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The Effect of Temperature on the Arrangement of Dislocations in CdI$_2$ Crystals

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X-ray *a*-axis diffraction photographs of solution-grown single crystals of cadmium iodide frequently show streaking, arcing and polytypism. When the crystals are treated below the melting point the streaking is reduced, the arcing increased and higher polytypes transform into the most common type 4*H*. These changes in streaking and polytypism are possibly due to the regular diffusion of partial and unit edge-dislocations formed during the crystal growth. An increase in the arcing may result from the creation of fresh dislocations which move into the existing tilt boundaries or form their own boundaries.

The effect of temperature on the phenomenon of streaking (in which the reflexions of constant h and k but different l values run into each other on the X-ray diffraction photographs), the phenomenon of arcing (which consists of an extension of the diffraction spots into small arcs in a direction perpendicular to the layer lines on the X-ray photographs), and the phenomenon of polytypism (in which the unit-cell c dimension is found to vary within wide limits for various crystals of a substance), in cadmium iodide crystals has been investigated. The crystals, grown from a supersaturated solution at room temperature, ranged in size from nearly 0·5 to 1·0 mm and in thickness from about 50 to 200 microns. They were tested for optical perfection under a polarizing microscope both before and after heating, which was carried out for about 90 minutes at about 300°C, *i.e.* well below the melting point (nearly 390°C).

As a representative case, Figs. 1 and 2 show the *a*-axis 15°-oscillation photographs, taken in the range 25 to 40°, of the upper and lower faces of the crystal respectively, as picked up from the crystallizing dish (before heating). The former shows strong spots from the common polytype 4*H*, with intervening faint spots of a higher polytype which, perhaps, is 20*H*, but cannot be exactly identified. The photograph shows both streaking and arcing. The latter shows spots of a higher polytype 46*H*, without any streaking or arcing.

Figs. 3 and 4 are the *a*-axis oscillation photographs of the same crystal after heating. Only spots of the type 4*H* are now seen in the photograph of the upper face (Fig. 3), with a considerable reduction in streaking and a corresponding increase in arcing. The photograph of the lower face (Fig. 4), now shows reflexions of the common type 4*H*, indicating a complete transformation of the earlier structure.

The observed changes can be understood as follows. All cadmium iodide structures consist of various vertical arrangements of 'minimal sandwiches', each 'sandwich' consisting of a sheet of cadmium ions in between two hexagonal close-packed sheets of iodine ions. The binding forces within a sandwich, *i.e.* between Cd and I layers, being ionic in nature, are very strong, but two neighbouring sandwiches, *i.e.* I–I layers, are held together by weak van der Waals forces of attraction. Therefore, the layers can easily slip along basal planes under a small stress, giving rise to edge dislocations. Slip along $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ directions will give rise to partial and unit edge-dislocations respectively. The movement of a partial dislocation on the basal plane will cause the displacement of a complete layer, creating a stacking fault, whereas the movement of a unit edge-dislocation will not affect the layer sequence. When the stacking faults are created randomly they are manifest as streaking on the oscillation photograph (Trigunayat, 1966). If the vibration entropy stabilizes the stacking faults, as proposed by Jagodzinski (1954), a stable polytype is formed. The partial or unit edge-dislocations may also align themselves vertically one on top of the other to form tilt boundaries, which divide a crystal into two or more blocks, giving rise to arcing on the X-ray diffraction photographs (Agrawal & Trigunayat, 1969*a*, *b*). Fig. 1 shows both streaking and arcing, revealing a random occurrence of partial edge-dislocations and the formation of tilt boundaries in the crystal during its growth. Heating of the crystal presumably allows the edge dislocations to move freely inside the crystal and it appears that many partial dislocations diffuse right out of the crystal, resulting in a reduction in the streaking, as seen in Fig. 3. At the same time, both the partial and unit edge-dislocations, which were earlier held up at some obstacles, may move into existing boundaries, thus increasing their angles of tilt, or may form new tilt boundaries, so that more diffraction spots occur on an arc. Also it is possible that fresh dislocations are created which may likewise move into existing boundaries or form their own tilt boundaries. The increased arcing observed in Fig. 3, and also the increase in the number of spots on an arc, corroborates this reasoning.

Comparison of Figs. 2 and 4 indicates a complete transformation of the crystal structure on heating. The original polytype, *viz.* 46*H*, has changed to the common polytype 4*H*. According to the disorder theory of polytypism (Jagodzinski, 1954) polytypes are formed

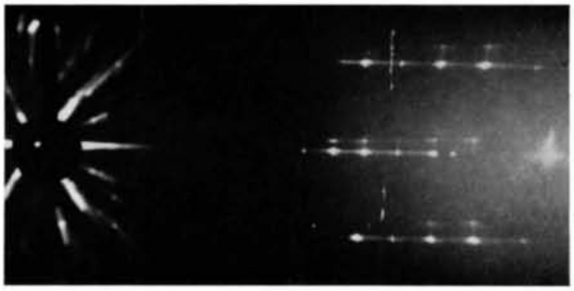

Fig. 1. X-ray *a*-axis 15°-oscillation photograph of the upper face of a CdI_2 crystal (before heating), showing both the 'streaking' and the 'arcing'. Camera radius 3 cm, Cu $K\alpha$ radiation. Mixture of polytype 4*H* and an unidentified polytype.

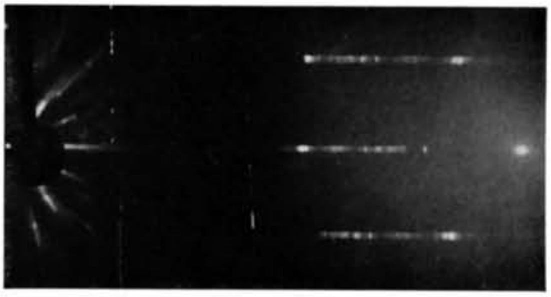

Fig. 2. X-ray *a*-axis 15°-oscillation photograph of the lower face of the crystal in Fig. 1 (before heating), with no 'streaking' or 'arcing'. Polytype 46*H* and other conditions as in Fig. 1.

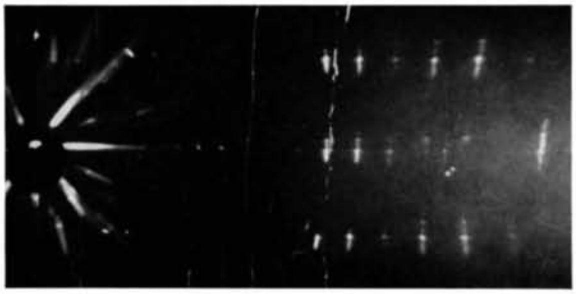

Fig. 3. X-ray *a*-axis 15°-oscillation photograph of the crystal in Fig. 1 after heating, showing a reduction in 'streaking' and an increase in 'arcing'. Polytype 4*H* and other conditions as in Fig. 1.

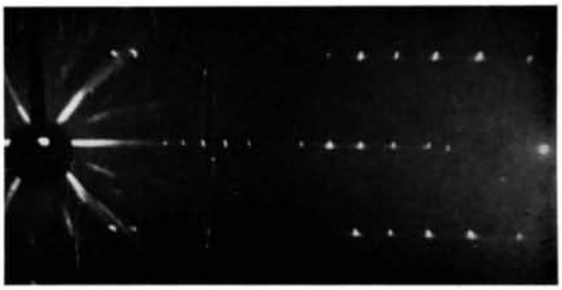

Fig. 4. X-ray *a*-axis 15°-oscillation photograph of the crystal in Fig. 2 after heating. Transforming into the common type 4*H* from the type 46*H*; other conditions as in Fig. 1.

because of the creation, in the common polytype, of edge dislocations of Burger's vector, $(\mathbf{a}/3+2\mathbf{b}/3)$ or $(2\mathbf{a}/3+\mathbf{b}/3)$ or an integral multiple of these, at regular intervals. The formation of a lower polytype is governed by potential energy considerations while that of the long-period structure (for which the difference of energy is vanishingly small) is determined by the vibration entropy. Since it occurs more commonly than all other polytypes, the type 4*H* is believed to possess the minimum free energy. The higher polytypes of cadmium iodide are supposed to be formed by the introduction of stacking faults resulting from partial dislocations. The heating of a high polytype will help the partial dislocations to diffuse out, as proposed above, the polytype thus reverting to the parent 4*H* structure. Such a process will be favoured thermodynamically, since the system will always tend to adopt a configuration of minimum free energy. Thus the observed transformation of the type 46*H* (Fig. 2) to 4*H* (Fig. 4) is explained. Such a transformation cannot be understood on the screw dislocation theory of polytypism (Frank, 1951) according to which very stable polytypes should be formed by the mechanism of spiral growth.

Studies carried out on other cadmium iodide crystals have revealed that the process of transformation from a higher to a lower polytype is a gradual one. For instance, on heating a polytype 32*H*, the intensity of its diffraction spots changed, showing that the polytype remained of the type 32*H* without any change in its unit-cell dimensions, but the sequence of layers along the *c* dimension changed. Also, the change in intensity was such that the intense spots occurred at the positions of spots of the common type 4*H*. On heating again for the same time and at the same temperature, the intensity sequence changed further, but the spacing between the diffraction spots still remained the same, showing that the polytype was still 32*H*. The intensity sequence now resembled still more that of the type 4*H*. On further heating, the polytype ultimately changed to the common polytype 4*H* (photographs not reproduced). It follows that not only do the partial dislocations diffuse out gradually from the crystal, but they do so with regularity.

The above observations clearly bring out the important role played by stacking faults in the formation of polytypes. The detailed experimental results will be presented elsewhere in due course.

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Bragg Reflexion Intensity Distributions of Small Distorted Crystals with Stacking Faults

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General equations (within the limitations of the geometrical theory) are given describing the intensity distributions of Bragg reflexions of small distorted crystals with stacking faults. In these equations functions occur representing the stacking-fault densities, the form of the average coherently scattering region and the distribution of the relative translations of the unit cells due to the distortions apart from a lattice vector. The equations describing the intensity distribution of a Debye–Scherrer line can be inverted and give then the stacking-fault density, the distribution of the relative translations of the unit cells, and the form function of the average coherently scattering region in the direction perpendicular to the reflecting planes. A general method is given for separating the three effects: distortions, stacking faults and the size of the average coherently scattering region.

Introduction

In the analysis of the structure of distorted crystalline materials by X-ray diffraction we distinguish three different types of effects, due to crystallite size, random translations of the unit cells from their 'ideal' positions, and stacking faults.

The work of Warren & Avergach (1952) for the case in which crystallite size effects occur in combination with the random shifts of unit cells is very well known. The results of Warren & Averbach hold when the distortions of the material are not too large. For a correct interpretation of the diffraction intensity distributions in the case of larger distortions it is necessary