

The crystallographic twofold axes at $x = \frac{1}{4}$, $y = \frac{1}{4}$, and $x = \frac{3}{4}$, $y = \frac{3}{4}$ are those running through the center of the dimeric units and these units are layered approximately perpendicularly to the z direction (Fig. 2). The distance between these layers is nearly 3.7 Å, a value typical of layered aromatic structures. Distances between dimeric units in the same layer approximate those values expected for van der Waals contacts, the shortest being 2.39 between H(3) and H(7). All short intermolecular contacts are listed in Table 6.

It is interesting to speculate on the structural changes that may occur in the transformation of the low-melting form to the high-melting form of di-(2-pyridyl)amine. If the ring containing N(1) is rotated about the N(2)–C(5) bond to attempt to bring N(1) and H(10) into proximity, the distance between H(4) and H(7) would be reduced to approximately 1.6 Å, making this an unacceptable configuration. This steric interaction could be relieved by a change from the planar geometry about the amine nitrogen to one approximating a tetrahedron (including the lone pair of electrons). If this change does account for the increased stability then it is likely due to more favourable packing of dimers than the actual strengthening of the dimeric unit, since in the melting process one would expect the van der Waals forces to be overcome before the dimer is destroyed.

With the structural data presently available for transition metal complexes with di-(2-pyridyl)amine, it is not possible to make a meaningful comparison between the coordinated and free ligand. It is hoped that future structure determinations (X-ray and/or neutron) of metal complexes with this ligand will provide structural parameters of sufficient accuracy to allow meaningful comparisons to be made.

Acta Cryst. (1973). B29, 1674

Feeble Occurrence of Polytypism Based on the 2H Basic Phase in Cadmium Iodide Crystals

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(Received 29 January 1973; accepted 19 March 1973)

In cadmium iodide, the most stable phase is the 4H structure. The next stable phase is the two-layered hexagonal structure known as the 2H polytype. Most of the polytypes of cadmium iodide are generally found to result from the 4H basic structure; but there seem to be only a few polytypes which are based on the 2H basic structure. The rare occurrence of polytypic structures based on the 2H basic phase seems somewhat strange and, until now, there seems to have been no explanation of this strange behaviour of CdI₂ polytypes. The purpose of this communication is, therefore, to explain this salient feature of cadmium iodide polytypes.

Recently Prasad & Srivastava (1972) have shown that the polytypes of cadmium iodide based on the 4H basic structure are formed through a layer-transposition

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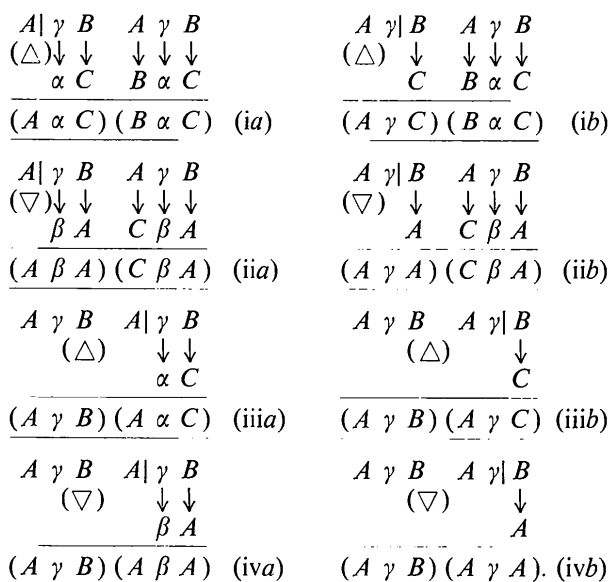
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mechanism involving only I/I glide and that the Cd/I glide produces structures which are energetically unfavourable. If the same idea is applied to the crea-

tion of polytypes from the $2H$ structure, it is found that the polytypic structures from $2H$ can be formed only when there is a very high density of ordered stacking faults.

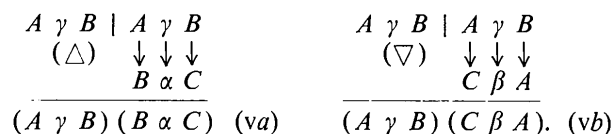
Results and discussion

The basic structure of the $2H$ polytype of cadmium iodide is (11) or $(A \gamma B)$. Taking more than one unit cell, it may be written as $(A \gamma B) (A \gamma B) (A \gamma B) \dots$ where A , B and C represent the position of the iodine layers and α , β and γ the position of the cadmium layers. Taking into account the fact that the orientation of the cadmium layer in an I–Cd–I sandwich is always different from the orientation of the two iodine layers in which it is sandwiched, the structure of the $2H$ phase can be written simply as AB or $ABABAB \dots$ for $(A \gamma B)$ or $(A \gamma B) (A \gamma B) (A \gamma B) \dots$. In the case of the $2H$ or $(A \gamma B) (A \gamma B) \dots$ structure, it is seen that not only the Cd/I glide, but also the operation of the I/I glide are not feasible up to a certain number of $2H$ units, and hence no polytypic structures should exist based on the $2H$ basic structure in cadmium iodide involving a low density of ordered stacking faults. The following represents the schematic representation of different glides in two units of the $2H$ structure:



In the above scheme, Δ denotes the cyclic change, *i.e.* $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow A$, $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, $\gamma \rightarrow \alpha$ and ∇ denotes the anticyclic change, *i.e.* $A \rightarrow C$, $B \rightarrow A$, $C \rightarrow B$, $\alpha \rightarrow \gamma$, $\beta \rightarrow \alpha$, $\gamma \rightarrow \beta$. The vertical line indicates the position of a glide plane. The above schematic representation deals with the Cd/I glide. It occurs in all the created structures from (ia) to (ivb), and therefore these structures are not energetically possible. All the above structures contain adjacent layers in the same orientation. The structure (ia), the sandwich $(A \alpha C)$, structure (ib), the sandwich $(A \gamma C)$, structure (iia), the sandwich $(A \alpha C)$ and the structure

(iiib), the sandwich $(A \gamma C)$ contain cadmium and adjacent iodine layers which are in the same orientation. Similarly, the structures (iia), (iib), (iva) and (ivb) contain adjacent iodine layers in the same orientation. Therefore all these structures are not possible. The above scheme deals only with the Cd/I glide in 2 units and now we will see the effect of I/I glide in 2 units of the $2H$ structure:



In the above scheme, the structures (va) and (vb) can be written for simplicity as $ABBC$ and $ABCA$ respectively. In these structures the adjacent iodine layers are in the same orientation and hence these structures are also not energetically possible. When the above mechanism was extended to the three units of $A \gamma B$ or AB , the following results were obtained.

A single fault gives the structures $ABBCBC$ and $ABCACA$. In the former structure, the two iodine layers in the B orientation and, in the latter structure, the two iodine layers in the A orientation are adjacent. Hence both the structures are energetically not possible. A double fault in three units of AB gives the structures $ABBCCA$, $ABBCAB$, $ABCAAB$ and $ABCABC$. We thus see that all the structures created through a double fault in three units of $2H$ are not possible either, since adjacent iodine layers are in the same orientation. The last sequence $ABCABC$ seems to be a structure that can be created out of (11) or $ABAB \dots$ units. Although this looks a possible structure since no adjacent iodine layers are in a similar orientation, the structure is actually purely cubic, or a $3C$ structure. Since cadmium iodide has the structure $(A \gamma B) (A \gamma B) \dots$, in which there is a strong binding between cadmium and iodine layers, *i.e.* within the sandwich $A \gamma B$, it appears very difficult to break the I–Cd–I sandwich. In other words, a polytype having an odd number of layers in its unit cell cannot be created from any basic structure, *e.g.* $2H$, $4H$ etc. The three-layered cubic structure $ABCABC \dots$ created by I/I glide is, therefore, not possible. We thus see that up to three units of $(A \gamma B)$, the stacking faults created through I/I glide or Cd/I glide are unable to create any new polytypic structure. We now give the results obtained when the above mechanism involving the I/I glide is applied to 4 units of $2H$.

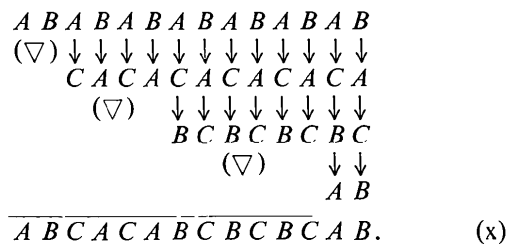
A single fault in four units of $2H$ or (11) produces the structure $ABCACACA$. In this structure, the two adjacent iodine layers are in the A orientation and hence the structure is not energetically favourable. A double fault produces the structures $ABCABCBC$ or 512, which is equivalent to (17), and $ABCACABC$ or 314, which is also equivalent to (17). A triple fault produces the structure $ABCABCAB$ or (71). Thus we see that

double and triple faults seem to produce a single new structure which is (17) in Zhdanov notation.

The structure (17) contains a large Zhdanov number 7 in its zigzag sequence. Large Zhdanov numbers are usually not found in cadmium iodide polytypes. All the known structures of cadmium iodide polytypes possess Zhdanov numbers limited to only 1, 2 and 3 in their zigzag sequence (Prasad & Srivastava, 1972). Also from the point of view of stacking-fault energy, the structural sequences containing a very high Zhdanov number and based on (11) or $ABAB\dots$ are not permissible as these will have a very high stacking-fault energy (Prasad & Srivastava, 1971). It is therefore expected that the creation of the structure having a sequence like (17) is not possible.

It should be mentioned in passing that a large number of polytypes are created from the 2H structure of ZnS during the $2H \rightarrow 3C$ phase transformation (Daniels, 1965). This is firstly because of the structural differences between ZnS and CdI_2 and secondly because of the role of growth faults in ZnS crystals (Rai, 1971). The growth faults or intrinsic stacking faults are manifested by the presence of point defects in the form of vacancies. It has been verified by Forty (1960, 1961) that the point defects in lead iodide crystals, which are isostructural with cadmium iodide crystals, are in the form of molecular vacancies. It therefore seems reasonable to assume that the growth faults in CdI_2 crystals will also be in the form of molecular vacancies. The molecular vacancy created in the 2H structure of CdI_2 crystals having the structure $A \gamma BA \gamma BA \gamma B \dots$ will leave the structure as such and will have no influence in producing a new polytypic structure.

We will now see the effect of layer transpositions in a large number of 2H units and investigate whether it can lead to the formation of polytypic structures which are energetically economic and contain the Zhdanov numbers within the allowed limits. The following depicts the scheme for a large number (seven for example) of basic 2H units.



The structure produced at (x) as a result of the I/I glide in 7 units is $ABCACABCBCBCAB$ or 31311131. This structure is probable in the sense that (i) it is energy-

tically economic, *i.e.* no two adjacent layers are in similar orientation, and (ii) it contains the Zhdanov numbers limited to 1, 2 and 3 only. A few other structures which are energetically economic are also possible through a different scheme of stacking faults in 7 units.

It is now clear that the formation of polytypic structures from the 2H basic phase requires a high density of stacking faults. A low density of stacking faults does not seem valid. The creation of a high density of ordered stacking faults in the basic phase seems to be difficult as compared with the creation of a low density of ordered stacking faults. Had the low density of ordered stacking faults (stacking faults in 2 or 3 units or so) been able to produce new structures, the basic phase 2H would also have been as active, in principle, as that of the 4H basic phase in producing the polytypic structures. Since a high density of ordered stacking faults seems to be rarely encountered, the polytypes based on the 2H phase should be rare and this is in keeping with experimental observations. It should be pointed out here that the polytypes resulting from the 4H basic phase and involving a very high density of ordered stacking faults are also rare.

The results obtained in the preceding discussion show that the rare occurrence of polytypic structures based on the 2H basic phase is easily understandable if it is taken that the polytypes of cadmium iodide are formed through layer transposition involving ordered stacking faults in the basic structure. This is because, when stacking faults occur in a limited number of 2H units, the sequences which are energetically improbable are produced. Structures based on the 2H phase are possible when the stacking faults occur in a large number of 2H units. This is less probable and, therefore, the rare occurrence of polytypic structures based on the 2H phase is obvious.

The author is thankful to Dr O. N. Srivastava, Physics Department, Banaras Hindu University and to Dr A. R. Verma, Director, National Physical Laboratory, New Delhi, India for their interest in the present work.

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