Crystal Structures of Two New Polytypes of Cadmium Iodide with Uncommon Space-Group Symmetry

By G. K. Chadha and G. C. Trigunayat

Department of Physics and Astrophysics, University of Delhi, Delhi 7, India

Crystal structures of two newly discovered polytypes, $8H_b$ and $24H_g$, of cadmium iodide have been determined. The structures are $(121)_2$ and $(2222211)_2$, respectively, in Zhdanov symbols. The polytypes show hexagonal symmetry (space group $P6_3mc$), so far shown only by the basic type $4H$. The rest of the 15 known cadmium iodide structures have been found to show the lower trigonal symmetry (space group $P3m1$, $P\bar{3}m1$ or $R3m$) which is usually expected for close-packed layer structures. The two polytypes also exhibit a transformation of the structure during crystal growth.

Cadmium iodide is now known to be a strongly polytypic substance. Over 80 cadmium iodide polytypes have so far been reported by various workers (Verma & Krishna, 1966; Chadha & Trigunayat, 1967a). These types differ in the stacking order of iodine and cadmium ions along the c direction as well as in the c period itself. Type $4H$ is found to occur most commonly and is therefore regarded as the most stable modification of cadmium iodide. On the average, in any X-ray investigation of cadmium iodide crystals, nearly 50% turn out to be the type $4H$. The atomic structure, given as (22) in Zhdanov (1945) symbols, of type $4H$ has been determined and is found to belong to space group $P6_3mc$. Detailed atomic structures of fifteen more cadmium iodide polytypes (Verma & Krishna, 1966; Chadha & Trigunayat, 1967b), which are relatively very rare, have also been worked out and found to belong to one of the space groups $P3m1$, $P\bar{3}m1$ and $R3m$. Cadmium iodide has a layer structure, all polytypes being built up by stacking molecular CdI_2-sheets in various close-packed arrangements, each sheet consisting of a layer of cadmium ions sandwiched between two close-packed layers of iodine ions. The close-packed iodine layers (as well as the cadmium layers) occupy the various A, B, or C positions in the stack. A close-packed arrangement of this kind is usually expected to result in a trigonal symmetry, which is actually found to be the case for almost all the cadmium iodide polytypes with known structures. The only exception is type $4H$ which, by virtue of the screw 6_3-axis, possesses hexagonal symmetry. In view of the fact that $4H$ happens to be the most common type of cadmium iodide, it is intriguing to find it possessing a symmetry higher than that normally expected. However, we have now found two more polytypes, *viz.* $8H_b$ and $24H_g$, to have the same space group as $4H$, *viz.* $P6_3mc$, showing that hexagonal symmetry, although rare, is not restricted to the common type $4H$ alone. This fact is likely to throw considerable light on the formation of polytypes, particularly as both

these polytypes also show interesting structure transformations during crystal growth. The detailed structures of these two polytypes have been worked out.

Experimental

The crystals under discussion had hexagonal shape and were selected from different batches of crystals grown from supersaturated solution. Since c-axis oscillation photographs of cadmium iodide often show streaking and smearing of diffraction spots (Trigunayat & Verma, 1962), a-axis photographs were used for identification and for the structure determination. As each of the two crystals consisted of two parts, *viz.* $(8H_b + 4H)$ and $(24H_g + 24H_h)$, respectively (referred to as crystals no. 1 and 2 respectively), the usual range of oscillation, *viz.* 25–40°, which gives the surface reflexion spots, was found to be most convenient for identification (Chadha & Trigunayat, 1967b). For the determination of structure, too, the intensities were compared in reflexion because the crystals were too thick to give diffraction spots in transmission (Fig. 6). As has been shown by Ramsdell (1944) and Mitchell (1955), for structure determination it is sufficient to compare the observed and calculated intensities for $10.l$ or $01.l$ reflexions alone. Therefore, only the zero-layer a-axis Weissenberg photographs were taken for structure determination.

Structures of polytypes

Polytypes $8H_b$

Crystal no. 1 has been identified as a combination of types $8H_b$ and $4H$ in syntactic coalescence with each other. The type $4H$ is known to have the space group $P6_3mc$ (Mitchell, 1956). The type $8H_b$ has also been determined to possess the same space group. Figs. 1 and 2 are the a-axis 15°-oscillation photographs, taken on a cylindrical camera of diameter 6 cm, of the two sides of the crystal showing the spots of types $8H_b$ and $4H$ respectively. Identification was done by the usual
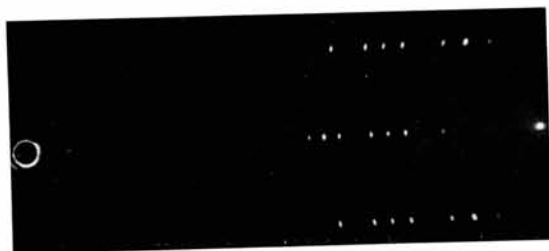
Fig. 1. A 15° a-axis oscillation photograph of polytype $8H_b$ (crystal no. 1); 3 cm camera; Cu $K\alpha$ radiation.
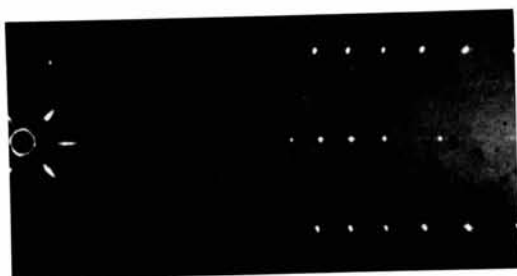

Fig. 2. A 15° a-axis oscillation photograph of polytype $4H$ (crystal no. 1); 3 cm camera; Cu $K\alpha$ radiation.

Fig. 3. Zero layer a-axis Weissenberg photograph of polytype $8H_b$; Cu $K\alpha$ radiation; camera diameter 5·73 cm; the festoons corresponding to the 10.l and $\overline{1}0.l$ rows of spots are recorded on the right and left side, respectively, of the straight row of 00.l spots; the l-value of two strong spots is mentioned on the photograph.

Fig. 4. A 15° a-axis oscillation photograph of polytype $24H_g$ (crystal no. 2); 3 cm camera; Cu $K\alpha$ radiation.

Fig. 5. A 15° a-axis oscillation photograph of polytype $24H_h$ (crystal no. 2); 3 cm camera; Cu $K\alpha$ radiation.

Fig. 6. Zero layer a-axis Weissenberg photograph of polytype $24H_g$; Cu $K\alpha$ radiation; camera diameter 5·73 cm; the festoon corresponding to 10.l row of spots is recorded on the right side of the straight row of 00.l spots; the l-value of two strong spots is mentioned on the photograph.

methods (Trigunayat, 1959). Fig. 3 is the zero-layer a-axis normal-beam Weissenberg photograph of type $8H_b$, showing 10.l spots which were used for comparing the calculated and observed values of intensities. As a polytype of the same c dimensions but different structure has earlier been reported by Mitchell (1956), we have labelled the present type $8H_b$. The type discovered earlier should now be referred to as $8H_a$. Because of the fact that $8H_b$ is the first polytype found, in addition to $4H$, showing hexagonal symmetry, attempts were made to work out its complete atomic structure. There are six possible ways in which different atoms can be arranged to form an eight-layered structure (Mitchell, 1956). But owing to the presence of a screw 6_3-axis in the space group of this polytype, atoms in the second half of the unit cell will be directly related to those in the first half. The Zhdanov symbol should consist of an odd set of numbers (*i.e.* a set with an odd number of terms) repeated twice (Srivastava, 1964). So for this type the problem is to find an odd set of numbers adding up to four. There can be two sets, (*a*) 4 and (*b*) $2+1+1$, and therefore two possible structures, (44) and (121121). However, since in cadmium iodide the Zhdanov number 4 has never been found to exist the only possible sequence is (121121). To verify that this is the correct structure intensity calculations were made for 10.l reflexions using the formula

$$I \propto [\{ \sum_{z_{A,\alpha}} f_{\mathrm{I,Cd}} \cos 2\pi lz + \sum_{z_{B,\beta}} f_{\mathrm{I,Cd}} \cos 2\pi (lz - \tfrac{1}{3})$$
$$+ \sum_{z_{C,\gamma}} f_{\mathrm{I,Cd}} \cos 2\pi (lz + \tfrac{1}{3}) \}^2$$
$$+ \{ \sum_{z_{A,\alpha}} f_{\mathrm{I,Cd}} \sin 2\pi lz + \sum_{z_{B,\beta}} f_{\mathrm{I,Cd}} \sin 2\pi (lz - \tfrac{1}{3})$$
$$+ \sum_{z_{C,\gamma}} f_{\mathrm{I,Cd}} \sin 2\pi (lz + \tfrac{1}{3}) \}^2] \quad (1)$$

where $z_{A,\alpha}$, $z_{B,\beta}$ and $z_{C,\gamma}$ denote the respective z co-ordinates of the iodine (Roman letters) and cadmium (Greek letters) atoms, on the vertical A, B and C axes, respectively, passing through $(0,0,0)$, $(\tfrac{2}{3},\tfrac{1}{3},0)$ and $(\tfrac{1}{3},\tfrac{2}{3},0)$ respectively. $\sum_{A,\alpha}$ represents the summation over iodine atoms at A sites and cadmium atoms at α sites, similar expressions being used for the other summations. The values of I for different l-values, obtained from equation (1) were multiplied by the Lorentz–polarization factor $(1 + \cos^2 2\theta)/\sin 2\theta$, where θ is the Bragg angle.

The calculated and observed intensities of 10.l reflexions for the structural sequence (121121) are given in Table 1. The intensities were compared from 10.16 to 10.32 as the spots in the range 10.0 to 10.16 are not purely due to one type. The calculated values in the Table are without any correction for absorption in the crystal, because no absorption factor was available for a crystal with a hexagonal shape. However, taking into account the shape and the orientation of the crystal it can be generally said that the change in the intensities due to absorption should be slight and gradual.

Table 1. *Calculated and observed relative intensities for the structure $8H_b$*

l	Calculated intensity	Observed intensity*
0	1	a
1	27	w
2	0	a
3	187	s
4	1000	vvs
5	347	vs
6	0	a
7	384	vs
8	236	s
9	300	vs
10	0	a
11	168	s
12	386	vs
13	58	ms
14	0	a
15	0	a
16	0	a

* The observed intensities were actually taken from the series 10·16 to 10·32, which have the same sequence as the series 10·0 to 10·16.

The detailed structure of $8H_b$ is, therefore, as follows:

Space group	$P6_3mc$
Zhdanov symbol	(121121)
ABC sequence	$(A\gamma B)(A\beta C)(A\beta C)(A\gamma B)$
$a = b = 4.24$ Å	$c = 27.34$ Å

Atomic coordinates can be easily found from the ABC sequence.

Polytype $24H_g$

Crystal no. 2 was identified as a combination of types $24H_g$ and $24H_h$ in syntactic coalescence with each other, showing once again a transformation of structure during growth. But in this case there has been a change of symmetry as well. Whereas the type $24H_g$ shows hexagonal symmetry (space group determined as $P6_3mc$), type $24H_h$ shows trigonal symmetry (space group $P3m1$ or $P\bar{3}m1$). Figs. 4 and 5 are a-axis oscillation photographs of the two sides of the crystal, showing the diffraction spots due to $24H_g$ and $24H_h$ respectively. As six polytypes of the same c dimension have been reported earlier (Mitchell, 1956; Srivastava, 1964), the present ones have been labelled $24H_g$ and $24H_h$. The earlier ones have already been labelled $24H_a$, $24H_b$, $24H_c$, $24H_d$, and $24H_f$. Once again, on account of its space group similarity with the common type $4H$, it was proposed to work out the complete atomic structure of type $24H_g$. Fig. 6 is the zero-layer a-axis normal-beam Weissenberg photograph showing 10.l spots.

To start with, 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 of the c dimension (82·02 Å) of $24H$. But making use of the presence of the screw 6_3-axis, as done in $8H_b$, the possible cases reduce to a small number. We have to find an odd set of numbers adding up to 12 (half the total

number for 24*H*). However, the majority of the structures of cadmium iodide already reported have only numbers 1 and 2 in their zigzag sequences of iodine atoms in the (11$\bar{2}$0) cross-section. Using this fact, the possible number reduces still more. Further elimination is possible by examining the intensity of the 10.*l* spots more carefully. The most intense spots were found to be either coincident with 4*H* spots (*i.e.* *l* = 12, 24, 36 ...) or lying around 4*H* spots (*i.e.* *l* = 5,7; 17, 19; 29, 31; ...) indicating that the structure is based on 4*H*. As the latter has the structure (22), it is concluded that type 24*H*$_g$ has a large number of (22) units in its structural sequence. These considerations reduce the possible number of structures to the following two:

$$\text{(i)} \quad (2222211)_2$$
$$\text{(ii)} \quad (2222121)_2$$

To decide the correct structure, intensities were computed for the two sequences and compared with the observed values. An excellent agreement was obtained for the first structure, *viz* .$(2222211)_2$. This structure gave all the extinctions observed in the 10.*l* row (Fig. 6).

The calculated as well as the observed intensities of 10.*l* spots are given in Table 2. As before, the intensities were compared from 10.48 to 10.96 and the calculated intensities in the Table are without any correction for absorption. The detailed structure is, therefore, as follows:

Space group $P6_3mc$
Zhdanov symbol $(2222211)_2$
$a = b = 4\cdot24$ Å $c = 82\cdot02$ Å

ABC sequence $(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)$
$(A\gamma B)(C\alpha B)(C\alpha B)(A\gamma B)$
$(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)$

The atomic coordinates can easily be found from the *ABC* sequence.

Discussion

As pointed out earlier, a close-packed arrangement of atomic layers is expected to result in a structure with trigonal symmetry. Except for the basic type 4*H* which has the space group $P6_3mc$, this has really been found to be so for all the cadmium iodide polytypes, numbering 15 in all (Verma & Krishna, 1966; Chadha & Trigunayat, 1967*b*), with known structures; these belong to one of the space groups $P3m1$, $P\bar{3}m1$ or $R3m$. Silicon carbide is another strongly polytypic substance with a close-packed layer structure, of which 47 polytypes have so far been discovered (Verma & Krishna, 1966). Of these, crystal structures of 32 have been worked out. Out of these, only 4 possess hexagonal symmetry, belonging to space group $P6_3mc$. The other 28 have trigonal symmetry, belonging to one of the space groups $P3m1$ or $R3m$. The four with hexagonal symmetry are the following:

Polytype	Crystal structure in Zhdanov symbols
2*H*	(11)
4*H*	(22)
6*H*	(33)
8*H*	(44)

Table 2. *Calculated and observed relative intensities for the structure* 24*H*$_g$

l	Calculated intensity	Observed* intensity	*l*	Calculated intensity	Observed* intensity
0	1	*a*	25	20	*vw*
1	0	*a*	26	0	*a*
2	0	*a*	27	33	*w*
3	3	*a*	28	0	*a*
4	0	*a*	29	214	*s*
5	57	*w*	30	0	*a*
6	0	*a*	31	176	*s*
7	103	*ms*	32	0	*a*
8	0	*a*	33	19	*vw*
9	21	*vw*	34	0	*a*
10	0	*a*	35	7	*vvw*
11	15	*vw*	36	386	*vs*
12	1000	*vvs*	37	5	*vvw*
13	18	*vw*	38	0	*a*
14	0	*a*	39	6	*vvw*
15	39	*w*	40	0	*a*
16	0	*a*	41	28	*w*
17	312	*vs*	42	0	*a*
18	0	*a*	43	14	*w*
19	322	*vs*	44	0	*a*
20	0	*a*	45	0	*a*
21	43	*w*	46	0	*a*
22	0	*a*	47	0	*a*
23	22	*vw*	48	0	*a*
24	236	*s*			

* The observed intensities were actually taken from the series 10.48 through 10.96.

Type $6H$ is known to occur very commonly and is regarded as the most stable modification of silicon carbide. Thus it is significant to note that in both cadmium iodide and silicon carbide, the basic types ($4H$ and $6H$ respectively) possess a higher symmetry than expected. At present it is very difficult to say what provides the ordering forces which bring about this intriguing situation. However, the restriction of the hexagonal symmetry to only small cells (the largest being $8H$ with $c = 20\cdot14$ Å) in silicon carbide appeared to suggest that these ordering forces, whatever their nature may be, could operate over only small distances. But the present discovery of hexagonal symmetry in a cell as large as $24H$ ($c = 82\cdot02$ Å) in cadmium iodide shows that the forces can indeed be operative over fairly large distances.

Crystal no. 1, found to be a combination of types $8H_b$ and $4H$ in syntactic coalescence with each other, shows that the structure transformed from $8H$ to $4H$ during growth (the lower face of the crystal, as picked up from the crystallizing dish, was found to be $8H$). The same is the case with crystal no. 2, which is found to be a combination of types $24H_g$ and $24H_h$, with the difference that the cell dimensions have remained unchanged during the transformation. However, recent work (Chadha & Trigunayat, 1967a) has shown that such transformations are observed very frequently in cadmium iodide. The two somewhat similar cases,

($30R + 30H$) and ($42R + 42H$), have been discussed earlier in detail by Chadha & Trigunayat (1967b), who concluded that the transformations can be understood on the basis of the layer transposition mechanism of Jagodzinski (1954). The present two cases of structure transformation can be explained on the same lines.

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The Structures of Two Polymorphic Forms of YAl₃*

By D. M. Bailey

Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames, Iowa, U.S.A.

Two structurally related polymorphic forms of YAl₃ have been corroborated: a low temperature form with the hexagonal Ni₃Sn-type structure and a high temperature form with a rhombohedral BaPb₃-type structure. The principal factor influencing the stability of the polymorphs appears to be the conservation of relatively short Al–Al bonds. The layered high temperature polymorph is subject to frequent faulting of the form previously observed in samarium.

Introduction

In an investigation of the aluminum-rich end of the yttrium–aluminum system, Savitsky (1959) reported that Y₂Al₅ is the phase most rich in aluminum. The entire system was investigated by Snyder (1960) who noted YAl₃ as the most aluminum-rich phase. Snyder's equilibrium diagram for the system is shown in Fig. 1. Lundin & Klodt (1961) substantially corroborate Snyder's work and, on the basis of X-ray powder data,

tentatively indicate YAl₃ to be hexagonal. Snyder, however, observed two distinct growth habits in crystals selected from a furnace-cooled alloy, *i.e.* needle-shaped crystals of approximately square cross section and truncated hexagonal bipyramids in degrees of development varying from hexagonal platelets to approximately equiaxed shapes. By examining crystals from furnace-cooled alloys of several compositions Snyder found that as the aluminum content of the alloy increased (corresponding, according to Fig. 1, to a reduced initial temperature of precipitation of the phase) the percentage of needle-shaped crystals present increased. He was unable to prepare alloys containing only needle-shaped crystals in any alloy richer in yttrium