Discussion

It is interesting to note that the second $69R$ type presently found is not the other simple structure $[(44)_2\,(43)]_3$ but a structure with a highly irregular stacking sequence. Thus it belongs to the rare groups of SiC polytypes with the three Zhdanov symbols 2,3 and 4 and emphasizes the importance of considering many more possible polytypes.

Unfortunately nothing conclusive can be said about the growth mechanism because we have no idea what the virgin crystal looked like. It is remarkable that a homogeneous core of 100 μm thickness remained after polishing and not a trace of another polytype could be found. Such observations have so far been restricted to $6H$ although there may be some platelets containing a $15R$ core. The extremely frequent occurrence of $6H$ (also in other growth furnaces under similar conditions) has led to the hypothesis (G. S. Kamath, personal communication) that $6H$ is the thermodynamically stable phase. Other polytypes would grow during the cooling period at non-equilibrium conditions. The two massive $15R$ crystals and the 100 μm thick core of $69R_b$ disagree with such a hypothesis since it is very unlikely that crystals of this size can grow in such a short time. Moreover from one of the pure $15R$ platelets two subsidiary crystals extend which obviously grew later.

Two-thirds of the growth spirals found are connected with unusual polytypes whereas less than a quarter of all crystals analysed contained rarer polytypes. This fact tends to support the Frank (1951) mechanism.

It should also be noted that the $69R_b$ polytype contains large building blocks of the $[(33)_n(34)]_3$ series of which the polytypes $21R$, $39R$, and $57R$ could be recovered. This may be an indication that the polymer theory (Ramsdell & Kohn, 1952) has some bearing on the growth of polytypes although a modification of it might bring it closer to reality. Such a modification should include the ideas of Bulakh (1969).

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Crystal Structures of Two 20-Layered CdI_2 Polytypes

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Crystal structures of two newly discovered 20-layered polytypes of cadmium iodide have been determined. One is found to be $(22)_4 1111$, belonging to the $(22)_n 1111$ series of CdI_2, three members of which are already known. The other structure is found to be (22111121122112). Their space group is $P3m1$. Their formation is discussed in terms of partial edge dislocations created at regular intervals during crystal growth.

Introduction

Cadmium iodide is known to be a strongly polytypic substance. Nearly 140 polytypes of CdI_2, grown from solution and vapour, have so far been reported by various workers (Mitchell, 1956; Trigunayat & Verma, 1962; Chadha & Trigunayat, 1967; Jain, Chadha & Trigunayat, 1970). Hitherto, complete crystal structures of only 25 polytypes have been determined. There have been two reasons for this relatively small number. First, the X-ray photographs of CdI_2 crystals frequently show streaking and arcing (Agrawal & Trigunayat, 1969), rendering them unsuitable for structure work, and secondly, the polytypes have the number 1 in their Zhdanov symbols, which enormously increases the number of possible structures to be considered. The structure determination of a polytype becomes

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easier if the intensity distribution of the diffraction spots happens to be similar to that of a smaller type (usually the common type $4H$). This factor has been helpful in the structure determination of the polytypes.

Recently 120 CdI_2 crystals have been examined with a view to studying the arcing phenomenon exhibited by them (Agrawal & Trigunayat, 1969). Of these, 17 turned out to be new polytypes, *viz.* $12H_g, 12R, 16H_d, 18H_h, 20H_p, 20H_q, 20H_r, 20H_s, 22H_h, 24H_j, 36H_i, 36H_j, 36H_k, 36H_l, 36H_m, 48R_b$ and $84R$. Of these, the crystal structure of the polytype $12R$ has already been determined (Agrawal & Trigunayat, 1968). The structures of two more polytypes, $20H_p$ and $20H_q$, are reported in this paper.

Experimental methods

The crystals were grown in a crystallizing dish from supersaturated solution. The crystals being extremely soft, great care was exercised to ensure that they were not deformed while being taken out of the solution or in mounting on the X-ray camera. The optically perfect single crystals were oscillated about the a axis in the range 25 to 40°, *i.e.* the c axis made an angle of 25–40° with the incident X-ray beam. This range covered a large number of $10.l$ reflexions from only one part, upper or lower, of a crystal platelet (Chadha & Trigunayat, 1967). A cylindrical camera of radius 3 cm and a collimator of aperture 0·5 mm were used. Zero-layer a axis Weissenberg photographs (5·73 cm camera diameter) were also taken and the observed intensities for $10.l$ reflexions were compared with the corresponding calculated intensities.

The polytypes of cadmium iodide

Cadmium iodide has a layer structure. The basic unit of CdI_2-polytypes consists of two hexagonal close-packed iodine layers with the small cadmium ions lodged between them. This can be represented by $(A\gamma B)$, $(B\alpha C)$, or $(C\beta A)$, where iodine ions are represented by Roman letters and cadmium ions by Greek letters. Various stacking arrangements of these layers can produce different polytypes with the same or different c dimensions.

Polytype $20H_p$

Fifteen polytypes of the same c dimension have already been reported by Mitchell (1956), Srivastava (1964) and Jain, Chadha & Trigunayat (1970), who did not determine their complete crystal structures. The present structure could be a new type by virtue of a different stacking sequence of layers in its unit cell. Hence it has been labelled as the type $20H_p$. It was found to occur in combination with an unidentified high polytype on one side of the crystal platelet, the other side of which was identified as $24H_j$. The a axis normal-beam Weissenberg photograph (Fig. 1) shows mixed diffraction spots of the type $20H_p$ and the unidentified high polytype. As the spots of the unidentified type had a smaller size and different characteristic shape, they did not interfere in the structure determination of the type $20H_p$. As seen in Fig. 1,

Table 1. *Comparison of calculated and observed intensities for* $10.l$ *reflexions of polytype* $20H_p$ *of cadmium iodide*

10.*l*	Calculated intensity	Observed* intensity	10.*l*	Calculated intensity	Observed* intensity	Further observed relations between intensities
10.0	1·7	*a*†	10.21	34·8	(*w*) ‡	$9>7\simeq 8$
1	0·6	*a*†	22	32·5	(*w*)	$12\simeq 13>11$
2	1·8	*a*†	23	29·9	(*w*)	$14>16>17$
3	3·9	*a*†	24	27·2	(*w*)	$15>25$
4	6·6	*vvw*†	25	391·9	*vs*	
5	158·9	*ms*	26	21·4	(*vw*)	
6	13·5	*vw*	27	18·8	(*vw*)	
7	17·5	*w*	28	16·1	(*vw*)	
8	21·4	*w*	29	13·4	(*vw*)	
9	25·3	*w*	30	642·5	*vs*	
10	1000	*vvs*	31	8·9	(*vvw*)	
11	32·1	*w*	32	6·9	(*vvw*)	
12	35·0	*mw*	33	5·2	(*vvw*)	
13	37·2	*mw*	34	3·7	(*vvw*)	
14	38·9	*mw*	35	40·9	*mw*	
15	639·3	*vs*	36	1·6	*a*	
16	40·5	*mw*	37	0·8	*a*	
17	40·3	*mw*	38	0·4	*a*	
18	39·7	*w*	39	0·1	*a*	
19	38·6	*w*	40	0·3	*a*	
20	344·7	*s*				

* As mentioned in the text, the observed intensities were actually taken from the series 10.40 to 10.80. This series has the same intensity sequence as 10.0 to 10.40.

† As can be seen in Fig. 1, the absorption is abnormally high for these reflexions because of the plate-like shape of the crystal.

‡ The reflexions in parentheses could not be well-resolved because of streaking.

the intense spots of $20H_p$ coincided with the $4H$ positions, indicating that the unit cell of the structure consisted mostly of (22) units. The same type of intensity sequences have previously been observed in three other polytypes, $8H_a$, $12H_c$ and $28H_c$, whose complete structures (Mitchell, 1956; Srivastava & Verma, 1965) have been found to belong to the $(22)_n1111$ series. Accordingly, the structure of $20H_p$ was postulated to be $(22)_41111$. The structure determination would otherwise have been an uphill task as there are an overwhelmingly large number of ways of arranging a 20-layered structure. To verify its correctness, the intensities of the $10.l$ reflexions were computed by using the formula,

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

where $z_{A,\alpha}$, $z_{B,\beta}$, $z_{C,\gamma}$ denote the respective z coordinates of the iodine (Roman letters) and cadmium (Greek letters) ions on the vertical A, B and C axes respectively, passing through (0,0,0), $(\frac{2}{3},\frac{1}{3},0)$ and $(\frac{1}{3},\frac{2}{3},0)$ respectively. $\sum_{Z_{A,\alpha}}$ represent the summation over the iodine ions at A sites and the cadmium ions at α sites, with similar expressions being used for the other summations. The values of I for different l values have been multiplied by the Lorentz–polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$, where θ is the Bragg angle. Excellent agreement was obtained between the observed and calculated values, listed in Table 1. The intensities were compared for reflexions from 10.40 to 10.80 as the spots in the range 10.0 to 10.40, occurring in transmission, do not result purely from one type. The detailed structure of this polytype is therefore as follows:

Space group $P3m1$
Cell dimensions $a=b=4{\cdot}24$, $c=68{\cdot}35$ Å
Zhdanov symbol $(22)_4$ 1111
ABC sequence $[(A\gamma B)\,(C\alpha B)]_4\,(A\gamma B)\,(A\gamma B)$

Atomic coordinates
6 iodine atoms at 0, 0, n_1z
$n_1=0,8,16,24,32,36$
10 iodine atoms at $\frac{2}{3},\frac{1}{3},n_2z$
$n_2=2,6,10,14,18,22,26,30,34,38$
4 iodine atoms at $\frac{1}{3},\frac{2}{3},n_3z$
$n_3=4,12,20,28$
4 cadmium atoms at $0,0,n_4z$
$n_4=5,13,21,29$
6 cadmium atoms at $\frac{1}{3},\frac{2}{3},n_5z$
$n_5=1,9,17,25,33,37$
where $z=\frac{1}{40}$.

Polytype $20H_q$

This polytype was found to occur in syntactic coalescence with another polytype of the same c dimension but having a different intensity sequence. Fig. 2 is its a axis normal-beam Weissenberg photograph. Close examination of Fig. 2 revealed that the intensities of the spots were quite symmetrical about the $4H$ positions and the intense spots on the photograph lay around the $6H$ positions, indicating that the structure contained a large number of (2211) units. A large number of structures were postulated and their calcu-

Table 2. *Comparison of calculated and observed intensities for* $10.l$ *reflexions of polytype* $20H_q$ *of cadmium iodide*

$10.l$	Calculated intensity	Observed* intensity	$10.l$	Calculated intensity	Observed* intensity	Further observed relations between intensities
10.0	1·1	*vw*†	10.21	63·7	*ms*	4 > 3
1	1·1	*vvw*†	22	34·5	*mw*	5 > 32
2	1·9	*vvw*†	23	106·3	*s*	6 > 9
3	13·9	*w*	24	75·6	*ms*	11 > 12
4	18·4	*w*	25	18·8	*mw*	
5	7·6	*vw*	26	59·6	*m*	13 ≃ 17 > 14 ≃ 16
6	37·7	*mw*	27	66·6	*m*	18 > 15
7	62·0	*m*	28	17·1	*w*	20 > 23
8	22·7	*w*	29	24·6	*mw*	24 > 21
9	46·3	*mw*	30	386·6	*vs*	22 > 29 > 25
10	1000	*vvs*	31	16·2	*w*	27 > 26
11	58·7	*mw*	32	7·3	*vw*	33 > 34 > 31
12	37·1	*mw*	33	18·4	*w*	
13	131·9	*s*	34	10·4	*w*	
14	108·1	*s*	35	1·9	*vvw*	
15	30·6	*mw*	36	4·4	*vw*	
16	112·4	*s*	37	3·1	*vw*	
17	143·0	*s*	38	0·4	*a*	
18	42·1	*mw*	39	0·2	*a*	
19	70·5	*m*	40	0·2	*vw*	
20	236·1	*s*				

* See first footnote to Table 1.
† See second footnote to Table 1.

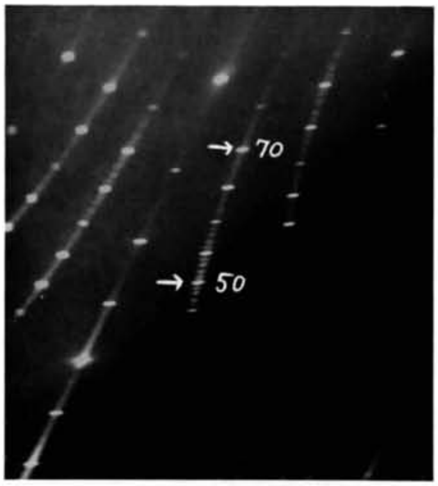

Fig. 1. Zero-layer *a*-axis Weissenberg photograph of the CdI_2 polytype $20H_p$. Camera diameter 5·73 cm; Cu $K\alpha$ radiation. The arrows indicate the *l* values of the reflexions on the 10.*l* festoon.

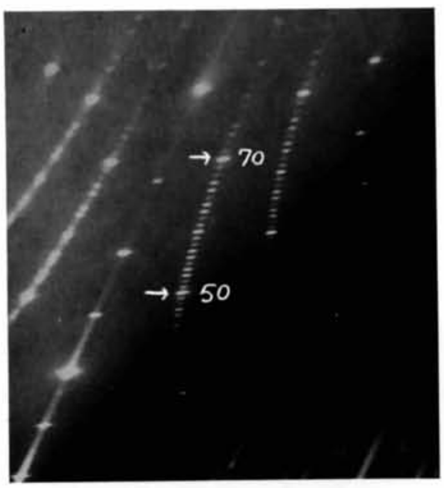

Fig. 2. Zero-layer *a*-axis Weissenberg photograph of the CdI_2 polytype $20H_q$. Conditions as for Fig. 1.

lated intensities for 10.*l* reflexions were compared with those observed on the Weissenberg photograph (Fig. 2). Excellent agreement was obtained for the structure (22111121122112), the calculated and observed values for which are given in Table 2. As in the previous case, the intensities of reflexions in the range 10.40 to 10.80 were compared.

The detailed structure of this polytype is therefore as follows:

Space group $P3m1$
Cell dimensions $a=b=4{\cdot}24$, $c=68{\cdot}35$ Å
Zhdanov symbol (22111121122112)
ABC sequence $(A\gamma B)(C\alpha B)(A\gamma B)_3(C\alpha B)_2(A\gamma B)(C\alpha B)_2$.

Atomic coordinates
5 iodine atoms at $0,0,n_1z$
$n_1=0,8,12,16,28$
10 iodine atoms at $\frac{2}{3},\frac{1}{3},n_2z$
$n_2=2,6,10,14,18,22,26,30,34,38$
5 iodine atoms at $\frac{1}{3},\frac{2}{3},n_3z$
$n_3=4,20,24,32,36$
5 cadmium atoms at $0,0,n_4z$
$n_4=5,21,25,33,37$
5 cadmium atoms at $\frac{1}{3},\frac{2}{3},n_5z$
$n_5=1,9,13,17,29$
where $z=\frac{1}{40}$.

Discussion

There are several theories of polytypism (Verma & Krishna, 1966) but those which have received the most serious attention so far are due to Frank (1951) and Jagodzinski (1954*a*,*b*). However, recent experimental evidence has shown that Frank's theory is unable to account for the generation of CdI_2 polytypes (Chadha & Trigunayat, 1967). Besides, both the polytypes whose structures have been determined here have been found to occur in syntactic coalescence with other polytypes having the same or different *c* dimensions, implying a transformation of structure during crystal growth. The dislocation theory is unable to explain such transformations. However, the structure transitions, as also the formation of rhombohedral and hexagonal polytypes of CdI_2, can be explained in terms of the creation of partial edge dislocations during growth, as proposed by Jagodzinski (1954*a*,*b*). The formation of polytype $20H_p$ from the common type $4H$ can be easily understood as follows. From its *ABC* sequence, $(ABCB)_4\,AB\underline{A}B$, it is clear that if a stacking fault occurs in the $4H$ structure $ABCB\underline{A}BCB$---at the position underlined in the *ABC* sequence, at a regular interval of 20 layers, the present structure will be formed. It is the fourth member of the structural series $(22)_n1111$. The formation of the polytype $20H_q$ can also be explained in similar terms. This polytype is not based on the common type $4H$ as it contains a large number of (11) units in its structure. It has the *ABC* sequence $(ABCBCB)_2\,(ABCB\underline{A}B)AB$, showing that it is based on the type $6H$, having the structural sequence $ABCBCB\,ABCBCB$---. Once again, a fault occuring in the $6H$ structure at the position underlined in the *ABC* sequence, at a regular interval of 20 layers, will generate the polytype $20H_q$.

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