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Studies on a New Polytype of Cadmium Iodide $28H_c$

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A twenty-eight layered new polytype of cadmium iodide, designated $28H_c$, with unit-cell dimensions $a = 4{\cdot}24$, $c = 95{\cdot}69$ Å, is described. The detailed atomic structure has been worked out and its zigzag sequence is found to be 2222222222221111. The growth of the polytype is examined in the light of the screw dislocation theory of polytypism. The screw dislocation theory is not able to explain fully the growth of this polytype. The polytype $28H_c$ is so far the largest cadmium iodide polytype with a known atomic structure.

Introduction

Polytypism, first observed in silicon carbide, found a simple explanation in terms of the screw dislocation theory of crystal growth (Frank, 1951). The theory gives a pictorial representation of the formation of various polytypes — and direct experimental evidence in support of it came from the observation of a correlation between the step-heights of growth spirals on silicon carbide polytypes and the heights of their X-ray unit cells (Verma, 1957). No such extensive and conclusive experimental support has yet been given for other existing theories of the origin of polytypism such as the polymer theory (Ramsdell & Kohn, 1952), vibration entropy — layer transposition theory (Jagodzinski, 1949; Jagodzinski & Arnold, 1960), and the impurity content theory (Lundqvist, 1948; Hayashi, 1960).

The main aim of the present work has been to carry the investigation further by testing the validity of the dislocation theory among other known polytypic substances. The substance chosen for the present work was cadmium iodide. From an interferometric and microscopic study of cadmium iodide crystals Forty (1952) predicted polytypism in this compound. Mitchell (1956) carried out an extensive X-ray diffraction study of cadmium iodide crystals and correlated the unit-cell dimensions with the step-heights measured by Forty (1952). However, for an unequivocal verification of Frank's dislocation theory of polytypism in the case of cadmium iodide, Trigunayat & Verma (1962) tried to find a correlation between the spiral step-height and the height of the unit cells by performing both the X-ray diffraction and the interferometric studies upon the same crystals. They found that no such correlation exists. Thus it is not completely understood why, even when a crystal shows a growth spiral and thus appears to have grown by the dislocation mechanism, there should not be a direct correlation between the spiral step-height and the X-ray unit cell.

We have examined numerous cadmium iodide crystals by X-ray methods and have isolated several long-period polytypes. Since only little work has been done on the structural analysis of cadmium iodide polytypes, we have directed our attention towards the structure determination of these long-period polytypes, to see whether these can be explained in terms of screw dislocation theory.

Generally, a cadmium iodide polytype is based on a certain ideal structure ($2H$ or $4H$) and has a repeat unit along c which is a non-integral multiple of the corresponding repeat unit of the basic structure. The formation of such polytypes is easily understood on the screw dislocation theory. However, we have isolated three polytypes, namely $22H$, $26H$ and $28H$, which are in contradiction to the above. The first two polytypes have c spacings respectively eleven times and thirteen times the c spacing of their basic $2H$ structure; and the third has a c spacing seven times the c spacing of its basic $4H$ structure. These polytypes are unusual since their creation requires a screw dislocation whose Burgers vector is an integral multiple of the c spacing of the basic structure. Their growth is not directly understood on the dislocation theory since such a screw dislocation could only cause further growth of the basic structure itself. Hence it was aimed to work out the detailed atomic structures of these polytypes, to see whether the structure could be explained on screw dislocation theory.

The results obtained on the $22H$ polytype have already been reported (Srivastava & Verma, 1963). This paper describes the detailed atomic structure of the polytype $28H$. This polytype is of special interest since, as shown later, the observations obtained on it furnish evidence both for and against the screw dislocation theory. Moreover, this is the first among the

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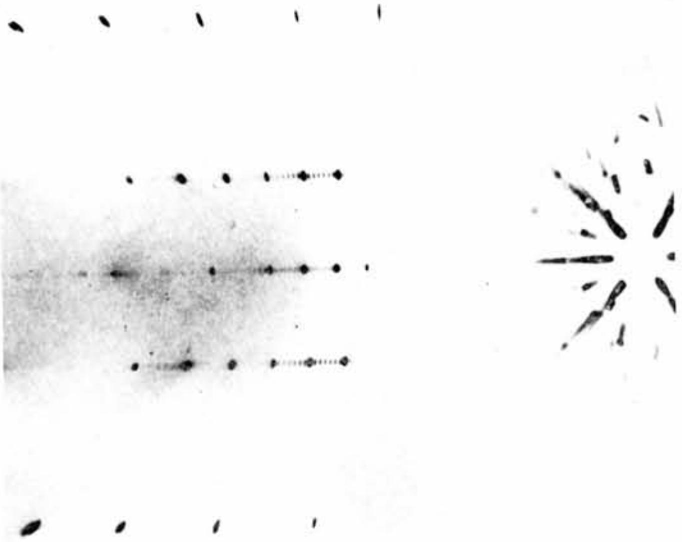

Fig. 1. 15° oscillation photograph about the a axis, with Cu $K\alpha$ radiation, on a camera of radius 3 cm (× 1·2).

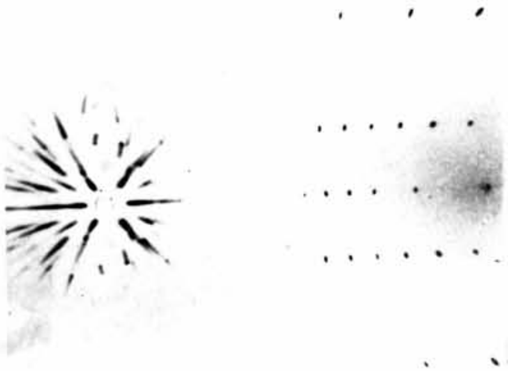

Fig. 2. 15° oscillation photograph about the a axis, of the other face of the crystal taken with Cu $K\alpha$ radiation, on a camera of radius 3 cm.

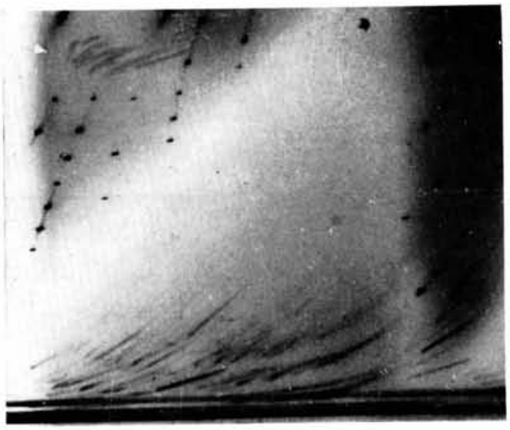

Fig. 3. First layer a-axis Weissenberg photograph taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm. The lowest festoon shows the $01.l$ row of spots. The spots on the festoon were indexed with the help of a Weissenberg photograph of a $4H$ polytype as well as with the help of a Weissenberg chart. The first visible intense spot corresponds to $l=63$; the visible series of spots have l values ranging rom $l=56$ to $l=112$.

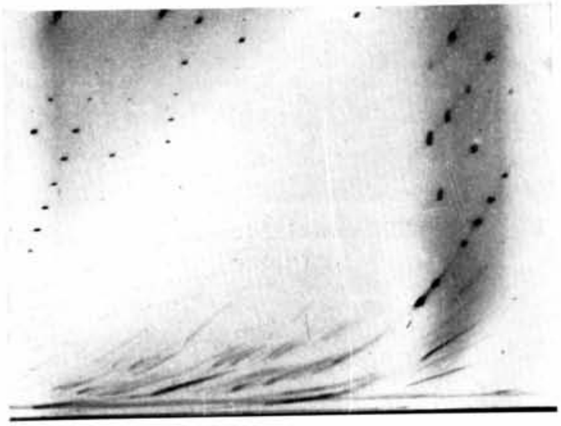

Fig. 4. First layer a-axis Weissenberg photograph of the other face of the crystal taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm.

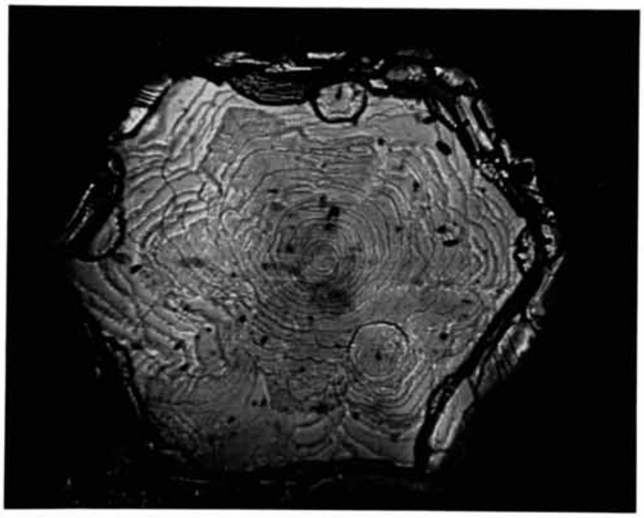

Fig. 5. Surface micrograph of the crystal obtained with narrow pencil of white light (× 25).

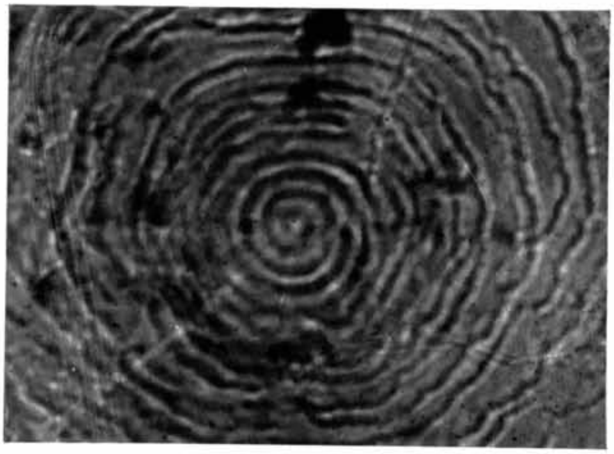

Fig. 6. Magnified view of the central portion of Fig. 5 (× 100).

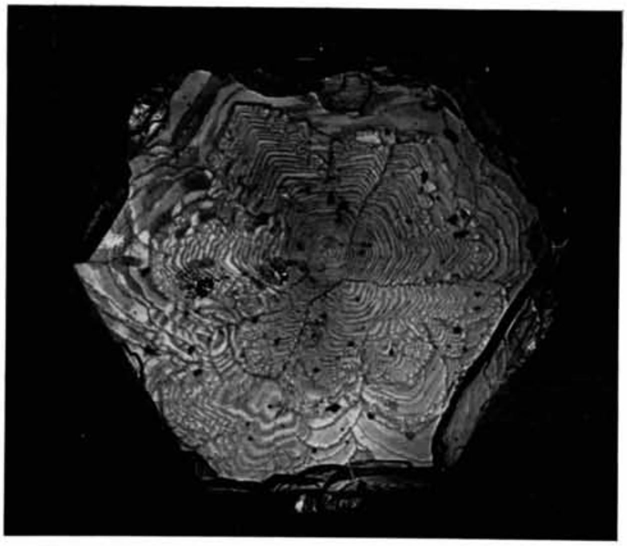

Fig. 7. Interferogram of crystal obtained with mercury light of wavelength 5461 Å (× 29).

Fig. 8. Magnified view of the central portion of Fig. 7 (× 100).

known polytypes which gives evidence as to what happens in the initial and final stages of growth of any polytype. This is now the longest cadmium iodide polytype with a known atomic structure.

Experimental

Crystals of cadmium iodide used in the present investigation were grown from aqueous solution at room temperature. The method is similar to that used by Mitchell (1957). The crystals were observed under a polarizing microscope and only those which showed uniform extinction were subjected to X-ray examination. The *c*-axis oscillation photographs generally showed smearing and streaking of diffraction spots and were found unsuitable either for identification of the polytype or for structure determination, while *a*-axis oscillation photographs showed discrete sharp spots. Therefore, *a*-axis oscillation photographs were taken for an oscillation range starting from the position when the *c*-axis (perpendicular to the crystal platelet) made an angle 25° with the incident X-ray beam, and was carried on to the position $(25+15)=40°$. This range was found most convenient for the identification of a polytype since it records a large number of $10.l$ spots. For the structure determination *a*-axis Weissenberg photographs recording either the $01.l$ or $10.l$ row were taken.

Fig. 1 reproduces a 15° *a*-axis oscillation photograph of the crystal, recorded on a 3 cm camera with Cu $K\alpha$ radiation. Fig. 2 shows the *a*-axis oscillation photograph of the crystal taken after it was rotated through 180° from the position for Fig. 1. Similarly Figs. 3 and 4 show the first layer *a*-axis equi-inclination Weissenberg photographs taken from the two sides of the crystal platelet, on a camera of diameter 5·73 cm with Cu $K\alpha$ radiation.

As is evident from Figs. 1 and 3, the present polytype is $28H$ since there are seven equal spacings between two consecutive $4H$ reflexions. However, Figs. 2 and 4, which represent photographs taken from the other side of the crystal, show it to be the ideal $4H$ structure. Thus there is a surprising situation in which one side of the crystal piece is the $4H$ ideal structure while the other side of the same piece is the polytypic $28H$ structure. By taking Laue photographs of different regions of the same face of the crystal it has been concluded that a single face contains a single polytype only. It has been possible to detect the presence of the two polytypes within the single crystal piece, because of the high absorbing property of both cadmium and iodine ions. The high absorption does not allow the weak diffracted beams from the polytypic structure $28H$ to be recorded on the film when this is facing the incident beam. When the crystal side containing polytypic structure $28H$ is away from the incident beam, evidently the polytypic spots of $28H$ are recorded since they have not to travel the whole thickness of the crystal.

Structure of 28*H*

The new modification exists in the form of a hexagonal platelet with a well developed and shining (0001) face. The *c* dimension evaluated from Fig. 1 is 95·7 Å. The known *c* dimension of the type $4H$ is 13·67 Å. The present polytype is thus $28H$. This is confirmed because of the presence of six diffraction spots between two consecutive intense $4H$ spots. Mitchell (1956) has reported two other 28-layered polytypes $28H_a$ and $28H_b$. In the absence of any structural data published by him and in view of the fact that in cadmium iodide almost all the polytypes with the same number of layers have different stacking sequence, the present polytype is designated $28H_c$.

For a large polytype such as this it is not possible to decide the correct structure by following the usual method of working out all possible structures involving Zhdanov (1946) numbers 1, 2, 3, 4, *etc.*, in their Ramsdell's (1944) zigzag sequence. Since almost all the polytypes of cadmium iodide have only the numbers 1 and 2 in their zigzag sequence, we shall also restrict ourselves to these numbers alone. Thus the problem of determining the probable structures reduces to arranging the numbers 1 and 2 in different ways so as to give a 28-layered unit cell and trying each structure separately. The number of such arrangements would be enormous because of the presence of number 1 and structure determination would become formidable. The correct structure was therefore anticipated as follows:

The diffraction spots which coincide in position with the spots of the $4H$ polytype are distinctively more intense than the rest of the spots. The unit cell of the polytype then must contain many (22)-units. The following possible structures are thus formulated with decreasing number of (22) units:

(i) 2 2 2 2 2 2 2 2 2 2 2 2 2 1 1
which for brevity can be written as $(22)_{6\frac{1}{2}}$ 11
(ii) $(22)_{6\frac{1}{2}}$ 2
(iii) $(22)_{6}$ 1 1 1 1
(iv) $(22)_{6}$ 2 2
(v) $(22)_{5}$ 1 1 2 2 1 1
(vi) $(22)_{5}$ 1 2 1 1 2 1
(vii) $(22)_{5}$ 1 1 1 1 1 1 1 1
(viii) $(22)_{4\frac{1}{2}}$ 2 1 1 1 1 1 1 2
(ix) $(22)_{4\frac{1}{2}}$ 1 1 2 1 1 2 1 1
(x) $(22)_{4\frac{1}{2}}$ 2 1 2 2 1 2
(xi) $(22)_{4\frac{1}{2}}$ 1 2 2 2 2 1

We cannot further decrease the number of (22) units since then the structure would not be based on a $4H$ ideal structure. As shown previously (Srivastava & Verma, 1963) all the polytypes of cadmium iodide necessarily have the hexagonal lattice. The above arrangements involving $(22)_{6\frac{1}{2}}$ and $(22)_{4\frac{1}{2}}$ do not represent a hexagonal lattice as for example the ABC sequence corresponding to first structure is

AB CB AB CB AB CB AB CB
AB CB AB CB AB CB C

In the above the number of △'s (reversal in one direction) is 15 and number of ▽'s (reversal in other direction) is 13. For an arrangement representing a hexagonal lattice the number of △'s and ▽'s should either be equal or should differ by a multiple of 3. Thus the arrangements (i), (viii), (ix), (x) and (xi) do not represent hexagonal structure and are, therefore, discarded. Structures (ii) and (iv), which are equivalent, are also disregarded since they represent the $4H$ structure itself. To decide the correct structure, intensities for six important $01.l$ reflexions were calculated for each of the remaining structures.

The intensity formula for $01.l$ reflexions for the space group $P3m1$ to which the polytype belongs is:

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

where $\sum_{zA,\alpha}$ denotes the summation over the z coordinates of I atoms at A sites and Cd atoms at α sites; similarly for $\sum_{zB,\beta}$ and $\sum_{zC,\gamma}$.

Here 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 cadmium ions. In cadmium iodide the basic polyatomic layer consists of two layers of hexagonal close-packed iodine ions with the small cadmium ions nested between them. The vertical I–I distance is 3·4175 Å and the vertical Cd–I distance is nearly half of this distance. The cadmium layer is thus midway between two iodine layers.

Table 1. *Comparison of calculated and observed intensities*

l	Calc. intensity	Obs.* intensity	l	Calc. intensity	Obs.* intensity
0	1·07	*a*	29	5·01	*a*
1	0·08	*a*	30	5·12	*vvw*
2	0·09	*a*	31	5·01	*vvw*
3	0·47	*a*	32	4·79	*a*
4	1·41	*a*	33	4·13	*a*
5	1·66		34	1·00	*a*
6	1·23	*a*	35	273·54	*s*
7	40·14	*m*	36	4·80	*a*
8	4·46	*vvw*	37	4·86	*a*
9	5·00	*vvw*	38	3·71	*a*
10	4·80	*vvw*	39	4·12	*a*
11	6·16	*vw*	40	4·10	*a*
12	6·23	*vw*	41	3·61	*a*
13	7·18	*vw*	42	262·57	*s*
14	1000	*vvs*	43	1·74	*a*
15	6·73	*vw*	44	2·40	*a*
16	6·83	*vw*	45	2·40	*a*
17	8·23	*vw*	46	1·70	*a*
18	7·81	*vw*	47	1·40	*a*
19	8·83	*vw*	48	2·60	*a*
20	6·23	*vw*	49	50·52	*m*
21	667·43	*vs*	50	3·29	*a*
22	8·41	*vw*	51	1·84	*a*
23	7·81	*vw*	52	3·08	*a*
24	7·61	*vw*	53	1·14	*a*
25	7·52	*vw*	54	1·21	*a*
26	8·00	*vw*	55	1·36	*a*
27	7·32	*vw*	56	4·51	*vvw*
28	149·20	*ms*			

* The observed intensities were taken from the series 10·56 through 10·112. This series has the same intensity sequence as 10·0 through 10·56 which is not visible on the film because of absorption caused by the non-equidimensional crystal plate.

The intensity values obtained from the above formula were multiplied by the Lorenz polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$. Fig. 9 shows plots of the calculated relative intensities for the 6 possible structures. A comparison of the calculated intensities with those observed on a Weissenberg photograph makes it evident that only the structure (iii) gives the right fit. For an unequivocal verification of the structure of an

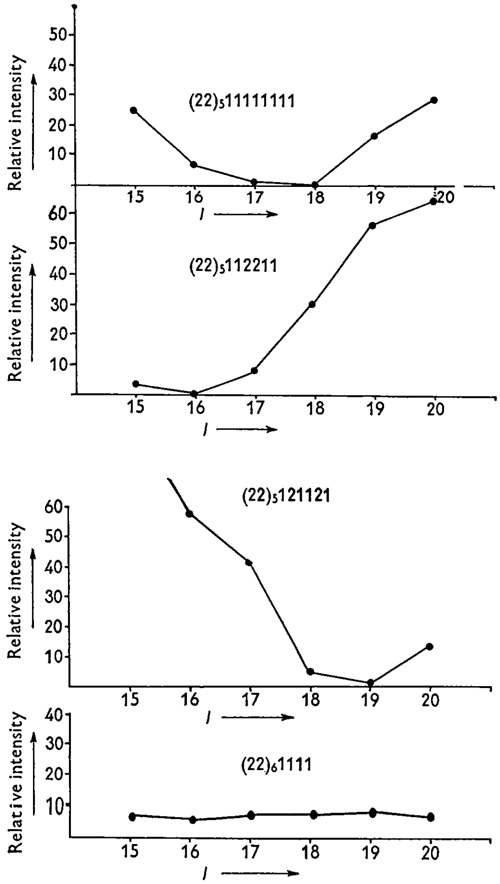

Fig. 9. Calculated relative intensity graph for possible arrangements.

nH polytype in cadmium iodide it is necessary to calculate intensities of reflexions $l=0, 1, 2, \ldots, 2n$ after which the intensities repeat themselves. Hence for structure (iii) the intensities for the complete range of fifty-six $01.l$ reflexions were calculated. Comparison of these with those observed on a Weissenberg photograph shows excellent agreement between calculated and observed intensities (Table 1). Owing to non-availability of suitable absorption factors for a thin platelet it was not possible to correct the intensities for absorption. However, it is the change in absorption which is of primary importance and this is not thought to be so abrupt as to cause appreciable difference in observed relative intensities within a small range.

The detailed structure of $28H_c$ is, therefore, as follows:

Space group $P3m1$

Zhdanov symbol 2222222222221111

ABC sequence

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

$a=4{\cdot}24$ Å $c=95{\cdot}69$ Å

Atomic coordinates

8 iodine at $0\ 0\ t_1$
$t_1=0, 8z, 16z, 24z, 32z, 40z, 48z, 52z,$
14 iodine at $\frac{2}{3}\ \frac{1}{3}\ t_2$
$t_2=2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z, 34z, 38z, 42z, 46z, 50z, 54z$
6 iodine at $\frac{1}{3}\ \frac{2}{3}\ t_3$
$t_3=4z, 12z, 20z, 28z, 36z, 44z$
6 cadmium at $0\ 0\ t_4$
$t_4=5z, 13z, 21z, 29z, 37z, 45z$
8 cadmium at $\frac{1}{3}\ \frac{2}{3}\ t_5$
$t_5=z, 9z, 17z, 25z, 33z, 41z, 49z, 53z$ where $z=1/56$

Discussion

According to Frank's (1951) screw dislocation theory, the crystals initially grow into thin plates of uniform thickness by a surface nucleation mechanism, as the supersaturation at the beginning is highest. Thus in cadmium iodide, regarding $4H$ as the ideal structure, this structure itself grows in the initial stages. Through non-uniform distribution of impurities the platelet containing the $4H$ ideal structure becomes self stressed and is, therefore, buckled. This buckling is relieved by slips of various magnitudes in the crystal platelet, resulting in the creation of one or more dislocations of various strengths. These very dislocations are responsible for the final creation of the polytype. The growth of polytype $28H_c$ is examined below in the light of these considerations.

The crystal platelet of the present polytype as shown previously has a $4H$ structure on one face and a $28H$ structure on the opposite face. This may be taken to furnish evidence that an initial $4H$ platelet has finally grown into a $28H$ polytype. Similarly the presence of the basic and polytypic structure within the same single-crystal piece has been detected in other cadmium iodide crystals also.

The polytype $28H_c$ is based on an ideal $4H$ structure. According to the screw dislocation theory the growth of a polytype from a single screw dislocation in an ideal $4H$ structure may result only if the Burgers vector of such a dislocation is a non-integral multiple of the c spacing of $4H$. In the present case, since the Burgers vector of screw dislocation which will create a polytype $28H_c$ will have to be a seven times integral multiple of the c spacing of $4H$, the growth cannot result by a single dislocation. A step of 24 layers formed in a $4H$ structure could only result in the further growth of $4H$.

To explain the growth of polytypes which cannot result from a single screw dislocation one may postulate two or more cooperating dislocations as was done by Mitchell (1956). Below it is shown how the growth of $28H_c$ can be visualized in terms of such an idea.

A single screw dislocation in a $4H$ ideal structure can easily create a step corresponding to the structure $(22)_6\,11$. Let there be another step corresponding to the structure 11 (obtained from $2H$) in the vicinity of the above. If the above two steps are close enough to cooperate in such a manner as to form a final step having the structure $(22)_6\,1111$, the growth of $28H_c$ can then take place. But if such is the case the surface observations must conform with the above.

At this stage, therefore, it was thought desirable to examine the crystal surface for growth features. However, there were difficulties. The crystal had been mounted on a glass fibre for X-ray diffraction studies, and had also been exposed to atmospheric moisture. Such exposure is known (Trigunayat, 1962) to be likely to blur the surface features. Secondly (Trigunayat, 1962), cadmium iodide crystals, because of their chemical reactivity with silver and other substances, cannot easily be coated to increase the reflectivity. Thus we were able only to get two-beam internal interference fringes and not multiple beam fringes which are much sharper. No attempt was made to dismount the crystal from the glass fibre because of the possibility of deformation. A micrograph of the (0001) face (mag. X 30) using bright field illumination is shown in Fig. 5. The phase contrast illumination did not show any improvement. The central part, shown enlarged in Fig. 6 (mag. X 120), illustrates the growth spiral observed on that face of the crystal which exhibited $28H$ polytypic structure. No spiral was observed on the opposite face of the crystal. This is a broken spiral, of symmetry intermediate between hexagonal and circular symmetries, with no clear evidence of cooperation of two dislocations. According to the screw dislocation theory of polytypism as shown above, the crystal should have exhibited two cooperating spirals of heights 89 Å and

7 Å respectively with a resultant spiral step-height of 96 Å for a direct correlation to exist between spiral step-height and c dimension of the unit cell. Fig. 7 shows the two-beam internal interferogram of the crystal obtained with green monochromatic light of mercury ($\lambda = 5461$ Å) (mag. X 30). An enlargement of the corresponding central part of Fig. 7 is shown in Fig. 8 (mag. X 120). The mean value of the spiral step height ($\bar{h}$), measured by counting the number of steps (n) and the member of fringes (m) between two points, by superimposing Figs. 6 and 8, is nearly 2580 ± 70 Å taking $\mu = 1{\cdot}8$ for cadmium iodide from $\bar{h} = (\lambda m)/(2\mu n)$. Thus it is evident that there is no direct correlation between the spiral step-height and the c dimension of the unit cell. However, it can be argued that the above large step-height results from multiple dislocation in the polytype $28H$ itself. This will require that at first the polytype $28H$ grows by the postulated cooperation of two dislocations; then that a further dislocation occurs in $28H$, which now acts as a basic structure to give a spiral step-height of 26 times the size of the unit cell of $28H$. Here we have assumed that the observed spiral step-height is an integral multiple of the c dimension of $28H$, but on account of the limitations of experimental techniques it has not been possible to determine the step-height very accurately. The matter will be still more complicated if the spiral step-height is a non-integral multiple of the c dimension of $28H$. However, even if the spiral step-height is an integral multiple of c of $28H_c$, the above explanation is far fetched. The surface spiral step-height does not seem to be in accordance with the screw dislocation theory of the growth of the polytype.

Jagodzinski & Arnold (1960) after examining fault-order phenomena in crystals of silicon carbide have postulated another theory of polytypism based on the vibration entropy of crystals. The essential features of Jagodzinski's theory are the 'diffuse' background and 'smearing' of diffraction spots. Trigunayat & Verma (1962) have observed high disorder and smearing phenomena on some crystals of cadmium iodide. They have indeed given evidence in favour of Jagodzinski's theory. However, as is evident from Figs. 1 to 4, the polytype $28H_c$ shows absence of any disorder. Thus it appears difficult to understand the growth of polytype $28H_c$ by Jagodzinski's theory.

It may be concluded that the growth of polytype $28H_c$ shows some evidence in favour of the screw dislocation theory, only as far as the initial growth, the dependence on $4H$ structure and the resulting order are concerned. However, the large spiral step-height, the kind of spiral observed on the surface, the integral multiplicity of the Burgers vector, and the repeat unit of the basic structure along c, are at variance with the screw dislocation theory of polytypism. In fact Trigunayat & Verma (1962) have concluded that the screw dislocation theory does not provide a satisfactory explanation for the growth of different polytypes of the compound. More recently Krishna & Verma (1962) have shown that the screw dislocation theory is also not able to explain fully the creation of all the polytypes in silicon carbide. Indeed no single theory is able to explain all the observed facts for any of the known polytypic substances.

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