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Anomalous Polytypic Structures: Investigation on Cadmium Iodide Crystals

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A direct correlation between the step heights of growth spirals and the heights of the X-ray unit cells, previously observed in silicon carbide crystals, furnished strong experimental support for Frank's dislocation mechanism for the genesis of various polytypes of this substance, but some recently reported anomalous polytypic structures cannot be directly understood in terms of screw dislocation theory. An X-ray diffraction and microscopic study of cadmium iodide has now revealed that these anomalies exist also for other polytypic substances. It is concluded that polytypism is influenced also by factors other than the spiral growth round screw dislocations.

X-ray diffraction studies of three new cadmium-iodide polytypes $26H_c$, $26H_d$ and $50H_c$ show that $26H_c$ and $26H_d$ have different structures but identical lattices with $a=b=4\cdot24$, $c=88\cdot8$ Å. Both belong to space group $P3m1$. $50H_c$ has the same a, b dimensions and space group as $26H_c$ and $26H_d$ but has $c=171$ Å; it has been identified from a diffraction photograph taken on a microfocus X-ray generator, and was found on the opposite face of the single-crystal piece which exhibited $26H_d$. The detailed structures of $26H_c$ and $26H_d$ have been worked out. While the determined structure of the polytype $26H_c$ has the Zhdanov sequence 211112 11 11 11 211112 11 11, that for $26H_d$ is 22 22 22 11 22 22 22. The former structure was solved by a graphical method which is a special case of Lipson & Taylor's Fourier Transform method. The method outlined may be helpful in determining structure of polytypes which are not highly based on a basic phase but show characteristic intense X-ray reflexions. Structures $26H_c$ and $26H_d$ come respectively from the parent structures $2H$ and $4H$, but it is shown that $50H$ has not originated from any of these basic phases.

The combined microscopic and X-ray studies of these structures reveal certain anomalies. In the case of $26H_c$ these are concerned with, firstly, the integral multiplicity of the Burgers vector and c spacing of the parent structure, secondly the absence of any spiral growth feature on its surface, and thirdly the inexplicable character of its atomic zigzag sequence. In $26H_d$ and $50H_c$ the anomalies are that there is no spiral growth feature on the surface of polytypic crystal $26H_d$ though its structure appears to have resulted from dislocation mechanism, that spiral growth feature is present on the surface of $50H_c$ whose structure does not appear to have originated by dislocation mechanism, and that both these unrelated structures exist in the same single-crystal piece.

Introduction

In a recent publication Krishna & Verma (1963) have reported a detailed X-ray diffraction and microscopic study of a large number of SiC polytypes, in which attention was mainly directed towards the analysis of the results in terms of the screw dislocation theory of polytypism. This theory, which was put forth by Frank (1951), and experimentally verified in the case of SiC crystals (Verma, 1952, 1957), gives a vivid and pictorial representation of the formation of different polytypes. However, the results obtained by Krishna & Verma (1963) revealed certain anomalous polytypic structures which could not be explained as having resulted directly by the dislocation mechanism. In particular the observation of polytypic structures which would require the Burgers vector of the generating screw dislocation to be an integral multiple of the lattice parameter of

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the parent structure was anomalous. It was concluded that the cause of polytypism in SiC needs to be reconsidered.

In the present work we were interested to investigate whether these anomalies were peculiar to silicon carbide crystals or whether they existed for other polytypic substances also. We therefore decided to investigate cadmium iodide, which is also known to exhibit a large number of polytypic modifications. An extensive investigation was carried out with the main emphasis on the identification and structure determination of long-period polytypic crystals; the determination of the structure of long period polytypes has not previously been done and it is mainly these polytypes that display anomalous features. However, such a study presents both experimental and theoretical difficulty. The experimental difficulties arise from the fact that X-ray diffraction photographs obtained with a conventional sealed off X-ray tube lack the high resolution which is necessary for the identification of the long period polytypes of cadmium iodide. Minute pieces of cadmium iodide, which would result in higher resolution of X-ray reflexions, could not be obtained. This was so since, unlike silicon carbide, cadmium iodide is soft and flexible and any attempt to cut the flake invariably leads to the distortion of the lattice. To overcome this difficulty we have used a microfocus X-ray tube in cases where higher resolution of X-ray reflexions was required. The theoretical difficulty arises since the usual trial-and-error methods of structure determination do not always lead to a successful solution of the long-period polytypic structures. In fact to work out the detailed structure merely by trial-and-error methods is practically impossible for these long period polytypes. We have, therefore, made use of a novel method to determine the structures by critically examining the intensity distribution in the $10\cdot l$ reciprocal lattice row.

Over 20 new polytypic modifications of cadmium iodide have been identified by us. These show a wide variety of growth features and structures. Among newly isolated polytypes, types $22H_c$, $28H_c$, $26H_c$, $26H_d$ and $50H_c$ are of special interest. The polytypes $22H_c$ and $28H_c$ have been described elsewhere (Srivastava & Verma, 1962, 1964). This paper reports the investigations on polytypes $26H_c$, $26H_d$ and $50H_c$ which show anomalies that cannot be explained by screw dislocation theory.

Experimental

Crystal growth

The crystals used in the present study were all grown by slow evaporation of an aqueous solution of the compound at room temperature. The hexagonal shaped crystals were gently removed from the dish with the help of a sharp needle after complete evaporation. This method is similar to that of Mitchell (1955) but differs in that the crystals were not taken out of the mother liquor but were removed only when they had grown fully and the water completely evaporated. As will be shown later, the crystals grown by this method are of added interest as their X-ray diffraction study throws light on what happens both in the initial and final stages of growth of the crystal.

X-ray methods

The *c*-axis oscillation and Weissenberg photographs of cadmium iodide crystals have invariably been found to show streaking between X-ray diffraction spots. This rendered their use practically impossible either for the identification of the polytype or for structure determination. However, *a*-axis oscillation photographs showed discrete sharp spots. Therefore, *a*-axis oscillation and Weissenberg photographs recording either $10\cdot l$ or $01\cdot l$ rows were taken. As had been shown by Ramsdell (1944) and Mitchell (1955) for SiC, for structure determination it is sufficient to compare the observed and calculated intensities for $10\cdot l$ or $01\cdot l$ reflexions alone.

For simple and moderately long-period polytypes diffraction patterns were obtained by employing conventional sealed off X-ray tubes. We have used a microfocus X-ray tube when higher resolution of X-ray reflexions and greater brilliance of the source are required. A commercial microfocus X-ray generator based on the design of Ehrenberg & Spear (1951) and manufactured by Hilger and Watts has been employed in the present investigation. This microfocus X-ray tube differs chiefly from the conventional tube in its small focus size so that the intensity per unit area in this tube is considerably larger, and also because of small focus size the resolution of X-ray reflexions is much higher. A line focus of 100μ and copper target were used for recording diffraction pattern shown in this paper.

Results

Figs. 1 and 2 refer to a hexagonal shaped crystal with a well developed and shining (0001) face of dimensions about $\frac{1}{2}$ mm × $\frac{1}{4}$ mm. This will be referred to as crystal No. 1. Fig. 1 shows a 15° *a*-axis oscillation photograph of this crystal recorded on a 3 cm camera with Cu $K\alpha$ radiation. Fig. 2 shows the corresponding zero-layer *a*-axis Weissenberg photograph of the same crystal taken on a camera of diameter 5·73 cm, using Cu $K\alpha$ radiation. Measurements on these photographs reveal that the *c* spacing of this crystal is 88·8 Å. The *c* spacing of the basic $2H$ structure is 6·835 Å. Therefore the present crystal is a 26 layered polytype. This is confirmed since there are 13 equal spacings (12 reflexions equally spaced) between two successive $2H$ reflexions and thus the polytype is $2 \times 13 = 26$ layered. As has been shown previously (Srivastava & Verma, 1962), all the polytypes of cadmium iodide are hexagonal. Thus the polytype under consideration is designated as $26H$.

Figs. 3 and 4 refer to another hexagonal shaped crystal with a well developed and shining (0001) face of dimensions about 2 mm × 1 mm. This crystal will be referred to as crystal No. 2. Fig. 3 shows a 15° *a*-axis oscillation photograph of this crystal recorded on a 3 cm camera with Cu $K\alpha$ radiation. Fig. 4 shows the zero-layer *a*-axis Weissenberg photograph of the same crystal taken on a camera of diameter 5·73 cm with conventional sealed off X-ray tube. This crystal is also of the polytype $26H$. However, since the intensity distributions of these two $26H$ crystals are different, their crystal structure must also be different. Mitchell (1956) has already reported two other 26 layered polytypes but no structural data were given. We have, therefore, referred to the polytypic structure of crystal No. 1 as $26H_c$ and to that of No. 2 as $26H_d$.

Fig. 5 represents a 15° *a*-axis oscillation photograph obtained with conventional sealed-off tube by reversing the crystal so that the opposite face of crystal No. 2 faces the X-ray beam. This shows it to be a high polytype. Thus two different polytypic structures are present in the same single crystal of the compound. As will be shown later it has been possible to detect the presence of these two polytypes in the same crystal because of the high absorbing property of both the cadmium and iodine atoms. However, the X-ray reflexions on this photograph do not show good resolution and it was therefore decided to use the microfocus X-ray tube.

Fig. 6 shows the same X-ray oscillation photograph as Fig. 5, employing the microfocus generator. For Fig. 5 the exposure time was 10 hours while for Fig. 6 it was 6 hours. Even with less exposure time, the diffraction spots obtained with the microfocus generator are brighter. The background is also considerably less than on Fig. 5. Each reflexion in Fig. 6 can be distinguished separately and accurate measurement revealed the crystal to be type $50H$. Since two such polytypes have already been reported (Mitchell, 1956; Trigunayat, 1960) the present polytype is designated $50H_c$.

Structure of polytypes

Structure of polytype $26H_c$

The usual method of structure determination consists in calculating all possible structures involving Zhdanov numbers 1,2,3,4 *etc.* (Zhdanov, 1945), in their Ramsdell zigzag sequence (Ramsdell, 1944, 1947) and deciding the correct structure by comparing the calculated intensities with the observed ones; this becomes practically impossible for a large polytype. The following simplifications are then made. Since almost all the cadmium iodide structures have only the Zhdanov numbers 1 and 2 in their zigzag sequence we shall restrict the structures to contain these numbers only. Even then there will be a large number of ways which will be geometrically possible for a 26-layered unit cell because of the presence of No. 1 in the zigzag sequence. However, the following are the important features observed on the X-ray diffraction patterns of the structure $26H_c$.

(i) All the reflexions which coincide in position with those from a basic $2H$ phase are intense and outstanding.

(ii) The $10\cdot l$ reflexions corresponding to $l=13n\pm 1$ ($n=1,2,3$) are either absent or are very weak. The reflexions $\bar{1}0\cdot 13n\pm 1$, $10\cdot\overline{13n\pm 1}$ and $\bar{1}0\cdot\overline{13n\pm 1}$ are also weak or absent.

(iii) The $10\cdot l$ reflexions corresponding to $l=13n\pm 2$ ($n=1,2,3$) are the second most intense reflexions. At some places they are almost as intense as the reflexions described in (i). Reflexions $\bar{1}0\cdot 13n\pm 2$, $10\cdot\overline{13n\pm 2}$ and $\bar{1}0\cdot\overline{13n\pm 2}$ are also strong.

The above observations suggest the presence of a large number of 11 units in the zigzag sequence of $26H_c$, *i.e.* the basic phase of this structure is $2H$. Mitchell (1956) has suggested that a polytypic series based on the basic $2H$ phase should not exist. However, this does not appear to be quite correct since in the present investigation as well as previously (Srivastava & Verma, 1962), polytypes showing X-ray reflexions having intensity distribution corresponding to the $2H$ phase have been observed. We expect therefore the structure $26H_c$ to be composed of many (11) units with some faults at the end of the sequence. The sequences derived in this manner will be of the type $(11)_{2n}\, p_1\, p_2 \ldots p_n\, p_n \ldots p_2 p_1$, where $p_1, p_2 \ldots p_n$ are either of the numbers 1 or 2. The maximum value of n is 5 and a value of n less than 3 is not considered because $2H$ spots will not come out intense in that case. For the twenty-six layered unit cell, there are twenty-one possible sequences, *e.g.* $(11)_{10}$ 2112; $(11)_8$ 212212; $(11)_6$ 22122122 *etc.* Intensities were calculated for some important $10\cdot l$ reflexions, namely the reflexions $l=13$ to 20. The intensity of a $10\cdot l$ reflexion from any cadmium iodide polytype may be written down as

$$I \propto A'^2+B'^2 \tag{1}$$

where

$$A' = \sum_{Z_{A,\alpha}} f_{\mathrm{I,\,Cd}} \cos 2\pi lZ + \sum_{Z_{B,\beta}} f_{\mathrm{I,\,Cd}} \cos 2\pi(lZ-\tfrac{1}{3}) + \sum_{Z_{C,\gamma}} f_{\mathrm{I,\,Cd}} \cos 2\pi(lZ+\tfrac{1}{3}) \tag{2}$$

$$B' = \sum_{Z_{A,\alpha}} f_{\mathrm{I,\,Cd}} \sin 2\pi lZ + \sum_{Z_{B,\beta}} f_{\mathrm{I,\,Cd}} \sin 2\pi(lZ-\tfrac{1}{3}) + \sum_{Z_{C,\gamma}} f_{\mathrm{I,\,Cd}} \sin 2\pi(lZ+\tfrac{1}{3}) \tag{3}$$

where $Z_{A,\alpha}$; $Z_{B,\beta}$ and $Z_{C,\gamma}$ denote the Z coordinate of iodine and cadmium atoms respectively on the A vertical axis passing through (000), the B vertical axis passing through ($\frac{2}{3}$ $\frac{1}{3}$ 0) and the C vertical axis passing through ($\frac{1}{2}$ $\frac{2}{3}$ 0), which can be written in short as A: 00z, B: $\frac{2}{3}$ $\frac{1}{3}$ z, and C: $\frac{1}{3}$ $\frac{2}{3}$ z. $\sum_{Z_{A,\alpha}}$ means summation over iodine atoms at A sites and cadmium atoms at α sites. Similarly for $\sum_{Z_{B,\beta}}$ and $\sum_{Z_{C,\gamma}}$. In cadmium iodide, as has been shown by Bozorth (1922), the basic polyatomic layer consists of two layers of hexagonal close packed iodine

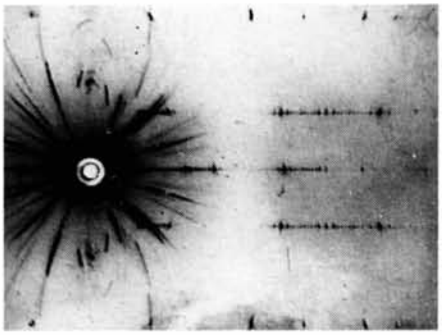

Fig. 1. A 15° *a*-axis oscillation photograph of the polytype $26H_c$, recorded on 3 cm camera with Cu $K\alpha$ radiation employing a conventional X-ray tube. (× $\frac{2}{3}$)

Fig. 4. Zero-layer *a*-axis Weissenberg photograph of polytype $26H_d$ taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm, employing a conventional X-ray tube. 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 first two visible reflexions towards the minimum correspond to $l=58$ and 59. (× $\frac{2}{3}$)

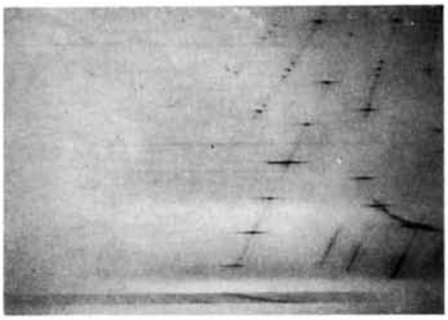

Fig. 2. Zero-layer *a*-axis Weissenberg photograph of polytype $26H_c$ taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm, employing a conventional X-ray tube. The festoon corresponding to the 10.*l* row of spots is recorded on the right side of the straight row of 00.*l* spots. The first intense spot from the top corresponds to $l=91$. The series $l=93$–62 of spots is visible in which the spot corresponding to $l=65$ is the most intense. (× $\frac{2}{3}$)

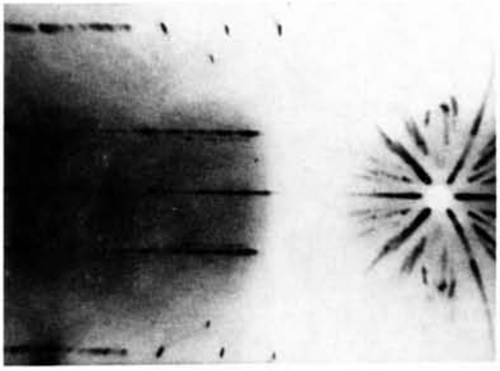

Fig. 5 A 15° *a*-axis oscillation photograph of the polytype $50H$, recorded on a 3 cm camera with CuK radiation employing a conventional X-ray tube. (× $\frac{2}{3}$)

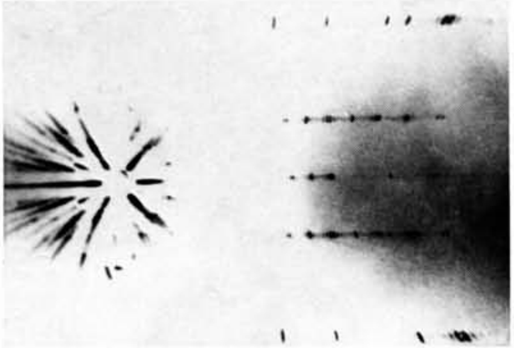

Fig. 3. A 15° *a*-axis oscillation photograph of the polytype $26H_d$, recorded on a 3 cm camera with Cu $K\alpha$ radiation employing a conventional X-ray tube. (× $\frac{2}{3}$)

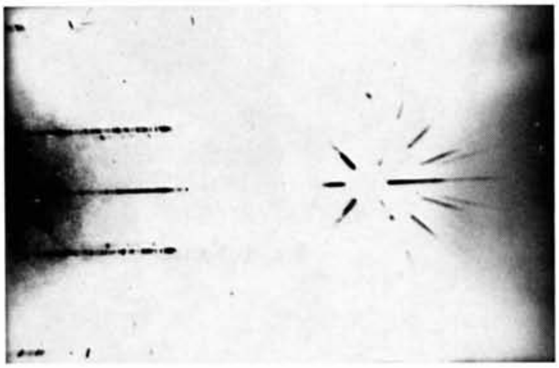

Fig. 6. A 15° *a*-axis oscillation photograph of the polytype $50H$, recorded on a 3 cm camera with CuK radiation employing a microfocus X-ray tube. (× $\frac{2}{3}$)

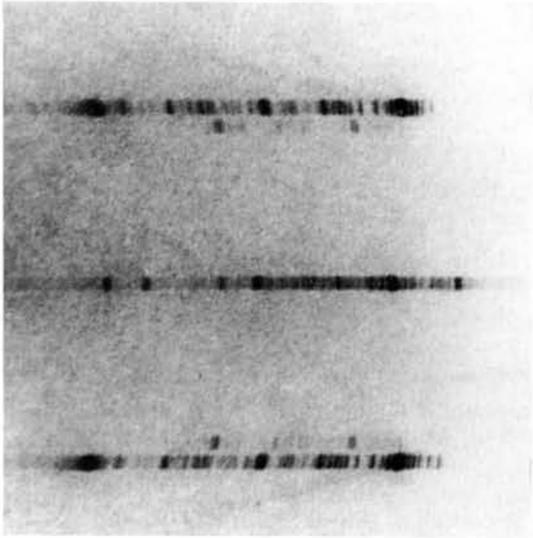

Fig. 7. A magnified view of the X-ray reflexions in Fig. 6. (× 2)

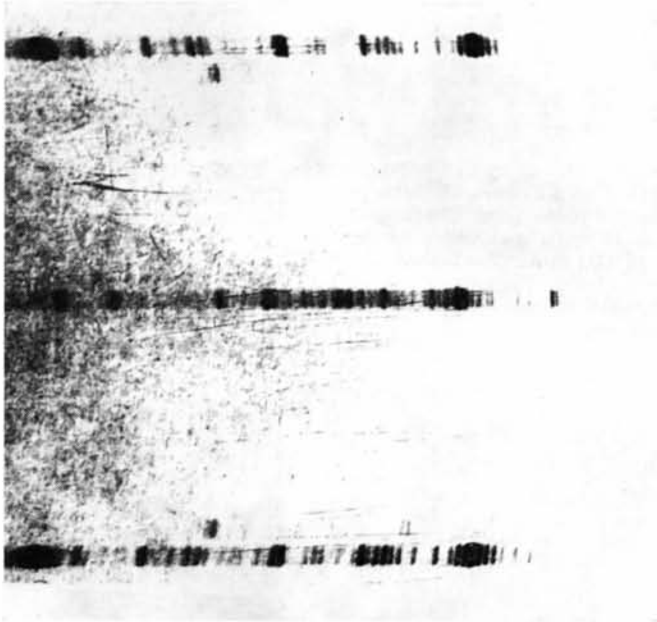

Fig. 8. Further magnification of X-ray reflexions in Fig. 6. (× 3)

ions with the small cadmium ions nested between them. The vertical I–I distance is $3{\cdot}41_5$ Å and the vertical Cd–I distance is nearly half of this distance. The cadmium layer is thus midway between two iodine layers.

The calculated intensities for none of the 21 structures matched with the observed intensity distribution on the X-ray diffraction photograph. It became then imperative to find other clues to the structure. Tomita (1960*a*, *b*) has theoretically shown in the case of silicon carbide structures that if there is a minimum intensity observed between two successive reflexions corresponding to the basic phase then the structure should consist of two separate multiple units of the basic phase separated by a few layers in between. Taking this into account we tried nine possible structures of the type $(11)_m\,(22)_p\,(11)_q\,(22)_r$, where m, p, q and r are integers.

However, these attempts also did not lead to success. It was then thought that the minimum corresponding to $l=13n\pm1$ may be structural extinctions. Since only few combination of atomic positions could produce these extinctions, it was tried to see if these extinctions could suggest some clue to the structure. Following Krishna & Verma (1962) it can be shown that if reflexions $10\cdot q$ $(q=13n\pm1)$ are absent the following relations must hold good for iodine atoms.

$$\sum_{Z_A}\cos 2\pi qZ_A=\sum_{Z_B}\cos 2\pi qZ_B=\sum_{Z_C}\cos 2\pi qZ_C=0 \quad (4)$$

$$\sum_{Z_A}\sin 2\pi qZ_A=\sum_{Z_B}\sin 2\pi qZ_B=\sum_{Z_C}\sin 2\pi qZ_C=0 \quad (5)$$

Similar relations should hold for cadmium atoms also. By trial and error in an Argand diagram it was found that only the sequence 11111411111111411111 satisfied the above relations. This sequence satisfied relations (4) and (5) only for even values of n and not for odd values. The sequence, however, contained Zhdanov number 4 which has never been found to exist in the cadmium iodide structural series. Calculation of intensities showed large intensity for odd values of n in $13n\pm1$, whereas the opposite has been experimentally observed. This solution was therefore rejected.

Having exhausted the above possibilities we thought it opportune to see whether the above described feature (iii), *viz.* the reflexions $10{\cdot}13n\pm2$ being very intense, could be of any help in finding a possible solution of the structure. The outstanding intense reflexions corresponding in position to $2H$ reflexions have already indicated the presence of many (11) units in the atomic sequence of $26H_c$. The next most intense reflexions corresponding to $l=13n\pm2$ should therefore be informative regarding the atomic position in the structure. This is so since there are comparatively few ways in which atoms can be placed to scatter in phase for a given reflexion, whereas there are many ways in which approximately zero scattering can be produced. Lonsdale (1929), Robertson & White (1945) and Abrahams & Robertson (1948) have made use of the criterion in determining certain organic structures. This consideration has helped us to solve the structure as shown below. The method used to deduce the atomic positions is in fact a special case of Fourier transform methods (Lipson & Taylor, 1958).

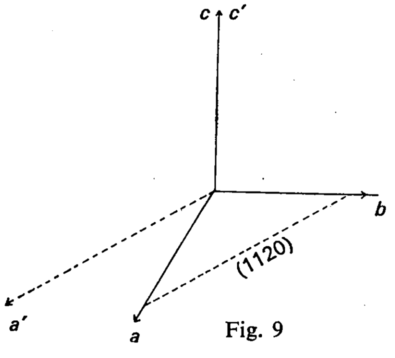

Fig. 9

All the cadmium iodide polytypes which are based on some ideal phase are formed by sandwiches of the type $(A\gamma B)$ or $(C\alpha B)$ in which A, B, C refer to iodine positions and γ and α to the cadmium positions. Therefore, it can well be concluded that atoms along the B axis are always fixed along odd sites only, the layer passing through the origin being taken as the zero layer. In the present case B atoms occupy positions 1,3,5 ... 25. Any sequence of $(A\gamma B)$ and $(C\alpha B)$ sandwiches to form the $26H$ structure will always give the above B position. Therefore, B atoms contribute significantly to the intensities corresponding to $2H$ positions only and give almost negligible contribution to other reflexions. Thus it remains to decide about the atomic positions along A and C axes only. Now keeping the atoms along the B axis fixed and interchanging the positions of atoms along A with those along C does not alter the structure. It merely means changing the origin and inverting the whole atomic sequence. Thus it remains to decide the positions of atoms along either of the two vertical axes A or C only. The positions of cadmium atoms are automatically fixed when the positions of iodine atoms are decided.

Since in cadmium iodide structures the plane $(11\bar{2}0)$ contains all the atoms along the three vertical axes A, B and C, it would be profitable to consider the $(11\bar{2}0)$ projection. As is obvious from Fig. 9 the matrix effecting the required transformation is:

$$\begin{vmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

In the special case of $10{\cdot}l$ planes the new indices will be

$$\begin{aligned} h' &= h-k=h \\ k' &= k \qquad =0 \\ l' &= l \end{aligned}$$

Thus the transformation does not lead to a change in the indices of planes of the type $10{\cdot}l$. Accordingly in the deduction below the same indices of the $10{\cdot}l$ planes have been used when the $(11\bar{2}0)$ projection is considered.

As has already been mentioned the reflexions which correspond in position to the basic $2H$ phase are most intense. Fig. 10 shows the traces of planes in the $(11\bar{2}0)$ projection so that the atoms lying on them would scatter in phase for each of the $10\cdot13n$ ($n=1,2,3$) reflexions. The atoms must lie on the intersection of these planes if all of the above reflexions are to be outstanding. As is evident from Fig. 10 the intersections are at heights 0,2,4, ... 26 along either of the A or C axes. Since the A or C atoms are present at even sites only the intersections in Fig. 10 represent the actual atomic sites. The presence of A or C atoms at heights 0,2,4, ... 26 means that the atomic sequence must contain many (11) units, *i.e.* many $(A\gamma B)$ or $(C\alpha B)$ sandwiches, which is in agreement with the previous deduction. Figs. 11 and 12 show the traces of planes in which the atoms should lie if they were to scatter in phase to make the reflexions $10\cdot13n\pm2$ ($n=1,2,3$) intense. These are the next most intense reflexions. Fig. 11 shows the case for $10\cdot13n+2$ ($n=1,2,3$) reflexions and Fig. 12 for $10\cdot13n-2$ ($n=1,2,3$). The atoms should lie at the intersection of the planes if all the reflexions in either of Figs. 11 or 12 are to be prominent. The places where atoms could be fitted on to the closest possible intersections of the traces of planes, and which lie either exactly or are near enough to atomic sites, are shown in Figs. 11 and 12. Now if all the reflexions corresponding to $10\cdot13n$, $10\cdot13n+2$, and $10\cdot13n-2$ are to be intense the atoms should lie at sites which are common to Figs. 10, 11 and 12. From Figs. 10, 11 and 12 it could be seen that in the first instance these sites are at heights 0,2,12,14,24 along either of the A or C axes. Among the thirty atomic sequences mentioned on pages 58 and 59 for the structure of $26H_c$, only those gave a rough fit for the calculated and observed intensities in which pairs of atoms along either of the A or C axes having a difference of either 12 or 14 units were present. Since 12 and 14 add to 26 in the case of polytype $26H$ the two atomic arrangements which have either 12 or 14 as the common difference among atomic positions along any axis give identical structures and any of them could be derived from the other by a shift of the origin. Keeping this in view the positions 0,2,12,14,24 were considered in two ways, firstly taking the positions 0,2,12,14 which represent two pairs of atoms with a common difference of 12 units and secondly taking position 24 also. Since the atomic positions along the B axis have already been fixed to have odd atomic positions only, the atomic positions on both A and C axes are automatically decided when positions on any of them are fixed at the heights mentioned above. These considerations gave the following two sequences:

(i) 2112 11 11 11 2112 11 11 11 11
(C atoms at heights 0,2,12,14)
(ii) 211112 11 11 11 2112 11 11 11
(C atoms at heights 0,2,12,14,24)

Intensities were calculated with the use of expression (1) for some important reflexions for the above sequences. It was found that though the above sequences gave comparatively large intensities for reflexions $10\cdot13n\pm2$, there were discrepancies in the observed and calculated intensities of other reflexions. At this stage other intersection sites common to Figs. 10, 11 and 12 were searched. These are at heights 4,10,16 and 22. Though these sites are not well represented by Fig. 12, these were considered since they were included in Figs. 10 and 11. As mentioned previously, only those structures gave a rough fit for the calculated and observed intensities which have C atoms at positions with a common difference of 12; therefore positions 4, 10, 16, 22 were considered with the positions of sequences (i) and (ii) in three different ways, firstly taking positions 4 and 16 together, secondly taking

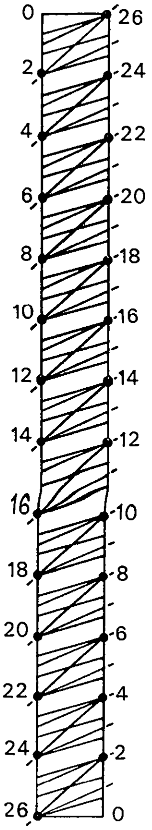

Fig. 10

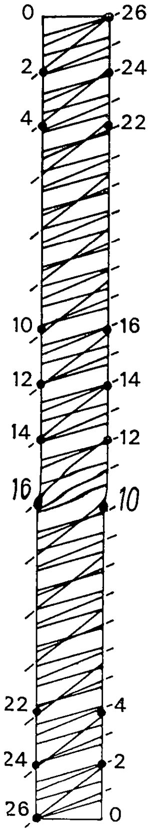

Fig. 11

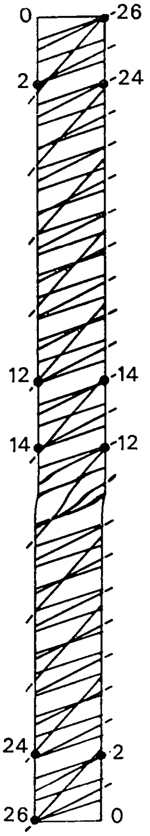

Fig. 12

Fig. 10. Traces of 10·13, 10·26 and 10·39 planes in the $(11\bar{2}0)$ projection. To distinguish between these planes the traces of 10·13 have been shown extended towards the left and those of 10·26 towards the right, while the traces of 10·39 are confined to the rectangular area itself.

Fig. 11. Traces of 10·15, 10·28 and 10·41 planes in the $(11\bar{2}0)$ projection. To distinguish between these planes the traces of 10·15 have been shown extended towards the left and those of 10·28 towards the right, while the traces of 10·41 are confined to the rectangular area itself.

Fig. 12. Traces of 10·11, 10·24 and 10·37 planes in the $(11\bar{2}0)$ projection. To distinguish between these planes the traces of 10·11 have been shown extended towards the left and those of 10·24 towards the right, while the traces of 10·37 are confined to the rectangular area itself.

positions 10 and 22 together and thirdly taking all the positions 4, 10, 16, 22. Above considerations led to the following sequences:

(i) 211112 11 11 211112 11 11 11
(C atoms at heights 0,2,4,12,14,16)
(ii) 2112 11 11 211112 11 11 22
(C atoms at heights 0,2,10,12,14,22)
(iii) 21111112 11 11 211112 11 11
(C atoms at heights 0,2,4,12,14,16,24 or 0,2,10,12,14,22,24)
(iv) 211112 11 21111112 11 22
(C atoms at heights 0,2,4,10,12,14,16,22)
(v) 2111111112 11 21111112 11
(C atoms at heights 0,2,4,10,12,14,16,22,24)

Calculation of intensities showed that all of the above sequences gave large intensities for reflexions 10·13$n \pm 2$. To decide the correct structure, the intensities for other reflexions were calculated and compared with the observed intensities. The first sequence, *viz.* 211112 11 11 211112 11 11 11, showed an excellent agreement as shown in Table 1. Other sequences gave discrepancies for reflexions other than 10·13n and 10·13$n \pm 2$. The detailed structure of polytype $26H_c$ is therefore as follows:

Space group: $P\,3\,m\,1$
Zhdanov symbol:
211112 11 11 211112 11 11 11

ABC sequence for iodine atoms:
$ABCBCBCBABABABCBCBCBABABAB$
ABC sequence for both cadmium and iodine atoms:
$(A\gamma B)(C\alpha B)(C\alpha B)(C\alpha B)(A\gamma B)(A\gamma B)(A\gamma B)(C\alpha B)$
$(C\alpha B)(C\alpha B)(A\gamma B)(A\gamma B)(A\gamma B)$

Atomic coordinates

7 iodine at 0 0 t
$t = 0, 8z, 10z, 12z, 20z, 22z, 24z.$
13 iodine at $\frac{2}{3}\ \frac{1}{3}\ t'$
$t' = z, 3z, 5z, 7z, 9z, 11z, 13z, 15z, 17z, 19z, 21z, 23z, 25z.$
6 iodine at $\frac{1}{3}\ \frac{2}{3}\ t''$
$t'' = 2z, 4z, 6z, 14z, 16z, 18z$
6 cadmium at 0 0 t_1
$t_1 = 5z', 9z', 13z', 29z', 33z', 37z'$
7 cadmium at $\frac{1}{3}\ \frac{2}{3}\ t'_1$
$t'_1 = z', 17z', 21z', 25z', 41z', 45z', 49z'$
where $z = \frac{1}{26}$ and $z' = \frac{1}{52}$

Structure of polytype $26H_d$

Here again the structure determination by mere trial and error would be an arduous task. This can be made easy if some information can be gathered from the intensity distribution on the X-ray diffraction pattern. The following significant features are observed:

(1) All the reflexions which coincide in position with the reflexions of the basic $4H$ phase are distinctly more intense than the others and have intensity distribution similar to that from a $4H$ structure.

Table 1. *Calculated and observed relative intensities for the structure $26H_c$*

l	Calculated intensities	Observed* intensities	l	Calculated intensities	Observed* intensities
0	0·13	*a*	27	1·43	*a*
1	0·17	*a*	28	243·29	*s*
2	9·43	*a*	29	13·69	*vw*
3	1·44	*a*	30	2·68	*vvw*
4	0·39	*a*	31	4·69	*vvw*
5	1·53	*a*	32	18·75	*w*
6	6·43	*a*	33	19·92	*w*
7	0·79	*a*	34	2·57	*vvw*
8	2·05	*a*	35	2·59	*vvw*
9	2·84	*a*	36	2·94	*a*
10	4·53	*vvw*	37	117·92	*ms*
11	170·96	*ms*	38	1·12	*a*
12	1·36	*a*	39	399·96	*s*
13	1000·00	*vvs*	40	1·21	*a*
14	1·81	*a*	41	56·27	*mw*
15	256·07	*s*	42	2·97	*a*
16	19·97	*vw*	43	0·30	*a*
17	2·51	*vvw*	44	0·89	*a*
18	8·16	*vvw*	45	2·09	*a*
19	34·35	*w*	46	1·80	*a*
20	46·02	*w*	47	0·24	*a*
21	3·99	*vvw*	48	0·86	*a*
22	7·22	*vw*	49	0·12	*a*
23	7·27	*vw*	50	1·81	*a*
24	276·57	*s*	51	0·45	*a*
25	1·86	*a*	52	0·01	*a*
26	253·51	*s*			

* The observed intensities were actually taken from the series 10·52 through 10·104. This series has the same intensity sequence as 10·0 through 10·52 which is not clearly visible on the Weissenberg photograph because of absorption caused by the non-equidimensional crystal plate.

(2) The reflexions which do not coincide with the corresponding $4H$ reflexions, but are nearest to them, are intense but not so much as their corresponding $4H$ reflexions.

The above features suggest the presence of a large number of 22 units in the zigzag sequence of the structure $26H_d$. Below are listed the possible structures with descreasing probability:

(i) 22 22 22 11 22 22 22
(ii) 22 22 21111112 22 22
(iii) 22 22 11122111 22 22
(iv) 22 22 1111111111 22 22
(v) 22 22 11211211 22 22
(vi) 22 22 12111121 22 22

It will be seen that each of the above arrangements has a mirror plane. This is because any number of (22) units have in themselves a mirror plane and after taking any number of (22) units the remaining layers could only be arranged taking the Zhdanov numbers 1 and 2 in sequences having a mirror plane. As for example, keeping 4 units of (22) the remaining 10 layers could be arranged in sequences 21111112, 112 112 11, 212212, 122221, and 11 11 11 11 11, each of which has a mirror plane. When two sequences each of which has a mirror plane are placed together as such, the resulting sequence also exhibits a mirror symmetry about either of the mirror planes of the two sequences. In fact all the determined sequences of cadmium iodide consisting of Zhdanov members 1 and 2 have mirror planes (Mitchell, 1956; Srivastava & Verma 1962, 1963). Intensities for a few important reflexions were calculated for each of the above structures. The intensity formula for $10.l$ reflexions corresponding to space group $P3m1$ to which the polytype belongs has already been given in (1). A comparison of the calculated intensities with those observed on the X-ray diffraction photograph showed that the first sequence in the above list gives a close agreement with the observed intensities. The calculated intensities for other sequences showed marked differences with the observed ones. Table 2 shows the good agreement between the two intensities. The detailed structure of the polytype $26H_d$ is, therefore, as below:

Space group: $P3m1$
Zhdanov symbol:
22 22 22 22 22 22 11
ABC sequence for iodine atoms:
ABCB ABCB ABCB ABCB ABCB ABCB AB
ABC sequence for cadmium and iodine atoms:
$(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)$
$(A\gamma B)(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)$

Atomic coordinates:
7 Iodine at $0\ 0\ t$
$t=0,\ 4z,\ 8z,\ 12z,\ 16z,\ 20z,\ 24z,$
13 Iodine at $\frac{2}{3}\ \frac{1}{3}\ t'$
$t'=z, 3z, 5z, 7z, 9z, 11z, 13z, 15z, 17z, 19z, 21z, 23z, 25z$
6 Iodine at $\frac{1}{3}\ \frac{2}{3}\ t''$
$t''=2z,\ 6z,\ 10z,\ 14z,\ 18z,\ 22z$
6 Cadmium at $0\ 0\ t_1$
$t_1=5z',\ 13z',\ 21z',\ 29z',\ 37z',\ 45z'$
7 Cadmium at $\frac{1}{3}\ \frac{2}{3}\ t'_1$
$t'_1=z',\ 9z',\ 17z',\ 25z',\ 33z',\ 41z',\ 49z'$
where $z=\frac{1}{26}$ and $z'=\frac{1}{52}$

The intensities of $10{\cdot}l$ reflexions obtained by expression (1) were multiplied by the Lorentz-polarization factor $(1+\cos^2 2\theta)/(\sin 2\theta)$ where θ is the Bragg angle and is calculated from the relation

$$\sin\theta_{10.l}=\tfrac{1}{2}\sqrt{\mathbf{a}^{*2}+l^2\mathbf{c}^{*2}}$$

where **a** and **c** represent unit-cell vectors of the reciprocal lattice given by $\mathbf{aa}^*=\lambda$, $\mathbf{cc}^*=\lambda$. To verify the proposed structure, intensities for a complete range of 52 reflexions in the $10{\cdot}l$ row were calculated in both cases. It is not necessary to check the agreement beyond this range since in a cadmium iodide structure nH intensities repeat themselves after $l=2n$. In cadmium iodide crystals high absorption occurs owing to the presence of both the heavy atoms cadmium and iodine. Moreover, since cadmium iodide crystals grow in the form of a thin hexagonal platelet, the absorption varies because of the shape effect. The absorption correction which would have improved the results could not be applied since suitable absorption factors for a thin platelet like the present crystal were not available. However, it is believed that this will not cause any abrupt change in the observed intensities, since the recorded reflexions correspond to the crystal face (0001) nearly perpendicular to the X-ray beam.

Discussion

It will now be examined how far the experimental results agree with those expected on Frank's (1951) screw-dislocation theory of polytypism originally proposed for silicon carbide. Forty (1952) has applied Frank's theory to explain the generation of cadmium iodide polytypes in the following manner. Regarding type $4H$ as the parent structure, slips of various magnitudes in this structure in the initial stages of growth create both even and odd dislocations, raising terminated steps of various heights. These steps will ultimately wind up into spirals so that the structure and height of the unit cell are controlled by the structure and height of this step. An even dislocation, *i.e.* a dislocation whose Burgers vector is an integral multiple of the c parameter of parent $4H$ structure, will leave the layers in perfect fit with each other, so that the parent structure itself continues during further growth. But odd dislocations of different strength leave a misfit in the structure at the initial step, so that the subsequent growth leads to the generation of various polytypic structures. Therefore, a polytype which has resulted by the screw-dislocation mechanism should exhibit spiral feature on its surface, should be based on a parent structure, should have the Burgers vector of the generating screw dislocation as a non-integral multiple of the c parameter of the parent structure, and also should be completely ordered.

The polytype $26H_c$ has been shown to be based on $2H$ phase; therefore the Burgers vector of the generating screw dislocation will be exactly 13 times the c parameter of $2H$. A step of 26 layers formed in a basic $2H$ structure could result in nothing else except in the further growth of type $2H$ itself. A single screw dislocation in basic $2H$ phase cannot, by itself, create any other polytypc. Other polytypes from basic $2H$ phase could then only result when a basic (11) step combines with another (22) step from a basic $4H$ phase. Though the Zhdanov sequence 211112 11 11 11 211112 11 11 of $26H_c$ contains a large number of (11) units the faults are not of the type 22 and are also at several places within the sequence. The atomic zigzag sequence of polytype $26H_c$ $2(11)_2 2\ (11)_3\ 2(11)_2 2\ (11)_2$ has stacking changes at intervals of 3, 4, 3, 3, in the sequence of basic polytype $2H$, $(11)_n$. If one wanted to explain the origin of this structure in terms of cooperation of dislocations, one would have to postulate at first the creation of step $8H$, (211112) by cooperation of basic $4H$, (22) and $2H$, (11) steps and then further two $8H$, (211112) steps would have to cooperate with a postulated presence of nearly (11) steps in the manner $211112\ (11)_3\ 211112\ (11)_2$. This is inconceivable and thus cooperation of dislocations cannot give rise to the polytype $26H_c$. The surface of this crystal (No. 1) was examined under a narrow pencil of white light in bright field illumination for any growth feature. It was also examined by incident phase contrast illumination but this did not show any improvement. The surface of the polytypic crystal $26H_c$ did not reveal any growth features at all. The above observations indicate that the structure $26H_c$ has not grown as visualized by dislocation mechanism.

X-ray diffraction photographs from crystal No. 2 show that it consists of a 26-layered polytype on one face called $26H_d$ and a 50-layered polytype on the other. The diffraction from the two opposite faces could be separately recorded because of the high absorbing property of both the cadmium and iodine atoms, owing to which at one time only that diffraction pattern is recorded which corresponds to the polytypic structure of the crystal face which is away from the incident radiation (Srivastava & Verma, 1962). We thus have a peculiar instance when a single-crystal piece possesses two modifications both of which have the same a, b dimensions and space group but differ in the c dimensions of the unit cell, one being 88·8 Å and the other 171 Å.

The polytype $26H_d$ with the Zhdanov sequence 222222222222 11 is one of the polytypes of the series which will be formed by dislocation mechanism from the $4H$ structure. However, surprisingly, no spiral was observed on this face of crystal No. 2. From this it may be concluded that though the structure of polytype $26H_d$ conforms to that expected on dislocation theory, there is no evidence from the surface features

Table 2. *Calculated and observed relative intensities for the structure* $26H_d$

l	Calculated intensities	Observed* intensities	l	Calculated intensities	Observed* intensities
0	1·20	*a*	27	4·41	*a*
1	0·13	*a*	28	5·27	*a*
2	0·16	*a*	29	6·12	*vvw*
3	0·78	*a*	30	9·49	*vvw*
4	1·71	*a*	31	26·65	*w*
5	0·84	*a*	32	187·95	*ms*
6	59·34	*mw*	33	218·05	*s*
7	106·40	*mw*	34	32·34	*w*
8	8·37	*a*	35	8·09	*vvw*
9	5·76	*vvw*	36	4·78	*vvw*
10	3·26	*a*	37	3·56	*a*
11	1·67	*a*	38	3·07	*a*
12	0·47	*a*	39	617·51	*vs*
13	1000	*vvs*	40	0·67	*a*
14	7·38	*a*	41	0·83	*a*
15	7·45	*a*	42	6·88	*a*
16	9·89	*vvw*	43	1·47	*a*
17	15·22	*vw*	44	6·06	*a*
18	30·17	*w*	45	18·97	*vw*
19	324·40	*s*	46	20·27	*vw*
20	384·12	*s*	47	7·61	*a*
21	27·82	*w*	48	1·03	*a*
22	13·86	*vw*	49	0·11	*a*
23	6·60	*a*	50	0·06	*a*
24	4·62	*a*	51	0·05	*a*
25	3·50	*a*	52	0·25	*a*
26	329·13	*s*			

* The observed intensities were actually taken from the series 10·52 through 10·104. This series has the same intensity sequence as 10·0 through 10·52 which is not clearly visible on the Weissenberg photograph because of absorption caused by the non-equidimensional crystal plate.

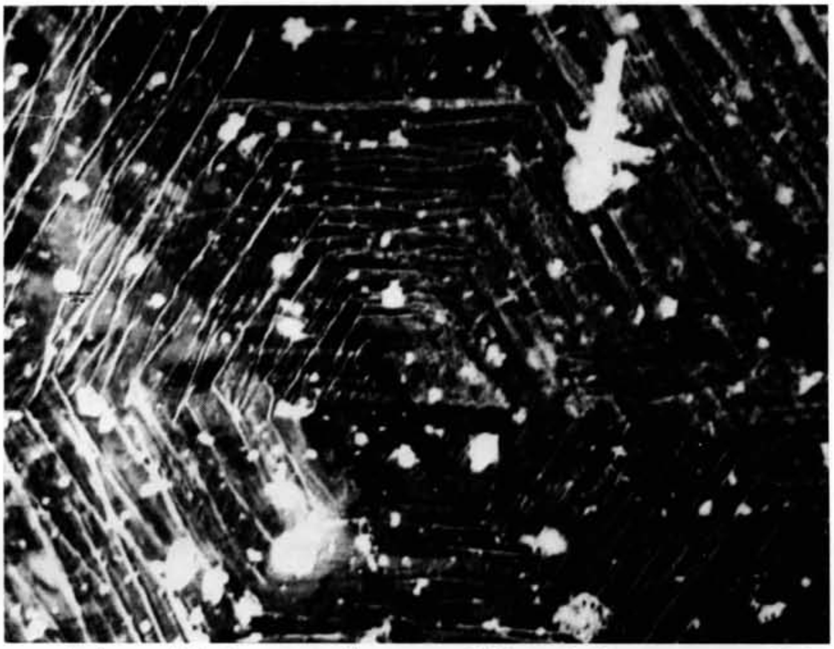

Fig. 13. Surface micrograph of crystal No. 2 corresponding to type $50H_c$ employing a narrow pencil of white light. (× 130).

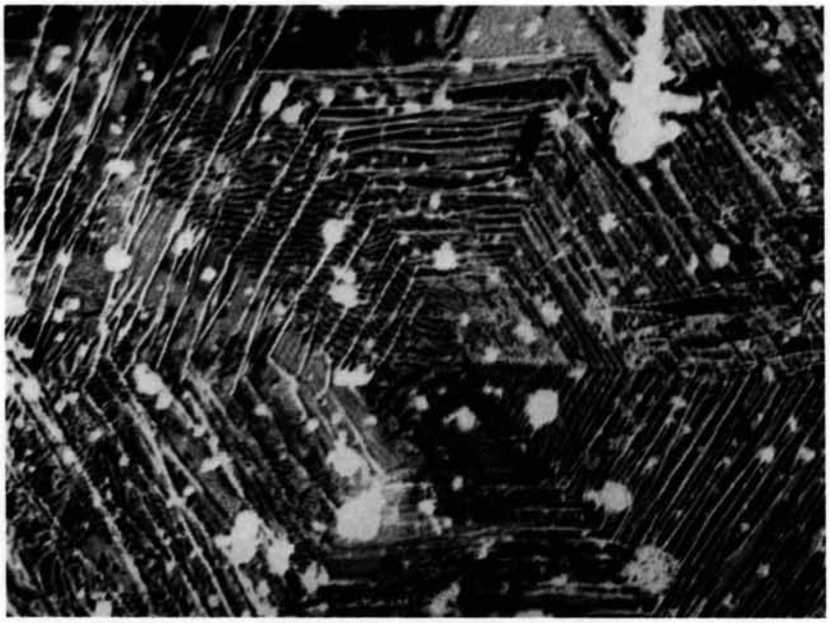

Fig. 14. Interferogram of crystal No. 2 corresponding to $50H_c$ structure employing green mercury light of $\lambda = 5461$ Å. (× 130).

to support this. The other face of crystal No. 2 which consists of polytype $50H_c$ shows a complicated growth pattern illustrated in Fig. 13. But the intensity distributions in X-ray patterns of $50H_c$ reveal that this is not based on either of the basic $2H$ or $4H$ phases, nor does it appear to have originated from $26H$. But the observation of a spiral feature corresponding to $50H_c$ polytype would indicate growth by dislocation mechanism. Thus we have the curious situation that in the same crystal piece on one side we have the polytypic structure $26H_d$ which can originate by dislocation mechanism but does not exhibit any spiral feature, whereas on the other face there is the polytype $50H_c$ which does not seem to have resulted by dislocation mechanism but still shows a complicated spiral feature.

Figs. 13 and 14 respectively show the surface micrograph and interferogram of that face of crystal No. 2 which exhibits the polytype $50H$. The interferogram in Fig. 14 shows the two-beam internal interference fringes. For step height estimation, only the method of two-beam internal interference (Forty, 1952) could be used. The method of multiple-beam interference similar to that used for stearic acid crystals by Verma & Reynolds (1953) could not be applied here since cadmium iodide reacts with silver. As is evident from Fig. 14 the fringes observed do not contour the growth steps. Owing to this an estimation of spiral step height and thus a verification of the correlation between this and the c dimensions of the unit cell was not possible. However, it is known (Trigunayat & Verma, 1962) that such a correlation is not observed on any of the cadmium iodide polytypes except for the basic $2H$ and $4H$ structures. This suggests that the formation of a polytype is not necessarily governed by dislocation mechanism. Jagodzinski (1949*a*, *b*, *c*, 1954) who has also arrived at a similar conclusion from thermodynamic considerations, has suggested that the formation of a polytypic structure is governed by its vibration entropy. Accordingly highly ordered long period polytypes like $26H_c$, $26H_d$ and $50H_c$ would become increasingly improbable.

To sum up the polytypes $26H_c$ and $26H_d$ show some evidence in favour of the screw-dislocation theory inasmuch as the dependence on the basic $2H$ and $4H$ structures and the resulting orders of the structure are concerned. The absence of any spiral features on the surfaces of the structures $26H_c$ and $26H_d$, the unexpected atomic zigzag sequence of the structure $26H_c$ and the fact that the Burgers vector for $26H_c$ is an integral multiple of the c dimension of the basic $2H$ structure, do not support the origin of these structures by the screw dislocation mechanism. However, the absence of spiral growth features on the crystal $26H_c$ and $26H_d$ can be explained if the growth conditions of the end surface were different from those ruling during the growth of underlying layers and were not based on dislocation mechanism. The polytype $50H_c$ furnishes a peculiar case where surface evidence indicates growth by the screw dislocation mechanism but the unit cell of the structure does not appear to have resulted by this mechanism.

In conclusion we find that anomalous polytypic structures first observed in silicon carbide, in which the Burgers vector of the generating screw dislocation is an integral multiple of the c parameter of the basic structure, exist for cadmium iodide crystals also. In addition, cadmium iodide polytypes exhibit the anomaly regarding the existence of two polytypic structures in the same single-crystal piece unrelated to each other and not being based on the same basic structure. All these facts put together indicate that the real cause of polytypism in cadmium iodide lies somewhere else and not just in the screw dislocation theory. In fact, no single theory is able to explain all the observed facts in any of the known polytypic substances.

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