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Arcing Phenomenon in Single Crystals of Cadmium Bromide

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Solution-grown single crystals of cadmium bromide have been found to exhibit arcing phenomena on their oscillation photographs and to give rise to closed rings of various shapes and sizes on Laue photographs. These have been explained in terms of the formation, during crystal growth, of tilt boundaries consisting of edge dislocations created by simultaneous slip along more than one close-packed direction on different basal and non-basal planes. The measurement of arc lengths on these oscillation photographs enables an estimate of the density of dislocations within the boundaries to be made.

Introduction

This X-ray study of single crystals of cadmium bromide is one in a series of studies on phenomena of arcing and polytypism in the MX_2 compounds, which have close-packed hexagonal layer structures. Other substances of this type, *viz*. CdI_2 and PbI_2, have already been investigated (Agrawal & Trigunayat, 1969*a*,*b*; Agrawal, Chadha & Trigunayat, 1970). Practically all the 12 crystals investigated in this study exhibit arcing phenomena on their X-ray photographs. This contrasts strongly with only 5% such instances in PbI_2 crystals and 42% in CdI_2 crystals. Reflexions of various shapes, *viz*. sigma, triangular ring, hexagonal ring, double rings, *etc*., have been observed on the Laue photographs. They have been explained in terms of tilt boundaries formed by vertical alignment of edge dislocations created by slip along more than one closest-packed direction on different basal and non-basal planes. In the crystals of CdI_2 and PbI_2 investigated earlier, the slip was found to be confined to the basal planes alone.

Experimental methods

The crystals were grown from aqueous solutions. At room temperature, 5 g of reagent grade $CdBr_2.4H_2O$ were dissolved in 20 cc of ordinary tap water in a shallow crystallizing dish. Hydrobromic acid was also added to prevent the formation of the hydrated bromide which forms in purely aqueous solutions. After several days, hexagonal crystal platelets of cadmium bromide, up to 1 mm across and 0.1 mm thick, formed in the dish. They were carefully removed from the solution and tested for perfection in a polarizing microscope before being mounted on the X-ray camera in order to obtain oscillation and Laue photographs. The *a* axis oscillation photographs were taken in the range 19 to 34°, *i.e*. the angle (referred to as φ in the following) between the incident X-ray beam and the *c* axis varied between 19 and 34°. This range was

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chosen in order to record a large number of $01.l$ reflexions whose l indices increased outwards from the centre of the photograph. This range was also suited to a separate identification of the upper and lower parts of a crystal since on a single X-ray photograph, spots were obtained by surface reflexion from one part alone (Chadha & Trigunayat, 1967). The Laue photographs were taken with the a axis vertical and the angle φ equal to 42°38′. This angle was particularly suitable for recording the $00.3n$ reflexion of an nH or nR polytype. On account of its high l value, this reflexion exhibits a large arcing effect.

The X-ray photographs of all the crystals were recorded with a camera of radius 3 cm and a collimator of aperture $\frac{1}{2}$ mm. The size of the focal spot was 1 mm^2. The oscillation photographs were taken with Ni-filtered Cu $K\alpha$ radiation and the Laue photographs with white Cu radiation.

Formation of tilt boundaries

The structure of the unit layer (minimal sandwich) of $CdBr_2$ is identical with those of CdI_2 and PbI_2. Consequently, the most probable slip planes and slip directions in $CdBr_2$ crystals should be the same as those in crystals of CdI_2 and PbI_2. The slip may take place along any one, two, or all three closest-packed directions, *i.e.* $[11\bar{2}0]$, $[1\bar{2}10]$ and $[\bar{2}110]$, in the basal planes. The processes of creation of edge dislocations, their dissociation into partials and their arrangement into macroscopic vertical tilt boundaries should all be similar to those in CdI_2 crystals (Agrawal & Trigunayat, 1969*a*). In the case of slip occuring simultaneously along all three possible directions of closest packing, the process of formation of triple nodes in common types of $CdBr_2$ and CdI_2 should, however, be slightly different on account of their different layer sequences. The most common structure of CdI_2 is the type $4H$, with layer sequence $(A\gamma B)$ $(C\alpha B)$ and that of $CdBr_2$ is the type $6R$, with layer sequence $(A\gamma B)$ $(C\beta A)$ $(B\alpha C)$, where A, B, C and α, β, γ represent the positions of anions and cations respectively. Within a sandwich, *i.e.* $(A\gamma B)$, $(C\beta A)$, or $(B\alpha C)$, the binding, being ionic in nature, is very strong, but any two adjacent sandwiches are held together by weak van der Waals forces of attraction. Consequently, as the atomic layers are laid down one after another during crystal growth, a slip in the first layer of the sandwich is far more likely than in the second. According to the well-known two stage process of slip, unit slip along a closest-packed direction $[11\bar{2}0]$, in an atomic layer parallel to the (0001) plane, is accomplished by the displacement of the layer in two stages, first along the $[10\bar{1}0]$ direction and then along the $[01\bar{1}0]$ direction, instead of a single displacement by one unit along the closest-packed direction, because the two-stage process requires less energy. Thus, in $CdBr_2$ crystals, a unit slip along a closest-packed direction in an A layer should be completed by the movement of an A atom first to an adjacent B position and then to the next A position (Fig. 1), since the preceding layer is always a C layer in the common type of $CdBr_2$. In the common type of CdI_2, however, a unit slip in the A layer is completed *via* a C position, as the preceding layer is a B layer. Therefore, in $CdBr_2$, a triple node in an A layer would be rotated through 180° with respect to that in a CdI_2 crystal. The position of a triple node in a C layer would be the same because the preceding layer is a B layer in both crystals. Thus, the triple nodes forming in the A and C layers in the common type of $CdBr_2$ would be of one type only. Further, as shown in Fig. 1, slip in a B layer would also form the same type of triple node. Therefore, all the triple nodes occuring in different basal planes in the $6R$ structure of $CdBr_2$ would be of one type. The strong interaction between dislocations of the same sign would bring them one on top of the other, leading to the formation of three tilt boundaries which divide the crystal into three blocks (Fig. 2). This is not the same as the formation of six boundaries in CdI_2 crystals (Agrawal & Trigunayat, 1969*b*).

In the common structure, $6R$, of cadmium bromide the $\{10\bar{1}2\}$ planes are equivalent to the basal planes in respect of close packing. Therefore, the probability of creation of dislocations by slip in the $\{10\bar{1}2\}$ planes in the common type of $CdBr_2$ crystals would be higher than in CdI_2 crystals. These dislocations might combine with other parallel dislocations created by slip in the basal planes to form asymmetrical tilt boundaries having their planes inclined to the c axis.

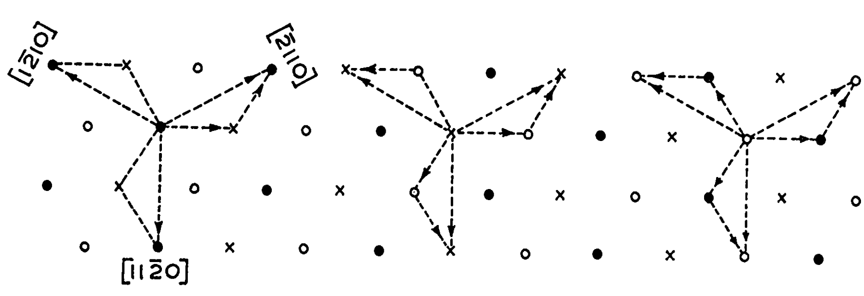

Fig. 1. Slip along close-packed directions. Black circles, crosses and open circles represent atoms in the A, B and C positions respectively.

Experimental results and discussion

Practically all the 12 crystals investigated in the present study, exhibited arcing on their oscillation photographs and closed rings on their Laue photographs. As the range of oscillation, ($\varphi \rightarrow 19$ to $34°$), permitted separate identification of the upper and lower parts of a crystal platelet, the oscillation and Laue photographs were taken from both parts of each crystal. Thus, a total number of 24 oscillation photographs and the same number of Laue photographs were obtained. The characteristic features of the various photographs will now be discussed.

(*a*) The lower part of crystal 1 gives rise to heavy streaking and large arcing on the oscillation photograph (Fig. 3). The Laue photograph (Fig. 4), taken with the *a* axis vertical and at $\varphi = 42°38'$, shows a nearly equilateral triangular ring for the $00.3n$ reflexion. The exact correspondence between the ring *ABC* (Fig. 4) and Fig. 2 is clear, *viz.* the blocks *a*, *b* and *c* give rise to reflexions *A*, *B* and *C* respectively, connected by the strips *AB*, *BC* and *CA* respectively, which originate from the continuous curvature across the intervening boundaries. Since all the three boundaries originate from one type of triple node, their angles of tilt will be essentially equal. The side *AB*, perpendicular to the central row of the ring, results from the tilt boundary consisting of dislocations perpendicular to the vertical *a* axis. Its length will be $\gamma x \theta$ (Agrawal & Trigunayat, 1969*a*), where γ is the camera radius, θ is the angle of tilt and x is equal to $(\lambda/c).l$. As $l = 3n$ for the ring *ABC*, the length *AB* is calculated to be approximately equal to $4{\cdot}4\theta$. The other two sides of the ring, *e.g.* *AC*, arise from the boundaries inclined at 30° to the *a* axis and will make an angle of $\tan^{-1}(x/2\sqrt{3}) \simeq 23°$ with the central row and will have a length of approximately $5{\cdot}6\theta$. Therefore, the ring *ABC*, because of its small size, has the appearance of a nearly equilateral triangle. During oscillation each block gives rise to its own spot. Hence, each layer line consists of three component lines on the oscillation photograph (Fig. 3). On irradiation of a particular small portion of the crystal, only one component line was obtained. The streaking along the layer lines has its origin in the stacking faults, created by partial dislocations, which occur randomly in the structure during crystal growth. The spots on the component lines belong to different unidentified polytypes, the reason for which could be that the partial dislocations are not created simultaneously at regular intervals in all the blocks. The upper part of the crystal gave a single spot for each reflexion.

(*b*) The Laue photograph (Fig. 5) of the lower part of crystal 2 exhibits hexagonal rings. As discussed in the preceding section, only one type of triple node of dislocations can form in the common type 6*R* of $CdBr_2$. However, if the crystal contains an admixture of other polytypes, the other type of triple node can also form, giving rise to hexagonal rings on the Laue photograph, as in CdI_2 crystals (Agrawal & Trigunayat, 1969*b*). Crystal 2 is a mixture of 6*R* and other unidentified polytypes, as seen from its oscillation photograph (Fig. 6). Here, the arcing is seen to start from a point lying nearly 1·5 cm to the left hand side of the centre of the photograph. This distance corresponds to the $0\bar{1}1\bar{2}$ reflexion. Similarly, in the oscillation photograph (Fig. 7) of the upper part, the arcing starts from a point lying at the same distance to the right-hand side of the centre of the photograph, which corresponds to the $01\bar{1}2$ reflexion. It follows that the axes of tilt and the planes of the boundaries are perpendicular to $\{01\bar{1}2\}$ planes, which is a departure from the normal situation in which the boundaries are perpendicular to the basal planes. The edge dislocations in the directions perpendicular to the $\{01\bar{1}2\}$ planes can be generated from a combination of slip along the closest-packed $\langle 11\bar{2}0\rangle$ directions in the basal and $\{01\bar{1}2\}$ planes. As stated in the preceding section, both these planes contain equally close-packed atoms. The effect of dislocations forming in the non-basal planes is manifested in the Laue photograph also (Fig. 5). One of the vertical sides of the $00.3n$ ring is seen to split up into two lines making a small angle with one another. One of them, that perpendicular to the central row, results from the boundary made up from dislocations lying in the basal planes and the other, slightly inclined to the former, results from the boundary of non-basal dislocations.

(*c*) The Laue photographs of a few crystals contain peculiarly shaped rings. The lower part of crystal 3 contains rings which look like the symbol used in mathematics for 'not smaller than' ($\nless$) (Fig. 8). These may result from a vertical tilt boundary giving rise to the side perpendicular to the central row, and from two other boundaries, normal to the $\{01\bar{1}2\}$ planes, giving rise to the other two sides of the ring. The reflexions on the central row of the Laue photograph (Fig. 9) of the upper part of the crystal form a shape similar to that of a laterally inverted sigma (Ƹ). Here each reflexion is made up of two parts which are mirror images of

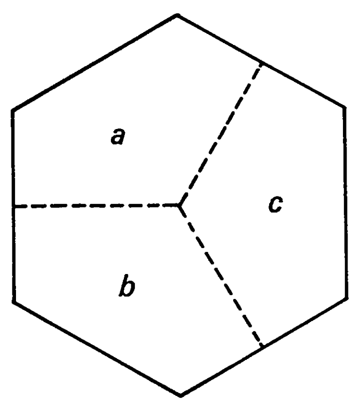

Fig. 2. A triple node of unit dislocations represented by dotted lines. The tilt boundaries along the dislocations divide the crystal into three blocks, *a*, *b* and *c*.

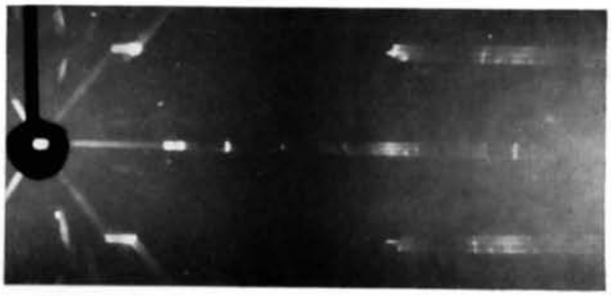

Fig. 3. *a*-axis 15° oscillation photograph of the lower part of crystal 1. φ varies from 19 to 34°; Cu $K\alpha$ radiation; camera radius 3 cm. Mixture of $6R$ and other unidentified polytypes.

Fig. 4. Laue photograph of the crystal in Fig. 3 at $\varphi = 42°38'$. *a* axis vertical; Cu white radiation; camera radius 3 cm.

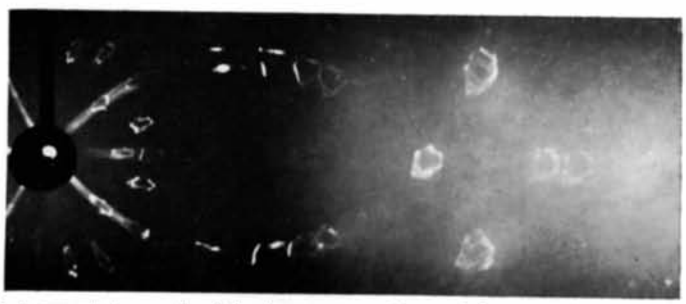

Fig. 5. Laue photograph of the lower part of crystal 2; conditions as in Fig. 4.

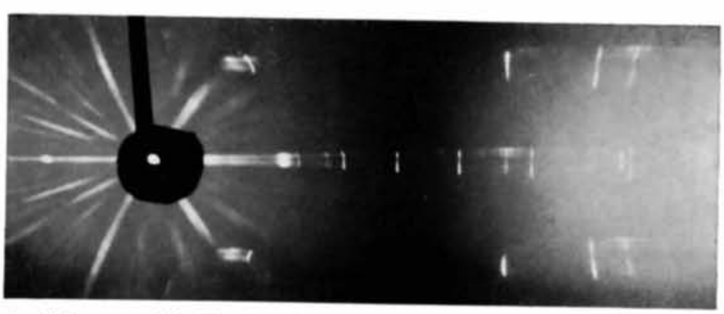

Fig. 6. Oscillation photograph of the crystal in Fig. 5. Mixture of $6R$ and other unidentified polytypes; conditions as in Fig. 3.

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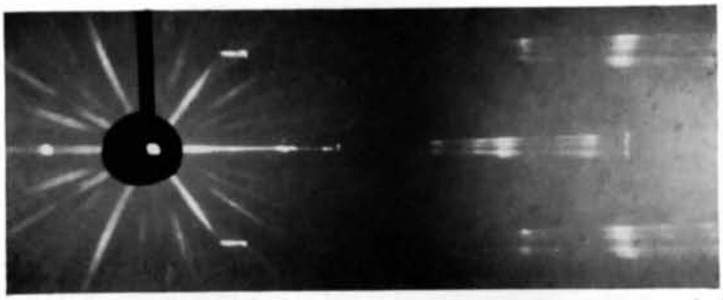

Fig. 7. Oscillation photograph of the upper part of crystal 2; conditions as in Fig. 6.

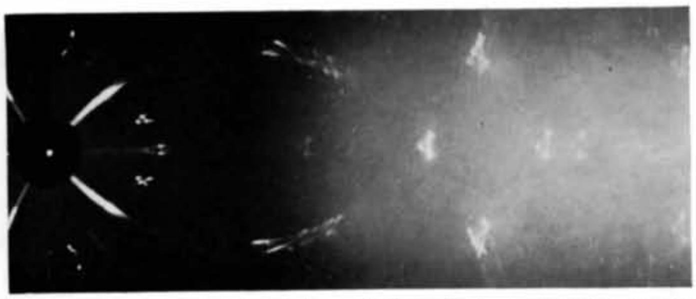

Fig. 8. Laue photograph of the lower part of crystal 3. Mixture of $6R$ and other unidentified polytypes; conditions as in Fig. 4.

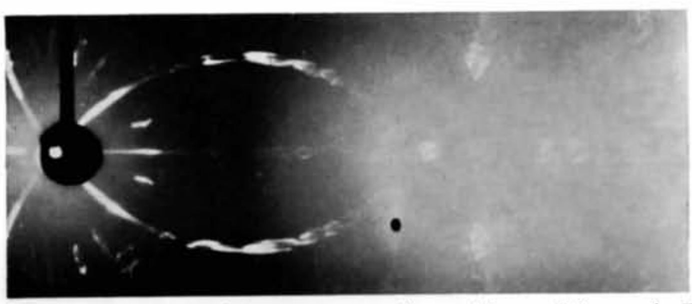

Fig. 9. Laue photograph of the upper part of crystal 3; conditions as in Fig. 4.

Fig. 10. Laue photograph of the upper part of crystal 4. Polytype $6R$; conditions as in Fig. 4.

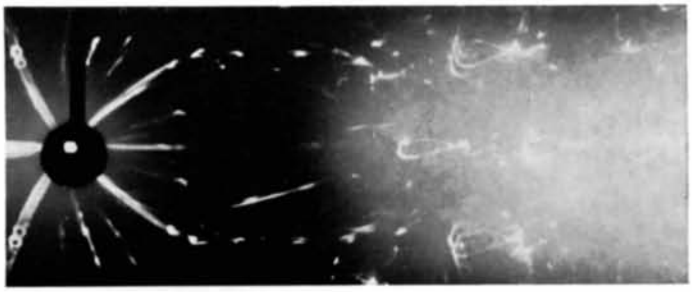

Fig. 11. Laue photograph of the lower part of crystal 5. Mixture of 6*R* and other unidentified polytypes; conditions as in Fig. 4.

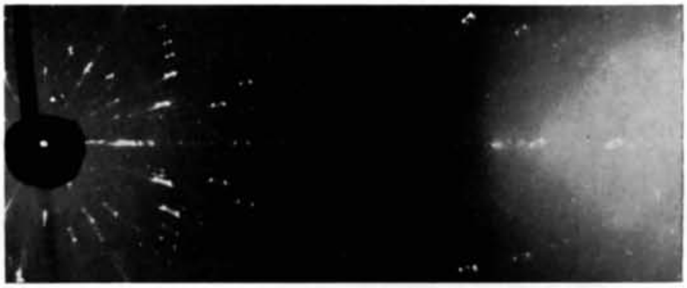

Fig. 12. Laue photograph of the upper part of crystal 6. Polytype 6*R*; conditions as in Fig. 4.

one another about the plane perpendicular to the plane of paper, and which pass through the central row. Each part results from two tilt boundaries whose planes and axes of tilt are normal to the $\{01\bar{1}2\}$ planes. The 00.3n ring, nearly triangular in shape, on the Laue photograph (Fig. 10) of the upper part of crystal 4 has one curved side, indicating the formation of a boundary of curved dislocations created during growth. The Laue photograph (Fig. 11) of the lower part of crystal 5 contains double rings of opposite orientation joined at a common point. The two rings are unequal in size. The bigger ring has a very irregular hexagonal shape, indicating the simultaneous formation of symmetrical and asymmetrical tilt boundaries. The smaller ring, having a triangular shape, could arise from triple nodes of non-basal dislocations, normal to the $\{01\bar{1}2\}$ planes. The Laue photograph (Fig. 12) of the upper part of crystal 6 shows typically shaped reflexions, each consisting of two spots joined by an intense straight strip on one side and by a faint curved strip on the other. The intense line having the two spots at its ends is due to a tilt boundary of unit edge-dislocations, inclined at 30° to the a axis. The appearance of an additional faint curved strip may be due to the dissociation of some of the unit dislocations into two partials to form extended dislocations.

The observation of arcing on the X-ray photographs of all the crystals during the present study shows that edge dislocations are created very frequently during growth. In addition, the oscillation photographs (*e.g.* Figs. 3, 6 and 7) of all the crystals exhibit streaking, showing that the stacking faults are not stabilized because of the rapid formation of dislocations. Thus the crystals always have some residual faults.

The measurement of arc lengths on the oscillation photographs affords a convenient method for estimating the density of dislocations within the boundaries. It has been estimated that the density of dislocations is of the same order, *i.e.* 10^5—10^6 dislocations cm^{-1}, as calculated earlier for crystals of cadmium iodide (Agrawal & Trigunayat, 1969*a*).

Conclusions

The significant conclusions emerging from the experimental findings are: (i) the creation of unit edge dislocations in one or more directions in different basal and non-basal planes, which then arrange themselves into tilt boundaries; (ii) the dissociation of unit dislocations into partials to form extended dislocations, and (iii) the creation of smooth curved dislocations which form their own tilt boundaries.

Using X-ray topographical methods, together with etching methods, Amelinckx, Strumane & Webb (1960) have conducted an extensive study of dislocation networks in SiC crystals, which possess layer structures like that of $CdBr_2$. They observed various types of dislocation networks in thin SiC platelets. Dislocations with $\langle 11\bar{2}0\rangle$ Burgers vector directions have been observed with evidence for slip in both the basal and non-basal planes. Pile-ups of non-basal dislocations were observed. Irregular crooked dislocations with a $[11\bar{2}0]$ Burgers vector direction, screw dislocations and smoothly curved dislocations have also been observed by them. These observations are quite similar to those described in the present paper.

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