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# Structure and Growth of Three New Polytypes of Cadmium Iodide 60*R*, 72*R*, and 32*H*. A New Possible Method of Determining Atomic Structure of Polytypes Based on Evaluation of Theoretical Stacking Fault Energy

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Three new polytypes of cadmium iodide, two rhombohedral 60*R* and 72*R* and one hexagonal 32*H* have been discovered. The detailed atomic structures of 60*R* and 72*R* have been worked out; these are $[(22)_3\ 1223]_3$ and $[(22)_4\ 1223]_3$. These structures indicate the existence of a structure series $[(22)_n\ 1223]_3$. The growth of the polytypes 60*R* and 72*R* has been discussed in terms of creation of periodic stacking faults in the basic structure. Evidences and arguments including electron microscope observations of dislocation dissociation have been presented to show that the proposed mechanism is the most likely one through which the above polytypes have resulted. Following Hirth & Lothe, theoretical stacking fault energies of the probable structures of the two polytypes have been calculated and it has been found that the stacking fault energies for the proposed structures are minimum. Based on this criterion the structure of 32*H* was deduced and was found to represent the correct atomic structure. It seems possible that the minimum stacking fault energy criterion may prove to be of value in general in determining the atomic structure of polytypes.

## Introduction

Cadmium iodide is a curious compound since it is known to exist in more than one hundred polytypic modifications (Srivastava & Verma, 1965; Chadha & Trigunayat, 1967). However, only two of these crystallographic modifications have been shown to be rhombohedral (Chadha & Trigunayat, 1967). The rhombohedral cadmium iodide polytypes present a very interesting feature since, unlike rhombohedral polytypes of other substances, these do not seem to result from any of the basic structures (Srivastava & Verma, 1965). Recently it has been suggested that these polytypes may form as a result of layer transpositions and creation of stacking faults (Chadha & Trigunayat, 1967). However, no evidence has been presented to show that a complex sequence of basal stacking faults can occur in cadmium iodide structures. The existence of the polytypes 60*R* and 72*R* suggests the occurrence of a structural series represented by the Zhdanov symbol $[(22)_n1223]_3$ in cadmium iodide polytypes. The scheme through which stacking faults could generate 60*R*, 72*R* polytypes has been described and discussed. Electron microscope observation which present evidence in favour of suggested mechanism has been presented. In order to test whether a polytypic structure corresponds to minimum stacking fault energy, which it should in principle if it has resulted from a basic structure through the occurrence of a stacking fault, theoretical stacking fault energies for the polytypes 60*R* and 72*R* were calculated. It was found that the atomic structure calculated, based on X-ray diffraction intensities, represented the atomic sequence with minimum stacking, fault energies. This procedure applied in the reverse way resulted in the determination of correct atomic structure for the polytype 32*H*.

## Observation and results

The crystals were grown from aqueous solution and were investigated by X-ray diffraction single-crystal oscillation and Weissenberg photographs. The polytypes 60*R* and 72*R* were found in the same batch of crystal whereas 32*H* was found in a different batch.

Figs. 1 and 2 represent the 15° *a*-axis single-crystal oscillation and Weissenberg photographs of a 60*R* polytype. Fig. 3 is a 15° *a*-axis single-crystal oscillation photograph of a 72*R* polytype. There are some closely spaced faint spots in Fig. 3 which are indicative of a polytype with a longer period superimposed on the polytype 72*R*. However the distinct spots represent polytype 72*R* and we will be concerned with these only in later discussions. The diffraction patterns of all the three polytypes exhibit strong spots near the 4*H* positions which clearly indicates the presence of a large number of (22) units in the Zhdanov symbol representing the structure of polytypes. Keeping this in view, the atomic structures were calculated by trial on an IBM 7044 computer. It is worth while mentioning that the determination of atomic structure here, as in the cases of all other polytypic crystals, is confined to the determination of only the stacking sequences of atomic layers. The strict extinction conditions observed for polytypic crystals ensures that the structures can be described in terms of closed packed layers of atoms (Verma & Krishna, 1966). The structure represented by the Zhdanov symbol $[(22)_3 1223]_3$ gave the best fit between experimental and calculated intensities of the polytype 60*R*. For 60*R*, the spots in the range 10.0 to 10.120 are not visible due to absorption, the comparison was made for the reflexions 10·120 to 10.240. This series has the same intensity sequence as 10.0 to 10.120. In order to verify the correctness of the proposed structure, we tried to match the calculated and observed intensities of a sequence which has only one cadmium and one iodine atom in orientations different from those in the proposed structure of 60*R*. It was found that even this small deviation caused certain serious discrepancies between calculated and observed intensities and this indicates that the proposed structure is the correct one. Fig. 3 which shows an oscillation photograph of polytype 72*R* also exhibits intensity features similar to those observed for 60*R*. Structure determination by a procedure similar to that adopted for 60*R* showed that the atomic structure of 72*R* corresponds to the Zhdanov symbol $[(22)_4 1223]_3$. The existence of these two similar structures indicates the existence of structural series $[(22)_n 1223]_3$. The detailed atomic structures of polytypes 60*R* and 72*R* are as follows. Tables 3 and 4 show the agreement between calculated and observed intensities for the proposed structures.

*Atomic structure of* 60*R*

Space group $R3m1$
Zhdanov symbol $[(22)_3 1223]_3$
*ABC* sequence
$(A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)\ (A\gamma B)\ (C\alpha B)\ (A\gamma B)$
$(A\beta C)\ (A\gamma B)\ (A\beta C)\ (B\alpha C)\ (A\beta C)\ (B\alpha C)\ (A\beta C)$
$(B\alpha C)\ (A\beta C)\ (B\alpha C)\ (B\gamma A)\ (B\alpha C)\ (B\gamma A)\ (C\beta A)\ (B\gamma A)$
$(C\beta A)\ (B\gamma A)\ (C\beta A)\ (B\gamma A)\ (C\beta A)\ (C\alpha B)\ (C\beta A)\ (C\alpha B)$

*Atomic structure of* 72*R*

Space group $R3m1$
Zhdanov symbol $[(22)_4 1223]_3$
*ABC* sequence

Table 1. *Theoretical stacking fault energy for the* 60*R polytype*

| | Structure | Theoretical stacking fault energy $E_{st}$* |
|---|---|---|
| (i) | $[(22)_3 1223]_3$<br>$(ABCB)_3 AB\ AC\ AB\ AC \dots,$ | $E_{st} = 3\psi_2 + (0)\psi_3 + (0)\psi_4 + \dots$ |
| (ii) | $[(22)_3 2213]_3$<br>$(ABCB)_3 AB\ CB\ AB\ AC \dots,$ | $E_{st} = 3\psi_2 + (0)\psi_3 + 2\psi_4 + \dots$ |
| (iii) | $[(22)_3 2313]_3$<br>$(ABCB)_3 AB\ CB\ AC\ AC \dots,$ | $E_{st} = 3\psi_2 + 1\psi_3 + 3\psi_4 + \dots$ |
| (iv) | $[(22)_3 2132]_3$<br>$(ABCB)_3 AB\ CB\ CA\ BA \dots,$ | $E_{st} = 3\psi_2 + 1\psi_3 + 4\psi_4 + \dots$ |

* In the above formulae the first term associated with $\psi_N$ denotes the number of pairs of nearest neighbours which are not in proper stacking sequence compared to basic structure sequence and $\psi_N$ denotes the distortional energy per pair.

Table 2. *Theoretical stacking fault energy for the* 32*H polytype*

| | Structure | Theoretical stacking fault energy $E_{st}$ |
|---|---|---|
| (i) | $(22)_5 3333$<br>$(ABCB)_5 ABC\ ACB\ ABC\ ACB$ | $E_{st} = 3\psi_2 + 3\psi_3 + 5\psi_4 + \dots$ |
| (ii) | $(22)_5 321123$<br>$(ABCB)_5 ABCA\ CBCB\ CACB$ | $E_s = 5\psi_2 + 1\psi_3 + 3\psi_4 + \dots$ |
| (iii) | $(22)_5 231132$<br>$(ABCB)_5 ABCB\ ACAC\ ABCB$ | $E_{st} = 5\psi_2 + 2\psi_3 + 6\psi_4 + \dots$ |
| (iv) | $(22)_5 11222211$<br>$(ABCB)_5 AB\ AB\ CB\ AB\ CBAB$ | $E_{st} = 6\psi_2 + (0)\psi_3 + 1\psi_4 + \dots$ |
| (v) | $(22)_5 1212\ 2121$<br>$(ABCB)_5 AB\ AC\ AC\ BC\ ACAB$ | $E_{st} = 6\psi_2 + (0)\psi_3 + 4\psi_4 + \dots$ |

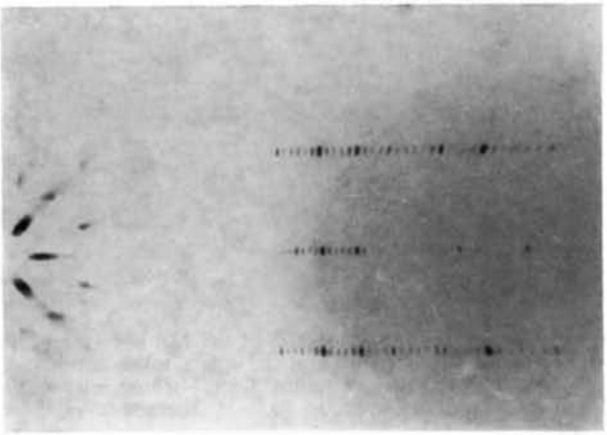

Fig. 1. 15° oscillation photograph of the $60R$ polytype of the cadmium iodide crystal about the $a$ axis, taken with Cu $K\alpha$ radiation on a camera of radius 3 cm. The first intense spot outwards from the centre on the $10.l$ row (the first layer) corresponds to 10.151.

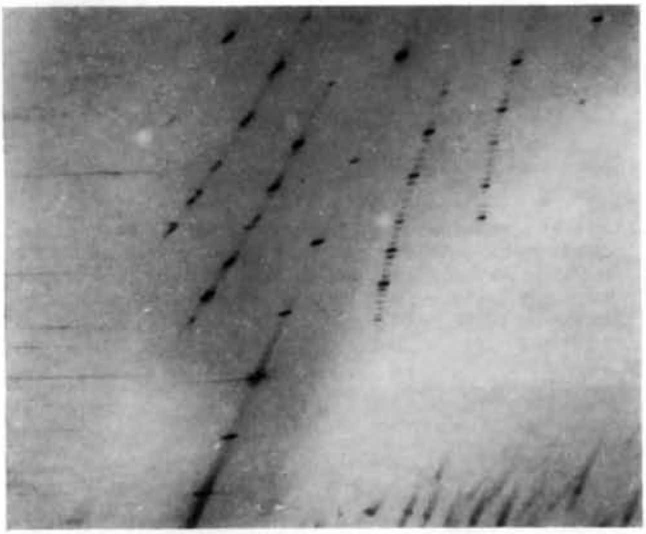

Fig. 2. Zero layer $a$-axis Weissenberg photograph of the $60R$ polytype of the cadmium iodide crystal taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm. The first intense spot on the $10.l$ row (which is next to the straight $00.l$ row) corresponds to 10.151

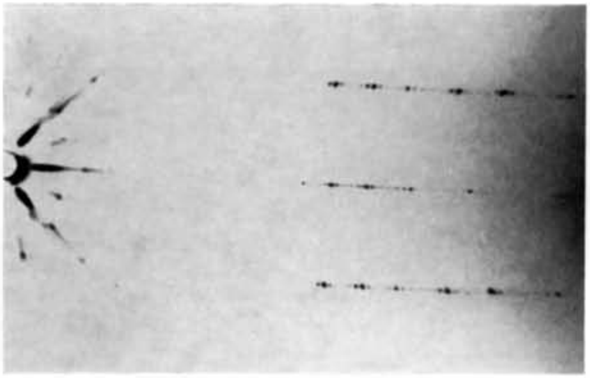

Fig. 3. 15° oscillation photograph of the $72R$ polytype of the cadmium iodide crystal about the $a$ axis, taken with Cu $K\alpha$ radiation on a camera of radius 3 cm. The first intense spot outwards from centre on the $10.l$ row (the first layer) corresponds to 10.181.

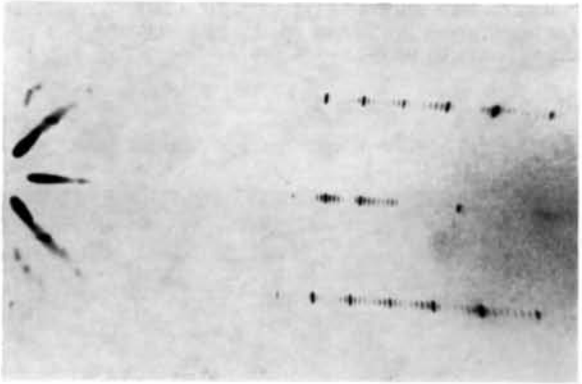

Fig. 4. 15° oscillation photograph of the $32H$ polytype of the cadmium iodide crystal about the $a$ axis, taken with Cu $K\alpha$ radiation on a camera of radius 3 cm. The first intense spot outwards from centre on the $10.l$ row (the first layer) corresponds to 10.48.

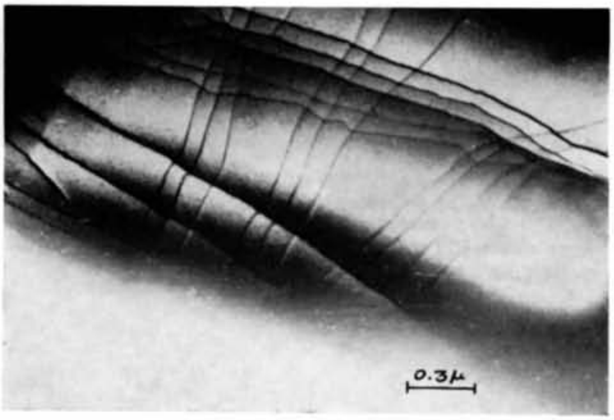

Fig. 5. Electron micrograph of $CdI_2$ crystals, widely dissociated dislocations in the form of twofold, threefold and fourfold ribbons.

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

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

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

$(B\gamma A)\ (C\beta A)\ (B\gamma A)\ (C\beta A)\ (B\gamma A)$
$(C\beta A)\ (C\alpha B)\ (C\beta A)\ (C\alpha B)$
$a=b=4\cdot24$, $c=81\cdot1$ Å.

We have reported only the atomic sequence and not the atomic coordinates as they can be derived from atomic sequence itself.

A look at the Zhdanov symbols of the polytypes indicates that these polytypes can be thought of as resulting from a basic 4*H* structure through the occurrence of stacking faults in it. This point will be analysed in detail later. There will be a large number of ways in which stacking faults may occur to produce a 60*R* from 4*H*. However, based on energy considerations it seems very probable that the sequence which has minimum stacking fault energy will be the most stable one and will represent the true atomic sequence of the 60*R* polytype. In order to test this, we calculated theoretical stacking fault energies for several possible atomic sequences representing the 60*R* polytype. The theoretical fault energies were calculated employing the procedure outlined by Hirth & Lothe (1968). The fault energy is simply represented by the number of pairs of separation $N$ which are not in the proper stacking sequence, multiplied by the distortional energy $\psi_N$ per pair. The fault entropy and specific surface free energy of the faults are neglected. Table 1 shows the stacking fault energies calculated for sequences which contain a large number of (22) units and which represent a rhombohedral polytype. We have considered only one third of the sequence, since, in the rhombohedral case, once this is determined the remaining sequence is automatically determined (Verma & Krishna, 1966). From Table 1 it is clear that the sequence $[(22)_31223]_3$ represents the minimum stacking fault energy; this is also the sequence determined from X-ray intensities. It is to be noted that as expected the stacking fault energies based on second nearest neighbour consideration are the same for all the sequences and the differences arise only when we consider third and fourth nearest neighbours. The above analysis of calculating theoretical stacking fault energies immediately indicates the usefulness of such calculations. Evaluation of stacking fault energies for 72*R* which has the Zhdanov symbol $[(22)_41223]_3$ gave similar results. In order to test the general usefulness of the above procedure, we calculated the atomic sequence of a 4*H* based new hexagonal polytype 32*H*. Fig. 4 represents this polytype. Table 2 shows the stacking fault energies for the sequences having a proper weightage of (22) units. The two structures representing minimum stacking fault energies are $(22)_53333$ and $(22)_5321123$; the first sequence does not seem very probable since unlike silicon carbide many (33) units are not found to exist in the atomic sequence of polytypic structures. Intensities for the $(22)_5321123$ were calculated and comparison of this with the observed intensities showed that the sequence represented the correct structure. Table 5 shows the comparison between calculated and observed intensities. In order to verify further, the intensities of some important reflexions were calculated for the sequences $(22)_53333$ and $(22)_5231132$; these structures

Table 3. *Observed and calculated intensities for the structure 60R of cadmium iodide*

| 10.*l* | Calculated intensity | Observed† intensity | 10.*l* | Calculated intensity | Observed† intensity |
|---|---|---|---|---|---|
| 1 | 8·2 | Region of high absorption X-ray diffraction spots could not be observed | 61 | 9·9 | *vvw* |
| 4 | 159·5 | | 64 | 7·1 | *vvw* |
| 7 | 28·3 | | 67 | 7·8 | *vvw* |
| 10 | 101·5 | | 70 | 4·4 | *vvw* |
| 13 | 709·1 | *ms** | 73 | 20·6 | *w* |
| 16 | 426·1 | *w** | 76 | 121·5 | *s* |
| 19 | 172·0 | *w** | 79 | 8·8 | *vvw* |
| 22 | 37·9 | *w* | 82 | 5·8 | *vvw* |
| 25 | 44·9 | *w* | 85 | 5·7 | *vvw* |
| 28 | 117·8 | *ms* | 88 | 22·4 | *vw* |
| 31 | 1000·0 | *vvs* | 91 | 102·0 | *s* |
| 34 | 48·0 | *w* | 94 | 5·6 | *vvw* |
| 37 | 16·6 | *vvw* | 97 | 0·6 | *a* |
| 40 | 27·9 | *vw* | 100 | 4·5 | *a* |
| 43 | 92·8 | *ms* | 103 | 19·6 | *vw* |
| 46 | 429·9 | *vs* | 106 | 4·1 | *a* |
| 49 | 22·9 | *vw* | 109 | 0·2 | *a* |
| 52 | 3·1 | *a* | 112 | 1·4 | *a* |
| 55 | 18·4 | *vvw* | 115 | 0·3 | *a* |
| 58 | 85·5 | *ms* | 118 | 0·3 | *a* |

* The absorption is abnormally high for these reflexions because of the plate-like shape of the crystal.

† As mentioned in the text, the observed intensities were actually taken for the spots 10.120 to 10.240. This series has the same intensity sequence as 10.0 to 10.120.

showed severe discrepancies between observed and calculated intensities and this showed the correctness of the proposed structure. The above analysis regarding the calculation of structure of 32*H* shows that the minimum stacking fault energy criterion may be of great help in determining atomic structure sequence of the polytypes. As no statistical data have been collected so far, the minimum theoretical stacking fault energy criterian can be treated at best as tentative only.

## Discussion

The atomic structures of the two polytypes, as is clear from their Zhdanov symbols, are very similar and in fact the polytypes can be thought as two members of the structural series $[(22)_n1223]_3$. The present polytypes have $n=3$ and 4 and in view of the frequent existence of structural series, it is likely that other members of the series will be found in future. In the following we will show that a similar sequence of stacking faults is necessary for the generation of the various polytypes of the series and this gives further credence to the existence of the proposed structural series.

It is generally agreed that the screw dislocation theory of polytypism is unable to explain the growth of most of the polytypes; however, growth of some of the polytypes can be explained based on this theory (Verma & Krishna, 1966). Also, in some cases, it is conjectured that the screw dislocations together with other dislocation may be partly responsible for the nucleation of polytypes (Bhide & Verma, 1959; Rai, 1971). Attempts to correlate the surface features with the atomic structure failed in the present case also and so we believe the present polytypes have not grown as a result of screw dislocation mechanism. It has been indicated previously by Chadha & Trigunayat (1967) that the rhombohedral polytype may grow as a result of layer-transpositions as suggested by Jagodzinski (1949 *a*,*b*). According to Jagodzinski's theory, a polytypic structure is nucleated due to layer-transposition, the resulting stacking faults and the ordering effect of the vibration entropy.

We will now describe the growth of the present polytypes based on Jagodzinski's theory. Since there is no evidence of stacking due to disorder in the diffraction patterns, we assume that the ordering effect of the vibration entropy is complete in the present polytypes. For the successful growth of the polytype, it then remains to explore the feasibility of periodic sequences of stacking faults which can create the polytypes in the present case.

Let us first consider the polytype 60*R*. We can break up the 60*R* structure sequence into three parts each consisting of 20 layers. The first part consisting of 20 layers can then be split in terms of (22) units as $(22)_3+(22)_2$. We then assume that up to the $(22)_3$ layers, the crystal grows as a 4*H* structure and then a sequence of stacking faults leads to the structure 1223. A schematic picture of the stacking fault chain is given below which creates 1223 from (22) units. The first term in the bracket on the left-hand side denotes the number of layers after which the stacking sequence changes and the second term denotes the nature of change, △ stands for cyclic change *i.e.* $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow A$ and ▽ stands for anticyclic change *i.e.* $A \rightarrow C$, $B \rightarrow A$ and $C \rightarrow B$.

Table 4. *Observed and calculated intensities for the structure* 72*R* *of cadmium iodide*

| 10.*l* | Calculated intensity | Observed† intensity | 10.*l* | Calculated intensity | Observed† intensity |
|---|---|---|---|---|---|
| 1 | 13·2 | X-ray diffraction spots could not be observed because of high absorption region. | 73 | 15·8 | *vw* |
| 4 | 10·9 | | 76 | 3·9 | *vvw* |
| 7 | 1·4 | | 79 | 6·4 | *vvw* |
| 10 | 7·6 | | 82 | 4·9 | *vvw* |
| 13 | 67·3 | | 85 | 3·2 | *vvw* |
| 16 | 342·0 | *ms** | 88 | 25·7 | *w* |
| 19 | 194·6 | *w** | 91 | 131·9 | *s* |
| 22 | 44·1 | *w* | 94 | 6·0 | *vvw* |
| 25 | 69·0 | *w* | 97 | 3·1 | *vvw* |
| 28 | 52·7 | *w* | 100 | 3·1 | *vvw* |
| 31 | 22·6 | *w* | 103 | 3·2 | *vvw* |
| 34 | 187·7 | *s* | 106 | 18·2 | *vw* |
| 37 | 1000·0 | *vvs* | 109 | 128·9 | *s* |
| 40 | 54·9 | *w* | 112 | 8·7 | *vw* |
| 43 | 13·4 | *vvw* | 115 | 1·0 | *a* |
| 46 | 60·0 | *vw* | 118 | 1·4 | *a* |
| 49 | 23·1 | *w* | 121 | 6·3 | *a* |
| 52 | 90·3 | *ms* | 124 | 16·5 | *vw* |
| 55 | 438·7 | *vs* | 127 | 5·4 | *vw* |
| 58 | 27·3 | *w* | 130 | 0·9 | *a* |
| 61 | 3·6 | *vvw* | 133 | 1·2 | *a* |
| 64 | 2·9 | *vvw* | 136 | 0·6 | *a* |
| 67 | 12·3 | *vvw* | 139 | 0·1 | *a* |
| 70 | 46·7 | *ms* | 142 | 0·0 | *a* |

* The absorption is abnormally high for these reflexions because of plate like shape of the crystal.

† Observed intensities were taken for the spots 10.144 to 10.288. This series has the same intensity sequence for 10.0 to 10.144.

$$\begin{array}{r}
A\;B\;C\;B\;A\;B\;C\;B\;A\;B\;C\;B\;A\;B\;C\;B\;A\;B\;C\;B \\
\downarrow\;\downarrow\;\downarrow\;\downarrow\;\downarrow\;\downarrow \\
\text{-------}\;(1\triangle)\;\text{-------}\,A\;C\;B\;C\;A\;C \\
\downarrow\;\downarrow\;\downarrow\;\downarrow \\
\text{--------}\;(1\triangledown)\;\text{--------}\,A\;B\;C\;B \\
\downarrow\;\downarrow \\
\text{---------}\;(1\triangle)\;\text{---------}\,A\;C
\end{array}$$

thus $(AB)\,(CB)_5$ changes to

$$(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(AC)\,(AB)\,(AC)$$

and this is the first part of the 60*R* sequence comprising 20 layers. The second part can be generated from the first part if each layer in the first part is shifted horizontally to a neighbouring orientation *i.e.* $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$. Similarly part three of the sequence can be generated from part two, the following depicts the stacking changes.

$$[(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(AC)\,(AB)\,(AC)] \quad (1)$$

The whole of the first stack shifts horizontally so that $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$

$$[(BC)\,(AC)\,(BC)\,(AC)\,(BC)\,(AC)\,(BC)\,(BA)\,(BC)\,(BA)] \quad (2)$$

The whole of the second stack shifts horizontally so that $A \rightarrow B$, $\mathrm{B} \rightarrow C$ and $C \rightarrow A$

$$[(CA)\,(BA)\,(CA)\,(BA)\,(CA)\,(BA)\,(CA)\,(CB)\,(CA)\,(CB)] \quad (3)$$

The three parts put together give the structure as follows:

$$[(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(AC)\,(AB)\,(AC)] \quad (1)$$

$$[(BC)\,(AC)\,(BC)\,(AC)\,(BC)\,(AC)\,(BC)\,(BA)\,(BC)\,(BA)] \quad (2)$$

$$[(CA)\,(BA)\,(CA)\,(BA)\,(CA)\,(BA)\,(CA)\,(CB)\,(CA)\,(CB)] \quad (3)$$

which is equivalent to the structure sequence $[(22)_3 1223]_3$.

A similar scheme can be presented for the growth of 72*R* polytype of cadmium iodide, *i.e.* we can break up 72*R* in three parts of 24 layers each. The first part of 24 layers can be split as $(22)_4+(22)_2$. Up to $(22)_4$ layers, the crystal grows as a basic 4*H* structure and then a sequence of stacking faults leads to 1223 in the same way as for 60*R*. The growth of polytype 32*H* can also be explained in a similar way; the stacking fault

Table 5. *Calculated and observed relative intensities for the structure* 32*H* *of cadmium iodide*

| 10.*l* | Calculated intensity | Observed intensity | 10.*l* | Calculated intensity | Observed intensity |
|---|---|---|---|---|---|
| 0 | 265·1 | Region of heavy absorption X-ray diffraction spots could not be observed | 33 | 23·9 | *w* |
| 1 | 204·3 | | 34 | 10·8 | *vw* |
| 2 | 19·1 | | 35 | 10·6 | *vvw* |
| 3 | 69·5 | | 36 | 18·0 | *vw* |
| 4 | 0·5 | | 37 | 16·9 | *vw* |
| 5 | 194·4 | | 38 | 7·1 | *w* |
| 6 | 20·5 | | 39 | 8·2 | *w* |
| 7 | 128·4 | | 40 | 238·2 | *s* |
| 8 | 537·9 | *s* | 41 | 50·5 | *w* |
| 9 | 51·9 | *w* | 42 | 60·0 | *a** |
| 10 | 83·0 | *w** | 43 | 39·5 | *a** |
| 11 | 31·1 | *w* | 44 | 9·9 | *vw* |
| 12 | 23·9 | *vw* | 45 | 0·6 | *vw* |
| 13 | 1·9 | *vvw* | 46 | 18·9 | *w* |
| 14 | 59·7 | *w* | 47 | 45·9 | *w* |
| 15 | 104·1 | *w** | 48 | 198·7 | *s* |
| 16 | 1,000 | *vvs* | 49 | 29·8 | *w* |
| 17 | 16·2 | *w* | 50 | 10·2 | *vw* |
| 18 | 11·2 | *w* | 51 | 0·6 | *vvw* |
| 19 | 11·5 | *vw* | 52 | 3·4 | *a* |
| 20 | 22·9 | *vw* | 53 | 8·8 | *a* |
| 21 | 35·2 | *w* | 54 | 9·5 | *a* |
| 22 | 37·5 | *w* | 55 | 6·4 | *a* |
| 23 | 39·7 | *w* | 56 | 25·0 | *w* |
| 24 | 435·5 | *s* | 57 | 1·1 | *a* |
| 25 | 62·8 | *w* | 58 | 1·1 | *a* |
| 26 | 69·0 | *w* | 59 | 0·8 | *a* |
| 27 | 50·1 | *vw** | 60 | 0·3 | *a* |
| 28 | 22·9 | *vw* | 61 | 0·1 | *a* |
| 29 | 10·5 | *vw* | 62 | 0·1 | *a* |
| 30 | 21·1 | *w* | 63 | 0·0 | *a* |
| 31 | 39·1 | *w* | 64 | 0·1 | *a* |
| 32 | 102·6 | *s* | | | |

* The absorption is abnormally high for these reflexions because of plate like shape of the crystal.

sequence creates 321123 out of $(22)_3$. It is to be noted that a scheme similar to ours has been put forward by Mardix, Kalman & Steinberger (1969) to explain the growth of ZnS polytypes. However, their work relates to transformation of polytypes in the same crystal and not to the growth of different polytypes. Also, their scheme always envisages stacking faults at equal intervals and up to a certain step the layers slip in a clockwise direction and for the rest of the steps in an anticlockwise direction, and this sequence of slip repeats periodically. The present scheme assumes only periodic stacking faults; the faults may not be at equal intervals as for example in the case of 32*H*. Moreover, the slip of layers is always alternately in clockwise and anticlockwise directions. Such a scheme of layer transposition is possible only when suitable partial dislocations, which nucleate stacking faults, sweep the basal plane; the sweeping occurs in the sequence after certain regular period in the parent structure. In order to find out whether chains of basal stacking faults occur in cadmium iodide crystals, we tried to observe the crystals directly in the electron microscope. Since cadmium iodide crystals are extremely susceptible to electron beam damage, it is not usually possible to observe the dislocation pattern in these crystals. However, by improving the thermal contact of the crystal with the specimen grid and employing full excitation of condenser lenses, we were able to observe the dislocation patterns in nearly 60% of the crystals. It is, however, not always possible to study completely each individual crystal. We found that dissociation of basal dislocations producing twofold, threefold and fourfold ribbons usually took place in all the crystals observed. Fig. 5 represents a typical example of twofold, threefold and fourfold partial ribbons. Thus it seems reasonable to believe that sequences of partial ribbons producing stacking faults occur in the cadmium iodide crystals and a regular sequence of stacking faults creating a polytype can easily occur. This lends support to the scheme of the growth of the polytypes that we have presented. Finally the determination of probable structure of a polytype based on calculation of theoretical stacking fault energy seems to be a new approach which needs to be explored further. Also the minimum stacking fault energy criterion lends credence to the above explanation of growth of polytypes in terms of creation and ordering of stacking faults.

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# Calculation of the Intensity of Secondary Scattering of X-rays by Non-crystalline Materials

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Equations that require numerical integration over only one variable were derived for calculating the intensity of secondary scattering of X-rays for non-crystalline samples of finite thickness. Both the reflection and transmission geometry cases were considered. Tables are given that allow the intensity ratio of secondary to primary scattering to be determined without making lengthy calculations. Modification of the normalization procedure when secondary scattering is important is discussed.

## Introduction

In studies of high molecular weight, petroleum-related, non-crystalline organic solids it was necessary to correct for secondary scattering. Warren & Mozzi's (1966) method of calculating secondary intensity for reflection geometry using samples of effective infinite thickness could not be used, because it was desired to use thin samples to avoid certain smearing corrections (Bragg & Packer, 1963; Keating & Warren, 1952) in the high angle scattering region. It also was desired to make secondary scattering corrections for trans-

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