have been computed using the formula

$$I=A^2+B^2 \qquad (1)$$

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

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

zA,α, zB,β, zC,γ denote the respective *z* coordinates of the iodine (Roman letters) and cadmium (Greek letters) atoms on the vertical *A*, *B* and *C* axes respectively, passing through (0,0,0), $(\tfrac{2}{3},\tfrac{1}{3},0)$, $(\tfrac{1}{3},\tfrac{2}{3},0)$ respectively. $\sum_{zA,\alpha}$ represents summation over iodine atoms at *A* sites and cadmium atoms at α sites, and likewise the other two summations. The intensities obtained by employing expression (1) were multiplied by the Lorentz–polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$ where θ is the Bragg angle. The calculated intensity values agree very well with the observed ones. The intensities were compared in reflexion because of heavy absorption about the central Laue streak; the thickness of the crystal was about 50 microns. In order to confirm the structure, the intensities of the $10.\bar{l}$ reflexions were also computed and were found to correspond with the observed values. These values are listed in Table 1. The intensities have been compared for the spots 10.48 to 10.96 and $10.\overline{48}$ to $10.\overline{96}$. The calculated values in the Table have not been corrected for absorption bacause no absorption factor was available for a crystal of hexagonal shape. However, taking into account the shape and the orientation of the crystal, it can be generally said that the change in intensities due to absorption should be slight and gradual.

The detailed structure of 24*R* is as follows:

space group $R3m$

Zhdanov symbol $(2213)_3$

Table 1. *Calculated and observed intensities of the structure* 24*R*

l	Calculated intensity	Observed intensity*	$\bar{l}$	Calculated intensity	Observed intensity*	Further observed relations between intensities
1	5	*a*	2	2	*a*	
4	21	*w*	5	9	*vw*	$13>19$
7	22	*w*	8	62	*ms*	$16>22>10$ $37\simeq 31$
10	34	*ms*	11	278	*vs*	$\overline{11}>\overline{17}$
13	264	*vs*	14	51	*ms*	
16	61	*ms*	17	184	*vs*	$\bar{8}>\overline{14}\simeq\overline{26}>\overline{32}$
19	208	*vs*	20	32	*w*	
22	59	*ms*	23	18	*w*	$\overline{35}>\overline{29}$
25	17	*w*	26	50	*ms*	
28	23	*w*	29	138	*s*	
31	103	*s*	32	32	*ms*	
34	23	*w*	35	110	*s*	
37	100	*s*	38	11	*w*	
40	18	*w*	41	6	*vw*	
43	2	*vw*	44	5	*vw*	
46	0	*a*	47	1	*vw*	

* As mentioned in the text the observed intensities were actually taken from the series 10·48 to 10·96. This series has a similar intensity sequence to that of 10.0 to 0.48.

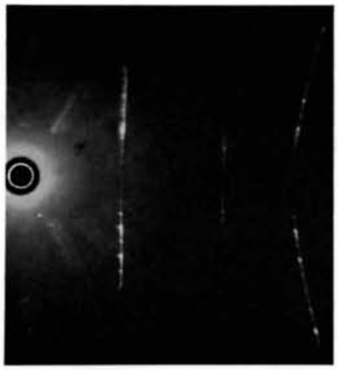

Fig. 1. A 15° c-axis oscillation photograph of polytype $24R$. Cu $K\alpha$ radiation; camera radius 3 cm.

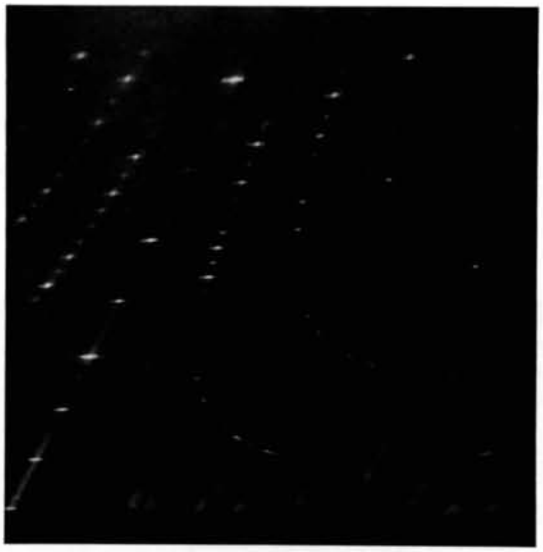

Fig. 2. Zero-layer a-axis Weissenberg photograph of polytype $24R$; Cu $K\alpha$ radiation, camera diameter 5·73 cm. The festoons corresponding to $10.l$ and $\bar{1}0.l$ rows of spots are recorded on the right and left side respectively, of the straight row of $00.l$ spots. The first intense spot from the top corresponds to $l=85$ in the $\bar{1}0.l$ festoon and to $l=83$ in the $10.l$ festoon.

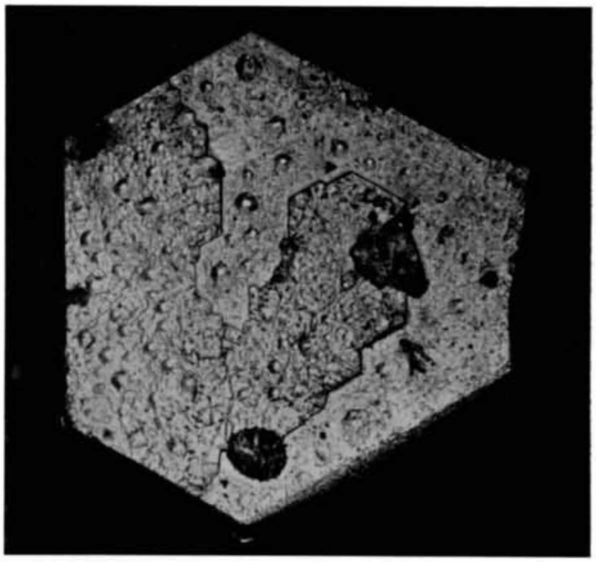

Fig. 3. Interferogram of a cadmium iodide crystal showing an overgrown layer on its (0001) face. Hg green light (× 67).

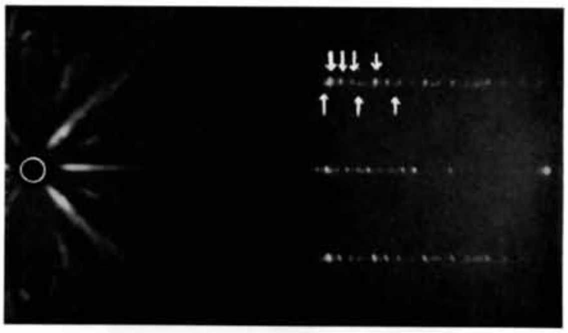

Fig. 4. A 15° a-axis oscillation photograph of the (0001) face of the crystal shown in Fig. 3, in reflexion showing spots of type $36R$ (upper arrow marks) and $4H$ (lower arrow marks); Cu $K\alpha$ radiation; camera radius 3 cm.

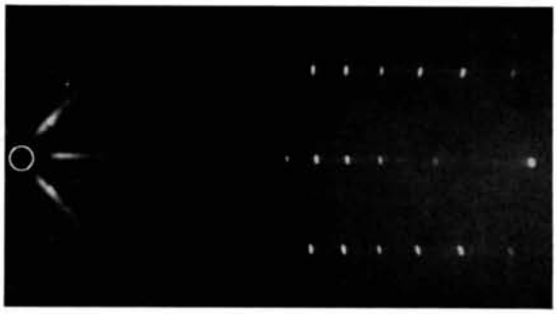

Fig. 5. A 15° a-axis oscillation photograph of the other face of the crystal (unidentified). Cu $K\alpha$ radiation; camera radius 3 cm.

Fig. 6. Zero-layer *a*-axis Weissenberg photograph of polytype 36*R*. Cu $K\alpha$ radiation; camera diameter 5·73 cm. The festoon corresponding to the 10.*l* row of spots is recorded on the right side of the straight row of 00.*l* spots; the *l* values of two strong spots are noted on the photograph.

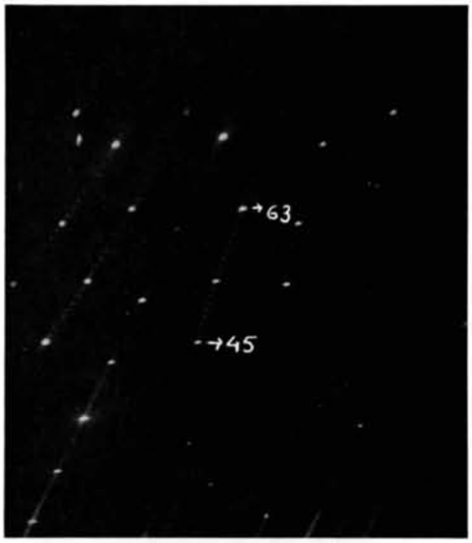

Fig. 8. Zero-layer *a*-axis Weissenberg photograph of polytype $18H_g$. Cu $K\alpha$ radiation; camera diameter 5·73 cm. The lowest festoon shows the 10.*l* row of spots. The *l* values of two strong spots are noted on the photograph.

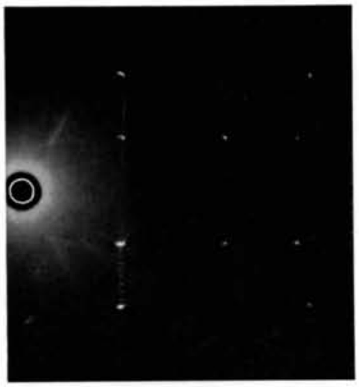

Fig. 7. A 15° *c*-axis oscillation photograph of polytype $18H_g$. Cu $K\alpha$ radiation; camera radius 3 cm.

Fig. 9. A 15° *a*-axis oscillation photograph of polytype $30Hd_\alpha$ Cu $K\alpha$ radiation; camera radius 3 cm. The *l* values of two strong spots along the 01.*l* row are indicated on the photograph.

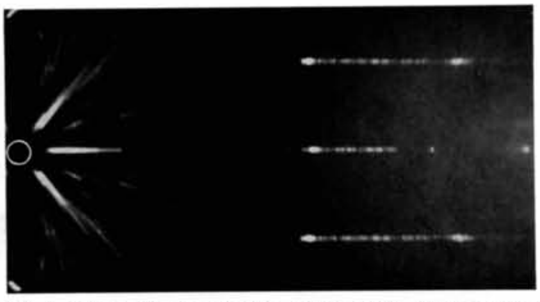

Fig. 10. A 15° *a*-axis oscillation photograph of the type 46*H*. Cu $K\alpha$ radiation; camera radius 3 cm.

ABC sequence
$(A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (A\beta C)$
$(B\alpha C)\ (A\beta C)\ (B\alpha C)\ (B\gamma A)$
$(C\beta A)\ (B\gamma A)\ (C\beta A)\ (C\alpha B)$
$a=b=4{\cdot}24$, $c=82{\cdot}02$ Å (hexagonal indexing).
Atomic coordinates
8 iodine atoms at $00z_1$
$z_1=0, 8z, 12z, 20z, 30z, 34z, 38z, 42z$
8 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 16z, 24z, 28z, 36z, 46z$
8 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z, 14z, 18z, 22z, 26z, 32z, 40z, 44z$
4 cadmium atoms at $00z_4$
$z_4=5z, 17z, 25z, 45z$
4 cadmium atoms at $\frac{2}{3}\frac{1}{3}z_5$
$z_5=13z, 21z, 33z, 41z$
4 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_6$
$z_6=z, 9z, 29z, 37z$
where $z=\frac{1}{48}$.

Structure of 36*R*

This new polytype was also discovered in a well-developed crystal showing no growth spiral on the (0001) basal plane (Fig. 3). It was found to have grown with a type 4*H* in parallel orientation on the same face of the crystal. The other face of the crystal was a high polytype (unidentified) based on 4*H*. The crystal forms an interesting case of epitaxic growth and has been discussed in detail elsewhere (Jain & Trigunayat, 1968*b*). Figs. 4 and 5 show the respective *a* axis oscillation photographs of the two sides of the crystal, obtained in the oscillation range 25–40°, *i.e.* the incident X-ray beam making an angle of 25–40° with the c axis. Fig. 4 shows two sets of diffraction spots corresponding to two structures, which were identified as 4*H* and 36 *R*. Fig. 5 shows the weak spots of a higher polytype based on 4*H*. Fig. 6 is an *a* axis normal-beam zero-layer Weissenberg photograph of the type 36*R* showing 10.*l* spots, which were used in the structure determination. *Prima facie*, the task of structure determination appeared exceedingly difficult because of a still larger number of possible atomic arrangements in the unit cell in this case. However, taking advantage of the fact that almost all the CdI_2 structures reported so far have Zhdanov numbers of only 1 and 2 in the zigzag sequence representing the sequence of iodine atoms in the $(11\bar{2}0)$ cross section, the possible number reduces to 55. Intensities arising from these possible sequences were computed using equation (1). Of all the sequences considered, only one gave values in agreement with the observed data and this agreement was exceptionally good as can be seen from Table 2. The intensities have been compared for the spots 10.72 to 10.144 and 10.$\overline{72}$ to 10.$\overline{144}$.

The detailed atomic structure of 36*R* is as follows:
Space group *R*3*m*
Zhdanov symbol $(22112121)_3$

Table 2. *Calculated and observed intensities for the structure* 36*R*

l	Calculated intensity	Observed intensity*	$\bar{l}$	Calculated intensity	Observed intensity*	Further observed relations between intensities
1	4	*a*	2	4	*a*	
4	16	*vvw*	5	7	*a*	
7	6	*vvw*	8	20	*vvw*	
10	19	*w*	11	37	*vw*	$25 \simeq 13 > 49 > 37 > 46 \simeq 58$
13	84	*ms*	14	96	*ms*	$55 > 22 > 16 \simeq 34 > 43$
16	146	*s*	17	434	*vs*	$\overline{17} > \overline{53} > \overline{41}$
19	852	*vvs*	20	45	*w*	$\overline{29} > \overline{23} > \overline{38} > \overline{50}$
22	157	*s*	23	149	*s*	$\overline{14} > \overline{35} > \overline{26} > \overline{56} > \overline{47}$
25	85	*ms*	26	54	*ms*	
28	5	*a*	29	186	*s*	
31	318	*vs*	31	28	*w*	
34	142	*s*	35	61	*ms*	
37	58	*ms*	38	127	*s*	
40	23	*w*	41	241	*vs*	
43	127	*s*	44	3	*a*	
46	31	*ms*	47	47	*ms*	
49	74	*ms*	50	74	*s*	
52	19	*w*	53	345	*vs*	
55	160	*s*	56	51	*ms*	
58	31	*ms*	59	25	*w*	
61	10	*vw*	62	5	*vw*	
64	5	*vw*	65	1	*vvw*	
67	2	*vw*	68	3	*vvw*	
70	1	*vw*	71	1	*a*	

* As mentioned in the text the observed intensities were actually taken from the series 10.72 to 10.144. This series has a similar intensity sequence to that of 10.0 to 10.72.

ABC sequence

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

$a=b=4{\cdot}24$, $c=123{\cdot}03$ Å (hexagonal indexing)

Atomic coordinates

12 iodine atoms at $00z_1$
$z_1=0, 8z, 12z, 22z, 26z, 30z, 34z, 38z, 42z, 52z, 64z, 68z$
12 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 28z, 40z, 44z, 48z, 56z, 60z, 70z$
12 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z, 16z, 20z, 24z, 32z, 36z, 46z, 50z, 54z, 58z, 62z, 66z$
6 cadmium atoms at $00z_4$
$z_4=5z, 17z, 45z, 49z, 57z, 61z$
6 cadmium atoms at $\frac{2}{3}\frac{1}{3}z_5$
$z_5=21z, 25z, 33z, 37z, 53z, 65z$
6 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_6$
$z_6=z, 9z, 13z, 29z, 41z, 69z$
where $z=\frac{1}{72}$.

Structure of $18H_g$

This polytype was found to exist in a well-developed hexagonal crystal which displayed no growth spiral on its (0001) basal plane. Both sides of the crystal were identified as the type $18H$. Fig. 7 is a *c* axis 15° oscillation photograph of the crystal. As six polytypes of the same *c* dimension have been reported earlier, the present one has been labelled $18H_g$. Fig. 8 is an *a* axis normal-beam zero-layer Weissenberg photograph of the polytype showing $10.l$ spots, which were used in the structure determination.

Although the number of ways in which the atoms could be arranged in the unit cell to form an 18-layered structure is extremely large, the correct structure could be anticipated from examination of the positions of the strong spots. The intense diffraction spots of this type were found to coincide with the type $2H$, indicating that its unit-cell contained a large number of (11) units. Thus, the structure was most likely to be one of the following two:

(1) 2211111111111111
(2) 22221111111111 .

The calculated intensity values for the first structure are given in Table 3; they are in excellent agreement with the observed values. The intensities of the spots from reflexions 10.36 to 10.72 were compared.

The detailed atomic structure of $18H_g$ is as follows:

space group $P3m1$
Zhdanov symbol (2211111111111111) or $(22)\ (11)_7$
ABC sequence
$(A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (A\gamma B)\ (A\gamma B)\ (A\gamma B)$
$(A\gamma B)\ (A\gamma B)\ (A\gamma B)$
$a=b=4{\cdot}24$ and $c=61{\cdot}515$ Å.
Atomic coordinates
8 iodine atoms at $00z_1$
$z_1=0, 8z, 12z, 16z, 20z, 24z, 28z, 32z$
9 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z, 34z$
1 iodine atom at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z$

Table 3. *Calculated and observed intensities for the structure* $18H_g$

l	Calculated intensity	Observed intensity*	*l*	Calculated intensity	Observed intensity*	Further observed relations between intensities
0	1	*a*	19	10	*ms*	18 > 9
1	0	*a*	20	9	*ms*	
2	0	*a*	21	8	*ms*	
3	1	*a*	22	7	*ms*	
4	2	*vvw*	23	6	*ms*	
5	3	*vw*	24	5	*w*	
6	4	*w*	25	4	*w*	
7	6	*w*				
8	7	*ms*	26	4	*w*	
9	107	*vvw*	27	278	*vvs*	
10	9	*ms*	28	2	*w*	
11	10	*ms*	29	1	*w*	
12	11	*ms*	30	1	*w*	
13	11	*ms*	31	0	*a*	
14	11	*ms*	32	0	*a*	
15	11	*ms*	33	0	*a*	
16	11	*ms*	34	0	*a*	
17	11	*ms*	35	0	*a*	
18	206	*vvs*	36	0	*a*	

* The observed intensities were actually taken from the series 10.36 to 10.72, which have a similar sequence to that of the series 10.0 to 10.36.

1 cadmium atom at $00z_4$
$z_4=5z$
8 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z, 9z, 13z, 17z, 21z, 25z, 29z, 33z$
where $z=\frac{1}{36}$.

Structure of $30H_d$

This polytype was discovered in a well-developed crystal which did display a hexagonal spiral on the (0001) basal plane. Fig. 9 is an *a* axis oscillation photograph of one side of the crystal, which has been identified as $30H$. The other side was identified as the type $46H$ (Fig. 10).

At first the structure determination of this polytype appeared to be a formidable task because of the large number of possible ways in which the various atoms can be arranged to give a unit cell with such a large *c* dimension (102·52 Å). However, an inspection of the intensity distribution revealed a striking feature, *viz.* the most intense diffraction spots of this type occurred at the positions of polytype $6H$ (Mitchell, 1956). As the latter type has the structure (2211), it implied the presence of many (2211) units in the unit cell of the unknown polytype. Bearing this intensity distribution in mind and using the numbers 1 and 2 only, the following structures were formulated as being probable:

(1) $(2211)_4$ 1221
(2) $(2211)_4$ 111111
(3) $(2211)_4$ 1122
(4) $(2211)_3$ 12211221
(5) $(2211)_3$ 12122121
(6) $(2211)_3$ 1111221111
(7) $(2211)_3$ 1112112111
(8) $(2211)_3$ 1121111211

The number of (2211) units cannot be decreased further, since the structure would then not be based on a $6H$ type. Intensities for 10.*l* reflexions were computed for each of the structures proposed above. Excellent agreement between the calculated and observed values, listed in Table 4, was found for the case of structure number (3). The intensities were compared from the *a* axis oscillation photograph (Fig. 9). A Weissenberg photograph could not be taken as the crystal was lost after taking the oscillation photograph. However, a large number of 01.*l* spots were recorded on the *a* axis oscillation photograph in the oscillation range 25–40°, which could be used for the intensity comparison. The intensities of the spots reflexions 01.75 to 01.115 (first layer) were compared. Although this does not cover the full range of reflexions from $l=60$ to $l=120$, the structure could be confirmed from these spots alone because of the symmetrical intensity sequence.

The detailed atomic structure of $30H$ is as follows:
space group $P3m1$
Zhdanov symbol $(2211)_4$ 1122
ABC sequence
$(A\gamma B)\,(C\alpha B)\,(A\gamma B)\,(A\gamma B)\,(C\alpha B)\,(A\gamma B)$
$(A\gamma B)\,(C\alpha B)\,(A\gamma B)\,(A\gamma B)\,(C\alpha B)\,(A\gamma B)$
$(A\gamma B)\,(A\gamma B)\,(C\alpha B)$
Atomic coordinates

Table 4. *Calculated and observed intensities for the structure* $30H_d$

l	Calculated intensity	Observed intensity*	*l*	Calculated intensity	Observed intensity*	Further observed relations between intensities
15	417	*vvs*	35	84	*s*	25 > 20 > 35 > 40
16	1	*a*	36	22	*ms*	22 ≃ 23 > 24 > 21
17	4	*vvw*	37	22	*ms*	36 ≃ 37 > 38 > 39
18	10	*w*	38	20	*ms*	
19	18	*w*	39	17	*ms*	
20	110	*s*	40	57	*s*	
21	31	*ms*	41	8	*w*	
22	35	*ms*	42	4	*vvw*	
23	35	*ms*	43	2	*a*	
24	32	*ms*	44	0	*a*	
25	117	*s*	45	376	*vvs*	
26	19	*ms*	46	0	*a*	
27	12	*w*	47	1	*vvw*	
28	5	*vvw*	48	2	*vvw*	
29	1	*a*	49	2	*vvw*	
30	206	*vs*	50	13	*ms*	
31	1	*a*	51	3	*w*	
32	5	*vvw*	52	2	*vw*	
33	10	*w*	53	1	*vvw*	
34	15	*w*	54	1	*vvw*	
			55	3	*vw*	

* The observed intensities were actually taken from the series 10·60 to 10·120, which have a similar sequence to that of the series 10·0 to 10·60.

10 iodine atoms at $00z_1$
$z_1=0, 8z, 12z, 20z, 24z, 32z, 36z, 44z, 48z, 52z$
15 iodine atoms at $\frac{2}{3}\frac{1}{3}z_2$
$z_2=2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z, 34z,$
$38z, 42z, 46z, 50z, 54z, 58z$
5 iodine atoms at $\frac{1}{3}\frac{2}{3}z_3$
$z_3=4z, 16z, 28z, 40z, 56z$
5 cadmium atoms at $00z_4$
$z_4=5z, 17z, 29z, 41z, 57z$
10 cadmium atoms at $\frac{1}{3}\frac{2}{3}z_5$
$z_5=z, 9z, 13z, 21z, 25z, 33z, 37z, 45z, 49z, 53z$
where $z=\frac{1}{60}$.

The polytype $30H_a$ is so far the largest polytype of cadmium iodide with a known atomic structure.

Discussion

Each of the four polytypes whose structures have been described above show a transformation of structure during growth. Each of the two rhombohedral polytypes, $24R$ and $36R$, occur in syntactic coalescence with a disordered high polytype (unidentified). In both the cases, the rhombohedral type was found to occur on the upper face of the crystal. The two hexagonal types, $18H_g$ and $30H_a$ grew together with other hexagonal types, one having the same cell dimensions (but different layer stacking sequence) and the other having different cell dimensions. Two nearly similar cases of structure transformation, *viz.* $30R \rightarrow 30H$ and $42R \rightarrow 42H$ have been described earlier by Chadha & Trigunayat (1967*a*). It was shown that the creation of rhombohedral polytypes in cadmium iodide and their subsequent transformation into hexagonal types could be explained on the layer-transposition mechanism of Jagodzinski (1954). The layer transpositions result from stacking faults generated during crystal growth. A stabilization of the faults into some definite structure is brought about by vibration entropy considerations. The structure-transformations observed by us for both the rhombohedral and the hexagonal types basically fit into the same pattern and can be similarly understood. For instance, in the case of type $24R$, found on the upper face of the crystal, stacking faults in the basic structure $4H$ could have created the disordered high polytype (unidentified) during the initial stages when the growth rate was rapid, which in turn could have developed more faults that became stabilized to give the type $24R$. A complete ordering of the faults is seldom possible. Hence the X-ray photographs of such crystals are usually expected to show 'streaking' in which the various reflexions on a layer line on the *a* axis oscillation photograph, and on a row line on the *c* axis photograph, run into each other. The 'streaks' may have varying intensities depending upon the proportion of residual faults inside the structure. Such 'streaking' was observed by Chadha & Trigunayat (1967*a*) on their X-ray photographs. This essential feature is also present on the X-ray photographs (Figs. 1, 4, 5, 7, 10) of all four crystals studied by us. Because of the more rapid rate of growth in the initial stages it is expected that the lower face of the crystal will have more residual faults, and hence will show more intense 'streaks' than the upper face. This has been found to be so in all the four cases discussed above. Evidence for the occurrence of stacking faults during growth of cadmium iodide crystals was reported in the recent work of Agrawal & Trigunayat (1969), who observed extensive arrangements of tilt boundaries of edge dislocations, partial dislocations, *etc.*, in these crystals.

The existence of rhombohedral polytypes of cadmium iodide, ten of which have been reported so far, is entirely inconsistent with the dislocation theory of polytypism (Chadha & Trigunayat, 1967*a*). The observed structure transformations cannot be explained on this theory either. Besides, no growth spirals have been observed on the surfaces of the present two rhombohedral types. The only polytype displaying a growth spiral on its basal plane, $30H_a$ could not have grown from a single screw dislocation because its structure, *viz.* $(2211)_4$ 1122, has been found to be based on the type $6H$ structure (2211). As the *c* dimension of $30H_a$ is an integral multiple of $6H$, the former can never be generated from the latter by creating a single screw dislocation. The observation of a single growth spiral also rules out the possibility of dislocations cooperation. The structure sequence, *viz.* 22 $(11)_7$ of the other hexagonal type $18H_g$ shows that it is based on the type $2H$[structure (11)]. As a screw dislocation of any strength created in $2H$ would always give rise to the basic structure $2H$ itself, it follows that the growth of the type $18H_g$ cannot be explained in terms of the dislocation theory either. Nor did this type display any growth spirals on its surface. To sum up, it appears that the growth of crystals by a spiral mechanism and the formation of a polytype during growth are two unconnected phenomena. The factor primarily responsible for the formation of polytypes is the stacking faults generated during the growth of crystals.

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The Conformation of Non-Aromatic Ring Compounds. LXV.* The Crystal and Molecular Structure of 3β-*p*-Bromobenzoyloxy-13α-androst-5-en-17-one

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The steroid 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one crystallizes in the orthorhombic system with four molecules per unit cell. The space group is $P2_12_12_1$ and the lattice constants are $a = 16{\cdot}216 \pm 0{\cdot}006$, $b = 19{\cdot}873 \pm 0{\cdot}009$ and $c = 6{\cdot}853 \pm 0{\cdot}003$ Å. The photographic data were collected at −180°C (Cu $K\alpha$ radiation) and estimated visually. The structure was determined by application of a minimum function and by Fourier techniques. Refinement by least-squares procedures resulted in an R value of 0·117. The results of separate refinements of *a*- and *c*-axis data are discussed. The molecule has a *cis* junction between rings *C* and *D* which causes flattening of ring *C*. Ring *D* has an approximate 'envelope' conformation with the atom C(14) as flap. The *A* and *C* rings have the usual chair conformation while *B* is a 'half chair'.

Introduction

This publication is a continuation of earlier reports on the molecular geometry of steroids with various configurations at the asymmetric carbon atoms (Hesper, Geise & Romers, 1969, and papers cited therein). The title compound 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one (hereafter APBA) has a *trans* junction between rings *B* and *C* and a *cis* junction between rings *C* and *D* (see Fig. 1). Accordingly, its configuration is 8β, 9α, 10β, 13α, 14α. The corresponding compound 3β-*p*-bromobenzoyloxy-androst-5-en-17-one with *trans C*/*D* coupling and belonging to the normal 8β, 9α, 10β, 13β, 14α-series will be discussed in a separate paper (Portheine, Romers & Rutten, 1970). This study was undertaken in order to investigate the conformational differences between the molecule under consideration and its 13β-isomer.

Experimental

Irradiation of the normal steroid 3β-hydroxy-androst-5-en-17-one (13β-configuration) with ultraviolet light in methanol solution induces partial conversion of the configuration at C(13) (Bots, 1958). From the isolated 13α-isomer the heavy-atom derivative APBA was prepared in benzene/pyridine solution with *p*-bromobenzoylchloride as reagent (Pot, 1964). Colourless orthorhombic needle-shaped crystals were obtained from a solution in acetone.

The unit-cell dimensions were determined from zero-layer Weissenberg photographs about [100] and the needle-axis [001]. The films were calibrated with superposed Al powder lines [a(Al) = 4·0492 Å at 20°C; λ(Cu $K\alpha_1$) = 1·54051 and λ(Cu $K\alpha_2$) = 1·54433 Å]. The observed density (flotation method) at 20°C corresponds to four molecules per unit cell (see Table 1). Absence of the odd reflexions $h00$, $0k0$ and $00l$ indicates the space group $P2_12_12_1$.

Table 1. *Crystallographic data of* APBA

3β-*p*-Bromobenzoyloxy-13α-androst-5-en-17-one	
Molecular composition	$C_{26}H_{31}BrO_3$, M = 471·4 g.mole^{-1}
Melting point	162–164°C
Space group	$P2_12_12_1$
a	16·216 (0·006) Å*
b	19·873 (0·009)
c	6·853 (0·003)
d_{obs}	1·35 (20°C)
d_{calc}	1·417 g.cm^{-3} (−180°C)
V	2208·5 Å^3

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* Part LXIV: de Hoog & Havinga (1970).