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# Solid State Structural Changes at High Temperatures in Cadmium Iodide

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Further experiments on the heating of polytypic crystals of cadmium iodide at high temperatures have yielded more information on the kinetics of stacking faults existing in the crystals and their role in structural transformations and polytype formation. The streaking of X-ray reflections progressively decreases in successive heating runs, showing that random stacking faults resulting from partial dislocations are gradually eliminated and that no fresh dislocations are created by heating. On the other hand, the extent of arcing of the reflections always increases, implying that more dislocations, both unit and partial, which had been earlier held up against some obstacles, move into existing tilt boundaries. The arc stays practically unchanged during further heating runs, thus indicating that the process of heating does not produce fresh dislocations and that no further significant movement of the dislocations takes place. The common type 4H has been established as the phase of maximum thermodynamic stability. The successive phase transformations in a crystal have revealed a systematic elimination of the stacking faults. The long period polytypes have been found to be thermally more stable than the short period polytypes.

## Introduction

Recent experimental studies have shown that stacking faults play a vital role in the formation of polytypes (*1*, *2*). Therefore, the knowledge of their kinetics in the growth and transformation of polytypes is useful in understanding the origin of polytypism. Most of the investigations in this direction have been made by heating the polytypic crystals at high temperatures. Some results on solid state transformations in cadmium iodide crystals, heated well below their melting point, have been reported earlier (*3*, *4*). More results, now extending over nearly 160 polytypes, have become available in the meantime, from which general conclusions can be drawn regarding the kinetics of faults in these crystals.

## Experimental Methods

The cadmium iodide crystals, measuring nearly 0.5–1 mm in cross section and nearly 50–200 $\mu$m in thickness, were grown from aqueous solution at room temperature (*5*). Using a polarizing microscope, optically perfect crystals were selected for X-ray examination. An *a*-axis oscillation photograph of each crystal was taken in a suitable range of oscillation, to yield a large succession of *10.l* spots in the region of reflection (*6*). This range is particularly suited for separately identifying the two faces of a crystal, which are usually different polytypes. All photographs were taken on a 3-cm camera, using Cu$K\alpha$ radiation. Subsequently, the crystal was heated in a furnace around 260°C and then reexamined by the optical and X-ray methods. The heating run usually consisted of 1.5–2 hr. This alternate heating and X-ray analysis were repeated as many times as found necessary.

## Experimental Results

The observed structural changes in a crystal, consequent upon its heat treatment, have manifested in four different ways on the X-ray photographs: (1) change in the intensity distribution of diffraction spots, (2) change in the spacing of spots, (3) change in streaking (the phenomenon in which the reflections of same *h* and *k* but of different *l* values run into each other, thus producing streaks, the intensity of which varies from crystal to crystal), and (4) change in arcing (the phenomenon characterized by the extension of spots into small arcs in a direction perpendicular to the layer lines); the phenomena of streaking and arcing in $CdI_2$ crystals have been

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described in detail by Agrawal and Trigunayat (7). All the polytypes have been ultimately found to change, in one or more heating runs, into the common polytype 4H, the oscillation photograph of which is shown in Fig. 1. This figure, as well as the subsequent figures, depicts only the first layer line, which adequately manifests the structural changes observed upon heating a crystal. The observed changes may be briefly summed up as follows (since the crystal plates grew with one of their flat faces in contact with the bottom of the petri dish, the two faces of a crystal have been referred to as upper and lower face, respectively, in the following).

### *Changes in Streaking*

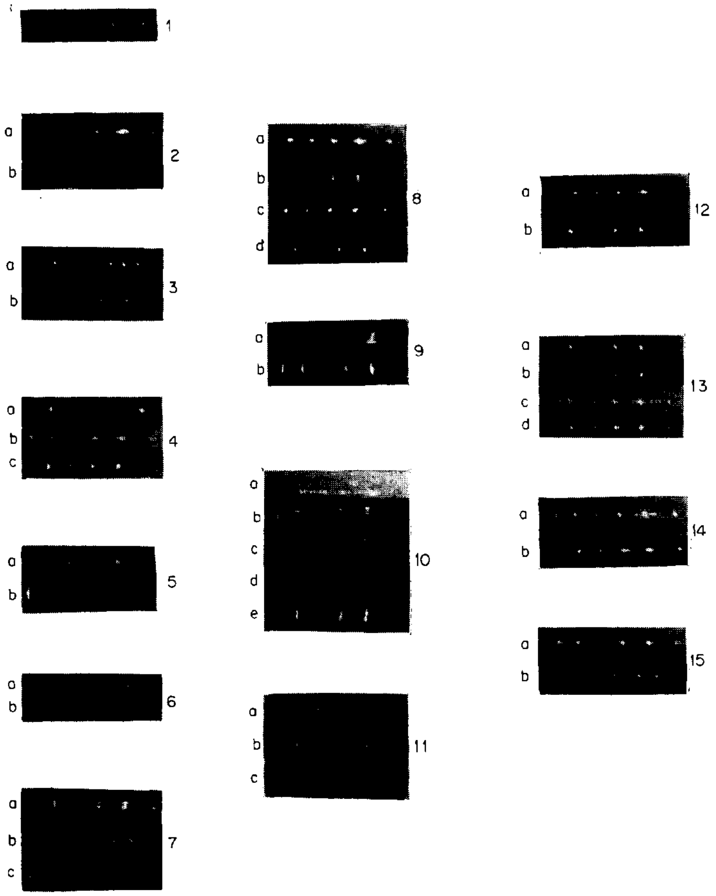
(1) The streaking generally reduces on heating a crystal and in some cases it completely disappears. One example of reduction and elimination has been depicted in Figs. 2 and 3, respectively.

(2) In about 50% of the cases, the continuous streaking has been found to become discontinuous upon heating, such that the streak is more intense near the main reflections than in between them. An example is shown in Fig. 4.

(3) The unidentified types displaying heavy streaking on their X-ray photographs invariably tend to transform into definite polytypes. An illustration is provided in Fig. 5.

(4) In a few exceptional cases, the streaking has been found to increase instead of reducing; e.g., see Fig. 6.

Besides the above structural changes observed upon heating the crystals, the following general observations have also been made: the X-ray photograph of the lower face of a crystal generally shows more intense streaks than the upper face. In the oscillation photographs of all 12R poly-



FIGS. 1-15.

types, streaks have been found to run between neighboring positions of the 12R and 4H reflections, as shown in Fig. 7.

### *Changes in Arcing*

(1) In about 50% of the cases, the oscillation photographs have shown development of arcing upon heating the crystal. A typical example is presented in Fig. 8, in which one face of the crystal showed development of arcing, but the opposite face did not.

(2) If the crystal originally displays arcing, the heat treatment has the effect of enhancing the extent of arcing. An example is presented in Fig. 9.

(3) If the arcing develops during heating, the arc length stays almost unchanged in subsequent heating runs. However, the resolution of the spots on the arcs improves, as described next. An example is shown in Fig. 10.

(4) The resolution of the spots on an arc steadily improves as the heating proceeds. If the arc looks continuous to begin with, spottiness develops upon it, so that it looks increasingly discontinuous. The effect is illustrated in the foregoing Figs. 9 and 10.

(5) In many cases the initially sharp reflections become diffuse upon heating the crystal. Each reflection may eventually split into two after more heating; e.g., see Fig. 11.

### *Polytypic Transformations*

(1) It has been observed that all polytypes, whether identified or unidentified, are ultimately transformed into the common polytype 4H upon heating. Sometimes the transformation occurs in

FIG. 1. The first layer line on an *a* axis 15° oscillation photograph of the common polytype 4H.

FIG. 2. Oscillation photograph of the lower side of a crystal (a) before heating showing reflections of the common type 4H, along with heavy streaking on the layer line; (b) after heating, showing appreciable reduction in streaking.

FIG. 3. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 8H along with moderate streaking on the layer line; (b) after heating, showing elimination of the streaking; the polytype has also transformed to 4H.

FIG. 4. Oscillation photograph of the lower face of a crystal: (a) before heating, showing heavy continuous streaking, along with reflections of an unidentified type and 2H; (b) after heating, showing discontinuous streaking; (c) after heating a second time, showing concentration of the streaks around the reflections of the type 4H, into which the original polytype has now transformed.

FIG. 5. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of an unidentified type, with heavy streaking; (b) after heating, showing reflections of the type 28H with reduced streaking.

FIG. 6. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 2H with very light streaking; (b) after heating, showing an increase in streaking.

FIG. 7. Oscillation photograph of the lower face of a crystal showing the existence of continuous streaking between successive reflections of the types 12R and 4H; (a) reflections of the type 12R and 4H are well defined; (b) the reflections of the type 4H are not well defined; (c) the reflections of the type 12R are not well defined.

FIG. 8. Oscillation photograph of the lower face of a crystal (a) before heating, showing combined reflections of the type 4H and 28H; (b) after heating, showing that arcing has developed; (c) before heating, displaying no arcing; (d) after heating, again displaying no arcing.

FIG. 9. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 18H, along with arcing; (b) after heating, showing an increase in the arcing; the polytype has transformed to 4H.

FIG. 10. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 42H; (b–e) after heating the crystal one, four, seven, and ten times, respectively; there has been practically no change in arcing but gradual improvement in the resolution of spots on the arcs.

FIG. 11. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 2H; (b) after heating, showing diffuse reflections of the type 4H; (c) after six heating runs, showing splitting of each reflections into a pair of closely situated reflections.

FIG. 12. Oscillation photograph of the upper face of a crystal (a) before heating, showing reflections of the type 48H; (b) after heating shows the transformation of the type 48H into the common type 4H.

FIG. 13. Oscillation photograph of the upper face of crystal, (a) before heating, showing reflections of polytype 84R, (b–d) after 1, 5, and 11 successive heating runs, showing slow transformation of 84R towards 4H.

FIG. 14. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the mixture (4H + 12R); 12R spots occur in both obverse and reverse position; (b) after heating showing that the mixture (4H + 12R) has transformed to the mixture (4H + 32H).

FIG. 15. Oscillation photograph of the lower face of a crystal (a) before heating, showing reflections of the type 20H; (b) after heating, showing that 20H has transformed into 12R.

just one heating run but in many cases intermediate polytypes appear before the final transformation into 4H takes place. Usually, intermediate types have the same cell dimensions as the original polytype, but different intensity sequences of the X-ray reflections. The number of heating runs needed for the ultimate transformation differs from polytype to polytype. Two representative examples are presented in Figs. 12 and 13 depicting the transformations after one and eleven heating runs, respectively.

(2) The small period polytypes, e.g., those consisting of up to nearly 16 layers in the unit cell, are usually transformed into the common type 4H in a single heating run, whereas the polytypes of larger periods generally need more than one heating run. However, there is a notable exception, viz., the polytype 12R. In spite of its small periodicity, this polytype, whenever it was encountered, required several heating runs for final conversion into 4H.

(3) Even the lower type 2H has been observed to transform into 4H, like all other polytypes. Not only that, the transformation has been found to be a quick one, occurring in a single heating run in all of the cases. The foregoing Fig. 11 depicts an example.

### *Anomalous Transformations*

Excluding the transformation 2H → 4H, one case each of structural transformation has been met with in which (1) a lower polytype has been found to convert into a higher polytype (12R → 32H), and (2) a higher type has been found to convert into a lower one (20H → 12R). These cases have been presented in Figs. 14 and 15, respectively.

## Discussion

Most observations are explicable in terms of movement of edge dislocations in the crystal caused by heating. The dislocations presumably generated during growth are already present in the crystals. The heterogeneous nature of crystal structure of $CdI_2$ provides for an easy creation of the dislocations during crystal growth by slip parallel to the basal plane (*7*). Thus, the bulk of the dislocations lie in the basal planes. Both unit and partial edge dislocations can be created. Substantial evidence regarding the existence and movement of these dislocations in $CdI_2$ crystals has been obtained in the investigation of the phenomena of arcing and ring formation, which are manifested on the X-ray photographs of the crystals (*7*, *8*).

The results of various large-scale investigations, e.g., (*5*), in cadmium iodide have shown that on an average nearly 50% crystals turn out to be type 4H. This predominant occurrence of 4H proves that this polytype has less free energy than any other $CdI_2$ polytype. Therefore, empirically, it may be regarded as the $CdI_2$ structure of maximum thermodynamic stability. The present observation that all the $CdI_2$ polytypes ultimately transform into 4H in one or more heating runs supports this contention. The supply of thermal energy during the heating runs helps the layer orientation to change suitably such that they eventually conform to the 4H structure. The change in the orientation should be brought about by the movement of partial dislocations along the appropriate layers, since the movement of a unit edge dislocation leaves the layer orientation unchanged. It is well known that a negligibly small driving force is needed for moving a dislocation. Most likely, the partials are already present within the original structure, being held up against some obstacles like impurity atoms, other dislocations, etc., because if they had to be created anew, random stacking faults would also be introduced, resulting in increase in streaking, which has been seldom observed. On the contrary, practically in all the cases the streaking has been found to reduce upon heating the crystals. That the dislocations are not created anew is also supported by the observation that any increase in arcing takes place only during the first heating run (see *Changes in Arcing* following).

Besides its dominating thermodynamic stability, the polytype 4H also has great thermal stability as is evidenced by the fact that its structure remains intact in spite of repeated heatings.

### *Changes in Streaking*

In most cases, the streaking has been observed to reduce or to be completely eliminated upon heating the crystals. Since streaking owes its origin to the existence of random stacking faults in the structure, this observation directly implies that the structure tends to "heal up" by a gradual elimination of the faults. The process of elimination presumably occurs by the movement of the existing partials as described above. However, the creation of fresh dislocations should not be completely ruled out, because in a very small number of cases the streaking actually has been found to increase upon heating (Fig. 6). But such instances have been extremely rare.

The presence of continuous streaking on an X-ray photograph is indicative of a completely random distribution of the stacking faults in the structure. Upon heating the crystals, the streaks tend to become increasingly discontinuous, with their intensities concentrating mainly around the positions of 4H reflections, thus revealing that the degree of randomness of faults gradually comes down, such that they increasingly approach the stacking sequence of the common type 4H. Such an approach towards the 4H sequence is quite expected, because the effect of heating on all the polytypes has also been observed to be the same, viz., to attempt for gradually attaining the stable 4H structure.

The tendency of unidentified polytypes with heavy streaking to form definite polytypes upon heating is understandable. The unidentified types usually show heavy streaking on their oscillation photographs. They remain unidentified because their reflections are unevenly spaced. Assuming that a polytype is produced during crystal growth by the introduction of stacking faults in the basic structure 4H, the presence of unevenly spaced reflections with heavy streaking means that the faults attempt to stabilize into a definite structure, possibly through the way suggested in the Jagodzinski's theory (*9*, *10*), but do not always succeed, so that in such unsuccessful cases most of them remain randomly distributed in the structure. The supply of thermal energy during the heating run helps the faults to complete the process of stabilization, although the structure, which now transforms into a definite polytype, may retain some stacking faults (Fig. 5).

The lower face of the crystal shows, in general, higher degree of streaking than the upper face. This is expected because in the method of growth employed in the present investigation, the crystals grow with their basal surfaces in contact with the bottom of the petri dish. Consequently, the lower face grows first, when the rate of growth is rapid on account of the higher supersaturation of the solution. The convection currents may also be strong then, on account of large differences in concentration in various parts of the solution, and hence the chances of generation of faults are high. The supersaturation gradually comes down during further growth, so that towards the end, when the upper face grows, the growth rate is slow and the convection currents are weak. Hence the chances of generation of the faults are considerably reduced.

The crystal structure of polytype 12R has been determined to be $(13)_3$ in Zhdanov symbols (*1*). This is equivalent to ABCBCABABCAC--- in ABC notation. The crystal structure of the common type 4H is represented as (22) in Zhdanov notation, and as ABCB---, or CABA---, or BCAC--- in the ABC notation. Clearly the 12R structure consists of three 4H units, each rotated with respect to its predecessor in an anticyclic manner, ABCB → CABA → BCAC. The experimental observation that a streak is always found to exist between the 4H and 12R position, whenever a polytype 12R is met with, simply shows that the type 12R always forms from the basic structure 4H. Such a formation of 12R during crystal growth is expected because, as seen above, this needs only single layer displacement after a 4H unit is completed. If the layer displacements occur at regular intervals, one will get a pure 12R structure. But this is not likely to happen on account of the close similarity between the crystal structures of 4H and 12R, and, consequently, negligibly small difference in their internal energies. Hence, the resulting structure will fluctuate between 4H and 12R. The original 4H structure may partly change into 12R (Fig. 7a), or mostly change into 12R (Fig. 7b), or may only tend to change into 12R (Fig. 7c).

### *Changes in Arcing*

The arcing observed on the X-ray photographs arises from a vertical alignment of edge dislocations of the same sign into tilt boundaries (*7*). The often observed development of arcing shows that some existing unit or partial dislocations have systematically moved into tilt boundaries. However, if the partials move, changes in streaking, or polytypic transformation, or both, should also occur simultaneously. If the arcing does not develop upon heating the crystal, it will mean that either the dislocations have failed to arrange themselves into the boundaries or dislocations of opposite sign have moved to annihilate each other, leaving behind a perfect lattice (*11*). It may also mean that the crystal is free from dislocations, but that will be a very remote possibility.

If the arcing exists before heating the crystal and enhances upon heating, it simply indicates that more dislocations, earlier held up against obstacles, have moved into the existing boundaries, increasing their angle of tilt ($\theta = |\mathbf{b}|/h$, **b** being the Burgers vector and $h$ the dislocation spacing).

The development of arcing in the first heating run and then staying as such in the subsequent heating runs shows that after the initial intense movement, the dislocations are either completely eliminated or held up against difficult obstacles. The obstacles are not altogether impossible to surmount, because it has been found that usually the reflections become diffuse upon heating, until after several repeated heating runs they split into a pair of close reflections (Fig. 11). Obviously the heat treatment constantly keeps on driving the dislocations. The smallness of the arc length (Fig. 11c) shows that the angle of tilt, $\theta$, of the corresponding tilt boundary is small, which, in turn, implies that the dislocations which move are only few and, therefore, they are widely spaced.

The observed near constancy of arc length after the first heat treatment also confirms that no fresh dislocations are produced upon heating the crystal, otherwise the arc length will have increased in the subsequent heating runs. The observed improvement in the resolution of spots on an arc upon heating shows that the alignment of the dislocations in the tilt boundary becomes more perfect, so that the two adjacent blocks of the crystal, situated on either side of the boundary, are separated by an increasingly sharp bend.

### *Polytypic Transformations*

The dominating thermodynamic stability of the common polytype 4H has already been pointed out. Sometimes it has been suspected that the lower polytype 2H may be more stable than 4H, since it has a smaller $c$ dimension and its unit cell corresponds to a "minimal sandwich" of cadmium iodide, which is very stable owing to the strong ionic bonds existing within it (*12*). Moreover, the greater relative abundance of both 2H and 4H than any other cadmium iodide polytype shows that they both represent modifications of true thermodynamic stability, yet the experimental fact that the 2H structure passes over to the 4H structure at high temperatures confirms that the former has a lower free energy than the latter.

The observed quicker transformation of the lower polytype into 4H is to be attributed to the increasing departure of the polytype structure from the stable 4H structure, with increase in the unit cell size. It should naturally require a smaller number of layer displacements, and therefore, lesser effort, for transforming the lower polytypes into 4H than the higher ones. Another reason for the greater stability of the higher polytypes may be that their transformations involve, from a purely statistical view point, more layer displacements within the sandwiches than in the lower types. Since strong ionic bonds have to disrupted for bringing about such displacements, greater energy is needed. However, sometimes, the crystal structure of a lower polytype may be such that its transformation into 4H mostly involves such difficult layer displacements. Then it shall also have a good thermal stability. Thus, the cell size cannot be regarded as the sole criterion for determining the thermodynamic stability of a polytype; the detailed crystal structure has also to be taken into account. A notable exception has been the polytype 12R, which has always required many heating runs for transformation into 4H. This is expected because the crystal structures of 12R and 4H are not very different [the 12R structure, $(13)_3$, can be generated from 4H (22) by introducing just single stacking fault] and therefore have close values of internal energy.

Excluding the transformation 2H → 4H, only two cases have been observed in which cell dimensions have changed upon heating the crystal (Figs. 14, 15). This includes both the conversion of a lower type into a higher type and vice versa. The rarity of such transformations shows that they take place under some exceptional circumstances. However, they again confirm that the cell size alone does not determine the thermodynamic stability of a polytype.

The intermediate polytypes observed during a phase transformation almost always have the same $c$ dimension as the original polytype, e.g., the transformation may proceed as $84R_1 \rightarrow 84R_2 \rightarrow \ldots \rightarrow 84R_{16} \rightarrow 4H$. As the transformation proceeds, the intensity distribution of the spots on the X-ray photographs increasingly resembles that of the 4H, which clearly shows that the stacking faults (with respect to the 4H structure) are eliminated gradually and in a systematic manner. It is possible that the whole process is governed by thermodynamic considerations of the type postulated in the Jagodzinski's disorder theory of polytypism. Another possibility could be that the presence of screw dislocations helps the stacking faults to expand regularly and thus bring about polytypic transformations, as suggested by Alexander et al.

for growth of ZnS polytypes (*13*). However, this can be decided only if such dislocations can be detected, e.g., by X-ray diffraction topographic methods, employed by Mardix et al. (*14*) in ZnS crystals.

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