Acta Cryst. (1972). A28, 494

On the Occurrence of Zhdanov Numbers 1, 2 and 3 in the Zigzag Sequence of Cadmium Iodide Polytypes

By R. Prasad and O. N. Srivastava

Department of Physics, Banaras Hindu University, Varanasi-5, India

(*Received* 26 *January* 1972)

It has been shown that the occurrence of only three Zhdanov numbers, 1, 2 and 3, in the zigzag sequence of cadmium iodide polytypic structures is not accidental but is directly attributable to the fact that the formation of cadmium iodide polytypes takes place through creation and ordering of stacking faults in the basic structure.

Introduction

Although in all the work relating to structure determination of cadmium iodide polytypes a limitation is put on the occurrence of the Zhdanov numbers and it is assumed that only three numbers 1, 2 and 3 should be present in the zigzag sequence (Zhdanov sequence), Srivastava & Verma, 1964, 1965; Verma & Krishna, 1966; Prasad & Srivastava, 1970*a*, 1971*a*), there seems to be no explanation available capable of explaining this fact. The purpose of this paper is to point out that the aforesaid limitation on Zhdanov numbers in cadmium iodide polytypes is a natural consequence of the well established result that cadmium iodide polytypes are formed due to creation and ordering of stacking faults in accordance with Jagodzinski's layer transposition mechanism (Jagodzinski, 1954; Prasad & Srivastava, 1971*a*, *b*; Trigunayat, 1971; Chadha & Trigunayat, 1967).

Results and discussion

We now proceed to show that when the genesis of CdI_2 polytypic structure is analysed in the light of the transposition mechanism, it becomes obvious that the possible Zhdanov numbers are limited to 1, 2 and 3. The basic CdI_2 structure is $4H$, whose structure is represented by the sequence (22) or $(A\gamma B)$ $(C\alpha B)$ where A, B, C represent the positions of iodine layers and α, β, γ the positions of cadmium layers. The basic structure thus consists of two sandwiches $(A\gamma B)$ and $(C\alpha B)$. Keeping in mind the fact that the orientation of the cadmium layer in between the iodine layers is automatically fixed (the orientation of the cadmium layer is always different from the two iodine layers in which it is sandwiched), the sandwich configuration for $4H$ basic structure can be written as $A\ B\ C\ B$. The creation of stacking faults bounded by partials is equivalent to a slip of one close-packed layer over the other; the slip vector being of the type $\mathbf{a}/3\ \langle 11\bar{2}0\rangle$. This slip amounts to a change in orientation of the close packed layers, *e.g.* $A\rightarrow B$, $B\rightarrow C$, $C\rightarrow A$ (we will represent this type of change in sequence, which may be considered as cyclic change, by the symbol $\triangle$) and $A\rightarrow C$, $B\rightarrow A$, $C\rightarrow B$ (this type of anticyclic change may be represented by the symbol ∇). It is also shown that the occurrence of stacking faults is more favourable when the slip or glide takes place between iodine layers (I/I glide) in comparison to the stacking faults which occur as a result of slip or glide between cadmium and iodine layers (Siems, Delvignette & Amelinckx, 1964; Prasad & Srivastava, 1970*b*); Prasad, 1971). The occurrence of stacking faults through I/I glide is much more feasible than those produced through Cd/I because the former produces a low-energy stacking-fault sequence. It can easily be seen that I/I glide implies that the glide plane is situated between the sandwiches and for Cd/I glide, it is within the sandwich. Based on the above described criterion the most likely stacking configuration in one unit (two sandwiches) of the basic structure is represented by the following:

$$\begin{array}{cccc} A & B| & C & B \\ (\triangle) & & \downarrow & \downarrow \\ & & A & C \\ \hline A & B & A & C \\ \hline \end{array} \qquad \begin{array}{c} \text{(i)} \\ \\ \\ \text{(ii)} \end{array}$$

In the above scheme the vertical line indicates the position of glide plane and $(\triangle)$ represents the cyclic nature of the change in the sequence of layers *i.e.* $A\rightarrow B$, $B\rightarrow C$, $C\rightarrow A$. The resulting sequence depicted by (ii) represents the basic $4H$ structure itself. It can be noted that the creation of stacking faults in one unit of the basic $4H$ structure through Cd/I glide leads to sequences which are energetically unfavourable This is shown by the following. Since Cd/I glide is involved, the orientation of cadmium layers has also been indicated.

$$\begin{array}{cc} A|\gamma B & C\alpha B \\ \downarrow\downarrow & \downarrow\downarrow\downarrow \\ \alpha C & A\beta C \\ \hline (A\alpha C) & (A\beta C) \\ \hline \end{array} \quad \text{(iii-}a\text{)} \qquad \begin{array}{cc} A|\gamma B & C\alpha B \\ \downarrow\downarrow & \downarrow\downarrow\downarrow \\ \beta A & B\gamma A \\ \hline (A\beta A) & (B\gamma A) \\ \hline \end{array} \quad \text{(iv-}a\text{)}$$

$$\begin{array}{cc} A\gamma|B & C\alpha B \\ \downarrow & \downarrow\downarrow\downarrow \\ C & A\beta C \\ \hline (A\gamma C) & (A\beta C) \\ \hline \end{array} \quad \text{(iii-}b\text{)} \qquad \begin{array}{cc} A\gamma|B & C\alpha B \\ \downarrow & \downarrow\downarrow\downarrow \\ A & B\gamma A \\ \hline (A\gamma A) & (B\gamma A) \\ \hline \end{array} \quad \text{(iv-}b\text{)}$$

```
AγB   C|αB
        ↓↓
        βC
(AγB) (CβC)     (v-a)

AγB   C|αB
        ↓↓
        γA
(AγB) (CγA)     (vi-a)

AγB   Cα|B
         ↓
         C
(AγB) (CαC)     (v-b)

AγB   Cα|B
         ↓
         A
(AγB) (CαA)     (vi-b)
```

It can be seen that the sequences represented by (iii), (iv), (v) and (vi) are all energetically quite unfavourable since these involve adjacent similar layers. Adjacent similar layers in a sequence of close-packed layers represent a very high energy configuration and are, therefore, not expected to occur, while in sequences (iv) and (v), iodine layers in similar orientations are present and in sequences (iii) and (vi) iodine and cadmium layers in similar orientation are present. These sequences are, therefore, unlikely to exist. We thus see that the possible stacking fault sequence in one unit of basic $4H$ structure does not create any new structure, it leads to basic $4H$ structure itself; this fact has been shown by the sequence represented by (ii). Let us now analyse the possible stacking fault sequences in two units (4 sandwiches) of the basic structure. These are sketched in the following, taking into account the I/I glide which creates feasible sequences.

```
A B|C B A B C B
    ↓ ↓ ↓ ↓ ↓ ↓
    A C B C A C
A B A C B C A C     (vii)
```

The sequence (vii) corresponds to Zhdanov sequence 13211 or 3212 (for details regarding the convention of writing Zhdanov sequences, refer to Verma & Krishna, 1966). It can be noted that the Zhdanov numbers present in this sequence correspond to 1, 2 and 3 only. The sequence represented by (vii) has been obtained from two units of basic structure $4H$ through the occurrence of single stacking faults; the occurrence of double and triple stacking faults is, however, also likely. The sequences created by these faults are shown schematically in the following.

(*a*) Double fault:

```
A B|C B A B C B
(△) ↓ ↓ ↓ ↓ ↓ ↓-----[(▽) not possible]
    A C B C A C
    (▽) ↓ ↓ ↓ ↓-----[(△) not possible]
        A B C B
A B A C A B C B     (viii)
```

(*b*) Triple fault:

```
A B|C B A B C B
(△) ↓ ↓ ↓ ↓ ↓ ↓-----[(▽) not possible]
    A C B C A C
    (▽) ↓ ↓ ↓ ↓-----[(△) not possible]
        A B C B
        (△) ↓ ↓-----[(▽) not possible]
            A C
A B A C A B A C     (ix)
```

In the above, [(▽) not possible] means that if anticlockwise shift of layers were considered, *i.e.* if the shift corresponded to $A \rightarrow C$, $B \rightarrow A$, $C \rightarrow B$, adjacent layers in similar orientation will be present; these sequences are, therefore, not possible; similar reasoning holds good for [(△) not possible]. The sequence (viii) corresponds to Zhdanov sequence 1232 which again represents $8H$ structure. The sequence (ix), however, represents the basic structure $4H$ corresponding to the sequence (22). While considering the above sequences, the I/I glide was taken to occur after the first sandwich; the I/I glide can also take place after two and three sandwiches, leading to other possible sequences. These situations are described below.

(*a*) Single fault:

```
A B C B|A B C B
    (▽) ↓ ↓ ↓ ↓-----[(△) not possible]
        C A B A
A B C B C A B A     (x)
```

(*b*) Double fault:

```
A B C B|A B C B
    (▽) ↓ ↓ ↓ ↓-----[(△) not possible]
        C A B A
        (△) ↓ ↓-----[(▽) not possible]
            C B
A B C B C A C B     (xi)
```

(*c*) Single fault:

```
A B C B A B|C B
        (△) ↓ ↓-----[(▽) not possible]
            A C
A B C B A B A C     (xii)
```

For the positions of the glide planes indicated by vertical lines it is evident that only single and double faults are possible for the position after two sandwiches and only a single fault is possible for the position after three sandwiches. The sequence shown in (x) is unstable (similar AA layers will be adjacent); the sequence in (xi) corresponds to the Zhadanov sequence 2123 and that in (xii) corresponds to 22121 which is equivalent to 2123. Here again we find that the numbers in the Zhdanov sequence for the possible sequences are confined to 1, 2 and 3. It should be noted that although all the three possible sequences 3212, 1232 and 2123 corresponding to (vii), (viii) and (xi) respectively represent the same periodicity, *i.e.* all of these represent the 8*H* polytype, the atomic structures (layer sequences) of these three 8*H* polytypes would be different since their Zhdanov sequences are different. This is in keeping with the experimentally established fact that in cadmium iodide each of the known polytypes has several structural variants (Srivastava & Verma, 1964, 1965; Trigunayat & Chadha, 1971).

It is thus clear that when polytypic structures are created by the occurrence of possible stacking faults in two units of basic 4*H* structure, the Zhdanov sequence of the structures always contains only three numbers, namely 1, 2 and 3. It will be worthwhile to analyse the resulting structures in two units of basic structure through the creation of stacking faults by I/I glide in conjunction with Cd/I glide. As shown previously, the Cd/I glide alone is not feasible since it leads to energetically unfavourable sequences. A possible sequence resulting through Cd/I together with I/I glide is shown in the following.

$$
\begin{array}{rrrrl}
A\gamma B & C\alpha B & A\gamma|B & C\alpha B & \\
 & & \downarrow & \downarrow\downarrow\downarrow & \text{(Cd/I glide)} \\
 & & C| & A\beta C & \\
 & & & \downarrow\downarrow\downarrow & \text{(I/I glide)} \\
 & & & B\gamma|A & \\
 & & & \downarrow & \text{(Cd/I glide)} \\
 & & & C & \\
\hline
(A\gamma B) & (C\alpha B) & (A\gamma C) & (B\gamma C) & \text{(xiii)} \\
\hline
\end{array}
$$

The above sequence is equivalent to Zhdanov sequence 242 which is equivalent to 44. This sequence is, however, energetically quite unfavourable since it has two sandwiches $(A\gamma C)$ and $(B\gamma C)$ where cadmium and iodine layers of similar orientation are adjacent. This reveals that the occurrence of a Zhdanov number other than 1, 2 and 3 (in the present case the number under consideration being 4) involves energetically unfavourable sequences and hence is not possible. It may be mentioned in passing that unlike the present case, in silicon carbide and zinc sulphide polytypes Zhdanov number 4 is most often encountered. Several other combinations of I/I + Cd/I glide in two units of basic 4*H* structure lead to sequences which have characteristics similar to that represented by (xiii); these often contain Zhdanov number 4 and also higher numbers but are not energetically possible.

The above results derived for two units of basic 4*H* structure can easily be extended to the cases of three and more basic units. The following lists various structures developed at different stages of stacking fault sequence (single and higher order faults) through I/I glide in three units of basic 4*H* structure.

A B A C B C A C B C A C (for glide after one sandwich) (xiv)

This is equivalent to Zhdanov sequence 322212 and corresponds to polytypic structure 12*H*.

A B A C A B C B A B C B (for glide after two sandwiches in structure xiv) (xv)

This is equivalent to Zhdanov sequence 123222 and corresponds to 12*H*; since the Zhdanov sequence for this is different from that in (xiv), the atomic structure (layer sequence) of this 12*H* polytype is different from that shown in (xiv).

A B A C A B A C B C A C (for glide after three sandwiches in structure xv) (xvi)

This corresponds to 223212 and is equivalent to 12*H* polytypic structure; this 12*H* is different than those in (xiv) and (xv).

A B A C A B A C A B C B (for glide after four sandwiches in structure xvi) (xvii)

This corresponds to basic 122232 and resembles the 12*H* structure given in (xvi).

A B A C A B A C A B A C (for glide after five sandwiches in structure xvii)

This is equivalent to basic structure 4*H* having the sequence 22.

The three sequences represented in (xiv), (xv) and (xvi) again reveal the fact that the only Zhdanov numbers which occur in cadmium iodide polytypic structures are 1, 2 and 3. The results obtained for other combinations of I/I glide in *n* basic units suggest the same result. It should be noted that when the above sequences which represent possible polytypic structures are analysed in terms of the occurrence of polytypic structural series (Prasad & Srivastava, 1971*c*) it becomes obvious that when these, instead of occurring individually, occur in conjunction with one or more units of basic structure, the corresponding polytypic structure series are generated. As, for example, the sequence represented by (vii) would result in the genesis of the polytypic structure series $(22)n$ 3212 with $n = 1, 2, 3, \ldots$, when the sequence of faults leading to (vii) would occur in conjunction with *n* units of the basic 4*H* structure *i.e.* with $(22)n$.

Conclusion

The results obtained in the preceding sections make it evident that the occurrence of three Zhdanov numbers

1, 2 and 3 in the sequences of cadmium iodide polytypic structures is understandable on the basis of formation of polytypes in terms of the creation of possible stacking faults in the basic structure. The occurrence of higher Zhdanov numbers is forbidden because these lead to sequences which involve adjacent layers in similar orientations; the higher Zhdanov numbers are, therefore, not feasible. Although the present investigation is confined to the understanding of the occurrence of certain specific Zhdanov numbers in cadmium iodide polytypic structures, similar analysis can be developed for the preponderance of certain specific Zhdanov numbers in polytypic crystals which have their basic structures resembling that of cadmium iodide, such as lead iodide, cadmium bromide *etc.*

The authors are thankful to Dr G. S. Verma, Head of the Department of Physics, Banaras Hindu University, Varanasi-5 and to Dr A. R. Verma, Director, National Physical Laboratory, New Delhi for their interest in the present work. The present work has been carried out with financial support from the Council of Scientific and Industrial Research, New Delhi.

References

CHADHA, G. K. & TRIGUNAYAT, G. C. (1967). *Acta Cryst.* **22**, 573.
JAGODZINSKI, H. (1954). *Acta Cryst.* **7**, 300.
PRASAD, R. (1971). Ph.D. Thesis, Banaras Hindu University.
PRASAD, R. & SRIVASTAVA, O. N. (1970*a*). *Z. Kristallogr.* **131**, 376.
PRASAD, R. & SRIVASTAVA, O. N. (1970*b*). *J. Phys. D: Appl. Phys.* **3**, 91.
PRASAD, R. & SRIVASTAVA, O. N. (1971*a*). *Acta Cryst.* A**27**, 259.
PRASAD, R. & SRIVASTAVA, O. N. (1971*b*). *J. Appl. Cryst.* **4**, 516.
PRASAD, R. & SRIVASTAVA, O. N. (1971*c*). *Z. Kristallogr.* In the press.
SIEMS, R., DELVIGNETTE, P. & AMELINCKX, S. (1964). *Phil. Mag.* **9**, 121.
SRIVASTAVA, O. N. & VERMA, A. R. (1964). *Acta Cryst.* **17**, 260.
SRIVASTAVA, O. N. & VERMA, A. R. (1965). *Acta Cryst.* **19**, 56.
TRIGUNAYAT, G. C. & CHADHA, G. K. (1971). *Phys. Stat. Sol. (a)*, *4*, 9.
TRIGUNAYAT, G. C. (1971). *Phys. Stat. Sol. (b)*, **4**, 281.
VERMA, A. R. & KRISHNA, P. (1966). *Polymorphism and Polytypism in Crystals.* New York: Wiley.

Acta Cryst. (1972). A**28**, 497

Twinning in 5,5'-Biisoxasole

BY M. CANNAS, G. CARTA AND G. MARONGIU
Istituto Chimico dell'Università, 09100 *Cagliari, Italy*

(*Received* 22 *March* 1972)

Weissenberg photographs from triclinic 5,5'-biisoxasole are explained in terms of three twinning laws defined as [001], (100) and (010). A structural interpretation of the twins is proposed using the results of the structure determination.

In a previous paper (Cannas & Marongiu, 1968) the crystal structure of 5,5-biisoxasole, determined by three-dimenisional X-ray diffraction data, was reported.

Crystal data

5,5'-biisoxasole $C_6H_4N_2O_2$, M.W. 136·11, m.p. 161 °C, $a=10{\cdot}47\pm0{\cdot}02$, $b=9{\cdot}01\pm0{\cdot}02$, $c=3{\cdot}78\pm0{\cdot}01$ Å,

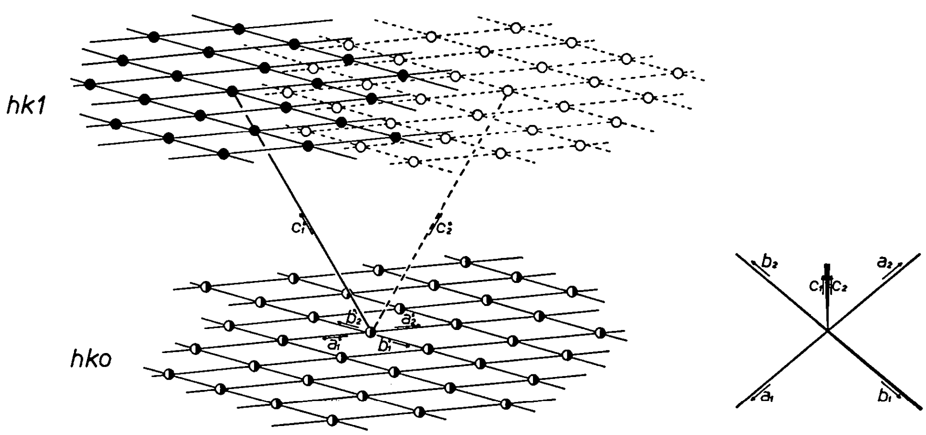

Fig. 1. The relative disposition of the reciprocal lattices of the two individuals in twinning I is shown on the left. On the right is given the relative orientation of the direct axes.