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Effect of Growth Conditions on the Genesis of CdI_2 Polytypes

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The growth history of solution-grown cadmium iodide crystals has been unfolded by successive cleavage. It has been revealed that all the crystals involve structural transformations during growth, including changes from lower to higher polytypes and vice-versa, as well as changes in the degree of disorder and the arrangement of the dislocations. The results can be explained in terms of the creation and ordering of stacking faults during growth.

Introduction

The upper and lower faces of a single crystal of cadmium iodide, as picked up from the crystallizing dish, very frequently turn out to be different polytypes. Also the two faces generally have different degrees of order, as judged from the intensity of *streaks* joining the main reflections on the oscillation photographs (*1*). These observations indicate the possibility of structural transformations during crystal growth. For the highly absorbing crystals of cadmium iodide, the diffraction spots are usually missing in the region of transmission on the X-ray photographs. Consequently, information about only small thicknesses (~5 μm) in the vicinity of the two crystal faces is available, through the diffraction spots obtained in the region of reflection. The polytypic composition of the larger thickness of the crystal remains unknown. Therefore, it was planned to study the entire composition of the crystal by removing its layers in succession and repeatedly subjecting it to X-ray examination. In this way the entire growth history of the crystal could be unfolded. The results of a preliminary study of 20 crystals were reported earlier (*2*). Since then, investigation of a total number of 45 crystals has been completed, from which general conclusions regarding the mode of growth of polytypes can be drawn.

Experimental Methods

The crystals were grown from aqueous solution. The details of method of growth and the optical and X-ray examination of the crystal have been provided earlier (*2*). The method of cleavage was found to be most suitable for removing crystal layers (*2*). Thin slices of a minimum thickness of nearly 20 μm could be peeled off in a single cleavage. Before starting to cleave the crystal, oscillation photographs of its basal faces were taken. Then the lower face of the crystal was stuck to a thin glass coverslip and the cleavages made in succession. The oscillation photograph of the top face of the crystal was obtained after each cleavage, until almost the entire thickness of the crystal had been removed and its bottom face had been reached.

Experimental Results

The observed structural changes relate to polytype transformation and to the changes in streaking and arcing of the X-ray reflections. The phenomenon of streaking, in which the diffraction spots seem to run into each other, owes its origin to the existence of random stacking faults in the crystal and the arcing, in which the spots are drawn in the shape of small arcs of a circle, result from the arrangement of dislocation into macroscopically vertical tilt boundaries (*1*). A total of 45 crystals were examined. The inferences drawn from the analysis of the experimental data may be condensed as follows.

(i) The polytype on the lower face (which is the initial product of growth) of a crystal has a higher unit cell height than the upper face (the final growth product). This upper face is usually the common type $4H$; of the 45 crystals examined, it has been found to be so in 34 cases.

(ii) Nearly all of the crystals have revealed changes of polytype during growth. The changes consist of one or more transformations.

In nearly 25% of the cases of transformation, the polytype has been found to change without a change in the cell height, i.e., as $nH_1 \rightarrow nH_2 \rightarrow nH_3 \rightarrow \cdots$. An example has been presented in Fig. 1. This and subsequent figures depict the first layer line of an *a*-axis oscillation photograph, repeatedly taken after each successive cleavage.

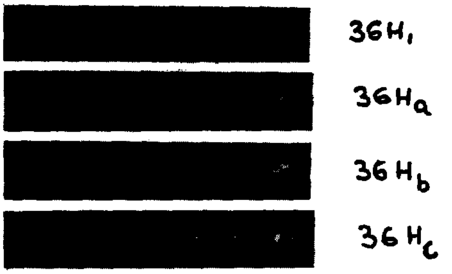

FIG. 1. Sequence of polytype transformation (without change in cell height) in crystal No. 42. Starting from the lower face (Polytype $36H_1$) downwards and going up to the upper face (polytype $36H_c$), each strip shows a succession of 01 *l* reflections on the first layer line of an *a* axis 15°-oscillation photograph. Cu$K\alpha$ radiation; 3-cm camera.

FIG. 2. Sequence of polytype transformation (accompanied with change in cell height) in crystal No. 43, depicted in the same manner as in Fig. 1.

In the rest of the cases of polytype transformation, the change from one polytype to another is such that the transformed polytype has a different value of the cell height. Thus, the transformation proceeds as $n_1H \rightarrow n_2H \rightarrow n_3H \rightarrow \cdots$. One example is shown in Fig. 2.

In four crystals, the complete atomic structure of the constituent polytypes could be worked out at each stage of transformation. This information has been very revealing, because in all these cases it has been found that the transformed structures closely resemble the parent structure. The transformations have been observed to proceed as follows in the respective cases:

(*a*) $6H_1 \rightarrow 12H_4 \rightarrow$ heavily disordered unidentified polytypes in nine successive cleavages $\rightarrow 4H$ (Fig. 3).

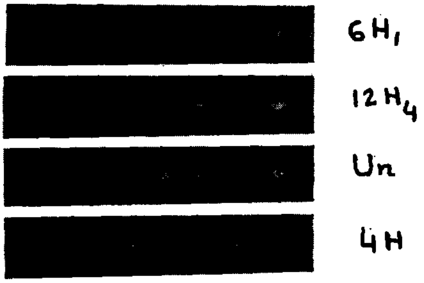

FIG. 3. Sequence of structural transformations in Crystal No. 7, depicted in the same manner as in Fig. 1. *Un* denotes unidentified polytype. Although the photograph of only one such type has been reproduced here, actually nine different unidentified types were encountered in succession (see text).

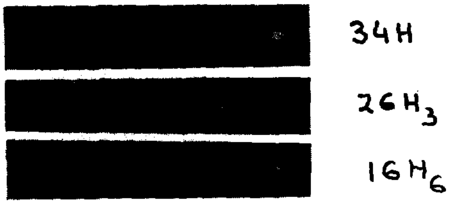

FIG. 4. Sequence of structural transformations in Crystal No. 28. The second strip shows a succession of 10 *l* reflections on the second layer line of an a^* axis oscillation photograph. Other two strips are depicted in the same manner as in Fig. 1.

FIG. 5. Sequence of structural transformations in Crystal No. 44, depicted in the same manner as in Fig. 1.

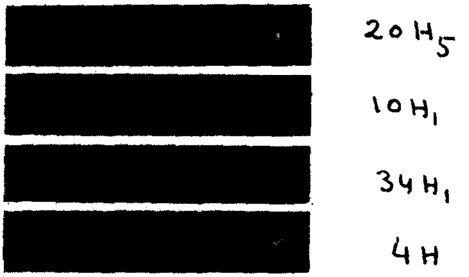

FIG. 6. Sequence of structural transformations in crystal No. 45, depicted in the same manner as in Fig. 1.

(*b*) $34H \rightarrow 26H_3 \rightarrow 16H_6$ (Fig. 4).

(*c*) $16H_4 \rightarrow 8H_1 \rightarrow 4H$ (Fig. 5).

(*d*) $20H_5 \rightarrow 10H_1 \rightarrow 34H_1 \rightarrow 4H$ (Fig. 6).

In case (*b*), it would not be possible to determine the crystal structure of polytype $34H$. However, the resemblance between the three constituent polytypes of the crystal was noticed in comparing the relative intensities of the 01 *l* reflections on the oscillation photographs of the polytypes (Fig. 4).

(iii) Even the lower polytype $2H$ has been observed to eventually transform into the common type $4H$. An example has been presented in Fig. 7.

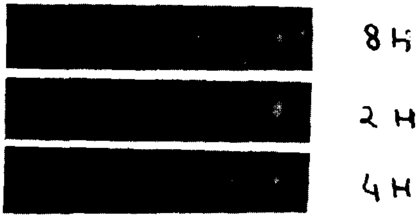

FIG. 7. Sequence of structural changes in crystal No. 33, depicted in the same manner as in Fig. 1. The eventual transformation of the lower polytype $2H$ into the common type $4H$ is to be particularly noted.

(iv) If a disordered polytype is encountered at some stage of transformation it does not persist through an appreciable thickness of the crystal.

(v) The region of the crystal situated in the vicinity of the layers where the transformation takes place, show an increase or fresh appearance of streaking. Fig. 3 serves as a representative example.

Discussion

The experimental observations can be analyzed in terms of the behavior of stacking faults created during crystal growth. The heterogeneous nature of CdI_2 structure favors mutual slippage of layers parallel to the basal plane under a small stress, giving rise to unit or partial edge dislocations, which can move easily during crystal growth (*3*). The movement of a unit dislocation across an entire layer leaves the orientation of the layer unchanged, but such movement of a partial dislocation does change the layer orientation, giving rise to a stacking fault. The fluctuations in the growth conditions, e.g., local changes in the concentration of solution due to differential rates of growth of the crystal, followed by the flow of convection currents, can provide the necessary forces for the creation and movement of the dislocations (*4*). In the beginning, the rate of growth will be rapid due to high supersaturation, and consequently, the conditions will fluctuate rather widely. Hence, the resulting faults are likely to be distributed randomly. In an attempt to lower the free energy of the crystal, these faults tend to arrange themselves in a regular manner, and thus, produce a polytype at the lower face. During further growth, more fluctuations in the growth conditions may take place, transforming the original structure into a different structure, which may still retain several faults and thus show streaking on its X-ray photograph. But as the supersaturation falls and the growth conditions gradually stabilize, the streaking should be reduced progressively and, in favorable circumstances, may disappear. However, the transition region of the crystal, grown under fluctuating conditions should necessarily show an increase or the fresh appearance of streaking on its X-ray photograph (Fig. 3). As the growth proceeds further, the growth rate slows down appreciably and the crystal naturally tends to acquire the configuration of least free energy. Since of all the polytypes of cadmium iodide, type $4H$ occurs most frequently and has been observed to have its structure unaffected even after prolonged heating at temperatures close to the melting point of cadmium iodide (*5*); it is believed to be thermodynamically most stable and to possess the minimum free energy. Hence, the end-product of the growth is expected to be $4H$, i.e., the upper face of a crystal is usually expected to be $4H$, which fully agrees with observations.

Even the lower type, $2H$, has been found to pass over to $4H$. All CdI_2 structures consist of composite I–Cd–I molecular sheets, each of which represents the unit cell of $2H$. Each molecular sheet consists of two I^- layers between which a Cd^{2+} layer is sandwiched. Due to the existence of strong ionic forces between the cadmium and iodine layers, prima facie the type $2H$ appears to be more stable than $4H$, the unit cell of which contains two such molecular sheets bounded by weak van der Waals' forces of attraction. However, the observed transformation $2H \rightarrow 4H$ clearly confirms the greater stability of type $4H$. Although this transformation has been encountered only once in the present investigation, the conclusion seems to be quite general. Earlier, exactly the same conclusion was reached during experiments on the heating of CdI_2 crystals (*5*).

If the fluctuation in the growth conditions is very strong, the transformation from one structure to another is likely to involve the rearrangement of the faults within the confines of the original unit cell. In such cases only the sequence of the layers in the unit cell will change, i.e., as $nH_1 \rightarrow nH_2 \rightarrow \cdots$. As mentioned earlier, several such transformations have been observed. If the fluctuations happen to be strong enough, they may upset the original structure to such a degree that both the layer sequence and the cell size change. Then the polytypes will change as $n_1H \rightarrow n_2H \rightarrow \cdots$, which also agrees with observation.

It may be pointed out that from energy considerations the conversion of one polytype into another should be a fairly easy process. The polytypes of a substance consist of various stackings of parallel identical unit layers. The atoms in a layer have essentially the same first nearest-neighbor relationships in all the polytypes. The difference between the various types appears only in the second or higher coordinations. Consequently, the polytypes negligibly differ in their internal energies, rendering their mutual conversions extremely facile.

During a transformation, it may be expected that the transformed structure will closely resemble with the parent structure, so that the change involved in the free energy of the crystal is least. This has actually been found to be so in four cases, where it has been possible to determine the complete atomic structure at each stage of transformation. For crystal No. 7, the original structure has been found to be (2211) (polytype $6H_1$; first reported by Mitchell (*6*)) and the transformed structure as (22211211) (polytype $12H_4$; first reported by Agrawal et al. (*7*)), in Zhdanov notation. Writing the structures in the expanded *ABC* notation, it is seen that the latter can be derived from the former by introducing just one stacking fault after every 12 layers, as follows (the faulted layer is in bold lettering):

ABCBABABCBAB··· ($6H_1$)
ABCBABCBCBAB··· ($12H_4$).

In crystal No. 44, the transformation has been found to proceed in an identical manner, i.e., from the structure $(22)_3(11)_2$ (polytype $16H_4$ (*8*)) to the structure $(22(11)_2)$ (polytype $8H_1$ (*6*)):

$ABCBABCBABCBABAB\cdots$ $(16H_4)$
$ABCBABABABCBABAB\cdots$ $(8H_1)$.

Crystal No. 45 shows the transformation of the structure $((22)_2 1122211)$ (polytype $20H_5$ (*9*)) to the structure $((22)_2 11)$ (polytype $10H_1$ (*6*)) which further changes to $((222211)_3 22)$ (polytype $34H_1$ (*10*)). The first transformation is realized in a similar manner by introducing a single stacking fault after every 20 layers in the parent structure:

$ABCBABCBABCBCBABCBAB\cdots$ $(20H_5)$
$ABCBABCBABABCBABCBAB\cdots$ $(10H_1)$

During further growth, polytype $10H_1$, with its structure as $((22)_2 11)$, may transform to the type $34H_1$ $((222211)_3 22)$ by increasing the size of its unit cell and including three of its complete original cells plus a (22) unit from the fourth cell to its sequence of layers. Thus, no creation of stacking faults may be involved here. The possible mechanism of increase in the cell size has been suggested in the following.

In the case of crystal No. 28 the transformation has been observed to proceed as $34H \rightarrow 26H_3 \rightarrow 16H_6$. The intensity distribution of the spots on the X-ray photographs of the three polytypes were found to be very similar (Fig. 4), which indicated a corresponding close resemblance between their crystal structures. However, despite the best possible attempts, the crystal structure of type $34H$ could not be determined. The structures of the polytypes $26H_3$ and $16H_6$ were determined as $((222211)_2 2112)$ and $((222211)2211)$, respectively (*10*). We now consider the possible mode of transformation in this case, as of $10H_1$ to $34H_1$ in the previous case. The preceding transformations were also accounted for by the introduction of stacking faults in the parent polytype, but it is difficult to understand how the faults can repeat periodically over large distances, e.g., the repeat period in the polytype $34H$ is nearly 116 Å. A very plausible way can be conceived for this purpose, in which the screw dislocations originating during crystal growth play a key role. Suppose that initially the crystal grows as a polytype nH when a screw dislocation appears and helps the crystal to grow further by the well-known spiral mechanism of Frank (*11*). If the initial step exposed by the dislocation on the crystal surface is free from stacking faults, it may or may not generate a new polytype, depending on whether the step height is an integral multiple of the c dimension of nH or not. But if the initial step happens to develop one or more such faults, then helped by the helical topology imparted to the crystal by the screw dislocation, the faults will tend to perpetuate themselves during further growth at a regular interval, fixed by the pitch of the screw. As in the creation of dislocations, the driving force for the expansion of faults is likely to be provided by the convection currents existing in solution. If the dislocation has a burgers vector strength equal to the c dimension of the polytype nH, the periodic recurrence of the faults will give birth to a new polytype that will again have n layers in its unit cell, but the layers will be arranged differently. The growth of this polytype will continue unabated as long as the pitch of parent screw dislocation remains unaltered and no new faults appear during further growth. However, if fresh faults are created in the crystal, these will perpetuate as before, giving rise to another new polytype of the same c dimension but with yet another sequence of the layers. Thus, the observed transformation $nH_1 \rightarrow nH_2 \rightarrow \cdots$ can be visualized.

The burgers vector strength of the dislocation may also change during further growth due to its dissociation into smaller ones. Adsorption of foreign particles on or near the dislocation may also alter the burgers vector. It is also possible that the existing dislocation vanishes altogether, either by ending at another dislocation or by moving out of the crystal, and a fresh dislocation of different burgers vector subsequently originates. These changes will give rise to new polytypes that will have their c dimensions different from that of the first polytype. In all likelihood, the arrangement of the layers also will be different, since the emergence of a new dislocation generally may be expected to be accompanied by new faults. Thus, the observed polytype transformations involving change in cell heights, $n_1H \rightarrow n_2H \rightarrow \cdots$ can be understood.

The nature of the transformation obviously will depend on the number and positions of the stacking faults and on the value of the burgers vector of the screw dislocation. In general the following possibilities will exist:

(i) A lower polytype may change into a higher one. In this case the screw dislocation necessarily has its burgers vector equal to the *c* dimension of the latter, e.g., in the foregoing transformation $10H_1 \rightarrow 34H_1$, the strength of the burgers vector of the dislocation should have been equal to the *c* dimension of $34H_1$. However, as discussed before, the energy considerations would dictate that the structure of the exposed ledge is very similar to the crystal structure of the substrate, i.e., the polytype $10H_1$. The polytype $34H_1$ $((222211)_3\text{-}22)$ will be obtained when the ledge results from a slip of magnitude equal to $(10n+4)$ layers in the parent structure, $10H_1(222211)$, where $n = 3$.

(ii) A higher polytype may transform into a lower polytype. It may happen by the emergence of a screw dislocation of burgers vector equal to the *c* dimension of either (a) the lower type or (b) the higher type. However, in the latter case, stacking faults should also appear at appropriate positions in the parent structure. They will be perpetuated with a period equal to the *c* dimension of the parent higher polytype but, nonetheless, will produce the lower polytype. The first mechanism should have been operative in the observed transformation $26H_3((222211)_2 2112) \rightarrow 16H_6$ $((2222211)2211)$ and the second in the transformation $20H_5(222221122211) \rightarrow 10H_1$ (222211).

It has been found that in general the polytype on the lower face of a crystal has a higher *c* dimension than the polytype on the upper face. Such behavior is to be expected because a screw dislocation of a relatively large pitch, necessary for producing a high polytype on the lower face, has a far greater probability of being generated during the early stages of crystal growth, when the high energy required for its creation may be available.

Whenever an appreciably disordered polytype has been encountered, it has not been found to persist through any appreciable thickness of the crystal. On the contrary, the transformation of a well-ordered polytype into another polytype has been observed to be a sluggish process. The disordered character of a polytype, arising from the existence of random stacking faults in the structure, manifests as streaking on its oscillation photograph. It may be qualitatively said that despite small differences in the potential energy, ordered states should be more stable than disordered ones. The display of heavy streaking by a disordered polytype means that the density of the random faults is high. As the growth proceeds, the energy consideration will demand that the faults attempt to arrange themselves to produce a well-ordered stable polytype. Therefore, a heavily disordered type should naturally have a tendency to transform itself into the ordered state. The existence of screw dislocations should aid in the process. If the growth conditions remain relatively stable, the attempts in this direction will succeed and an ordered state will be achieved. But if the conditions fluctuate rather widely, the attempts may only partially succeed, as manifested by the occurrence of irregularly spaced reflections superimposed on the streaks, e.g., in crystal No. 7 (Fig. 3).

The idea of the exposed ledge of a screw dislocation developing stacking faults, and thus, producing new polytypes was first noted by Frank (*12*) and Vand (*13*). It was perfected into an elaborate form by Alexander et al. (*14*) to account for the genesis of ZnS polytypes. The mechanism of formation of the CdI_2 polytypes, as suggested by us here, differs from that of the Zn*S* polytypes in that while the former are generated during crystal growth, the latter are produced after the completion of growth, during the cooling down period of the furnace (*15*).

Jagdozinski (*16*) has visualized the role of vibration entropy in the stabilization of stacking faults into periodic arrangements to produce polytypes. While such thermodynamic conditions may be pertinent for the growth of polytypes of substances like SiC and ZnS, which grow at high temperatures ranging from nearly 1000°–2500°C, they may be hardly applicable to the polytypes of substances like CdI_2, growing from solution at room temperatures.

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