

The Arcing of X-ray Diffraction Spots in X-ray Photographs from Cadmium Iodide Crystals

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The X-ray diffraction photographs from cadmium iodide crystals exhibit extension of diffraction spots in directions nearly perpendicular to the c^* axis. The reason for this extension (termed arcing) is not well understood. It has been shown in this communication that the arcing in cadmium iodide crystals may arise as a result of paracrystalline distortions introduced during the growth of crystals. Evidence and arguments have been advanced to show that whereas the arcing phenomenon cannot be explained on the basis of the presence of lattice defects, it can be readily explained on the basis of the presence of paracrystalline distortions.

Introduction

The X-ray diffraction spots from cadmium iodide crystals often exhibit a type of extension which is termed 'arc-ing'. In arcing, extension is such that the diffraction spot is elongated along directions which are inclined to the c^* axis (often the direction of extension is nearly perpendicular to c^*). Although arcing of X-ray diffraction spots from CdI_2 crystals was observed long ago (Trigunayat, 1962; Srivastava, 1964), attempts to explain arcing have been made only recently (Agrawal & Trigunayat, 1969*a,b*). Agrawal & Trigunayat proposed that arcing originates from division of crystals into several blocks which result from the occurrence of macroscopic tilt boundaries during crystal growth. The tilt boundaries are thought to be formed from partial dislocations which originate as a result of dissociation of unit dislocation in the basal plane. However, extensive investigations carried out to study dislocation configuration in CdI_2 crystals employing decoration as well as electron microscopic techniques do not reveal the presence of any tilt-boundary configuration (Prasad & Srivastava, 1970, 1971). It may also be noted that the suggestion put forward by Agrawal, Chadha & Trigunayat (1970) in support of their explanation of arcing, that the arcing is intimately connected with the occurrence of polytypism, does not appear valid. Arcing is not exhibited by other polytypic crystals such as silicon carbide, zinc sulphide *etc.* (see *e.g.* Verma & Krishna, 1966; Mardix & Brafman, 1968). It thus seems apparent that the cause of 'arc-ing' needs to be reconsidered. It is the purpose of this paper to present results which have been obtained while exploring the possible causes of the arcing phenomenon in cadmium iodide polytypic crystals. It is suggested that the arcing of diffraction spots may result from paracrystalline distortions introduced during growth of CdI_2 crystals. It is also shown that the arcing is characteristic of lattice distortions and is not connected with the occurrence of polytypism as proposed by Agrawal, Chadha & Trigunayat (1970).

Results and discussion

As suggested in the Introduction, the explanation proposed by Agrawal & Trigunayat (1969) for the cause of arcing in terms of the occurrence of tilt boundary configurations is unsatisfactory. When the disorder inherent in the arcing is analysed in the light of disorders produced by other imperfections (see *e.g.* Guinier, 1963) it becomes clear that arcing cannot be explained on the basis of other types of lattice defects (such as stacking faults) either. On the other hand, the diffraction patterns exhibiting arcing in cadmium iodide crystals are very similar to those observed in the case of chain molecules (see *e.g.* Vainshtein, 1966), micro-lattices of synthetic fibres (Hosemann, Balta-Calleja & Wilke, 1966) and atomic lattices in the ammonia catalyst (Hosemann, Preisinger & Vogel, 1966). The extension of X-ray diffraction spots in these crystals is known to result from paracrystalline distortion of the lattice. It would thus appear that in the case of CdI_2 crystals too, the paracrystalline distortion may be responsible for arcing of spots. We have tried to explain the arcing in terms of paracrystalline distortions; we find that such an explanation is in broad agreement with the observed facts. We now proceed to describe and discuss this explanation.

A paracrystalline distortion is produced when the units forming the lattice do not have the same size and/or shape and these units are inhomogeneously distributed. It is apparent that a lattice possessing paracrystalline distortion does not have long-range order. The idea of paracrystallinity was first introduced by Hosemann (1950). Paracrystallinity and its influence on the observed diffraction patterns have been described and discussed in detail by Hosemann & Bagchi (1962), Guinier (1963) and Vainshtein (1966). We will use these methods in describing the influence of paracrystallinity on the diffraction pattern in the present case. The terminology used by these authors to describe paracrystallinity is largely retained in the present discussions. Paracrystallinity in cadmium

iodide crystals may be introduced during growth in two possible ways. Firstly, water molecules may be adsorbed on the surface of layers forming the crystal during growth giving rise to fluctuations in axial parameters. Secondly, the growth of incoherent nuclei on top of a flat crystal surface may result in small gaps between different domains of the crystal. The above postulates were based on two observations. First, most of the cadmium iodide crystals exhibiting arcing showed loss of weight when heated between 200 and 250°C. The loss of weight varied from crystal to crystal, ranging from 5 to 20%. It is expected that the loss of weight results from dehydration of the crystals when water is lost as a result of heating. Heating observations involving crystals of approximately similar size revealed that the weight loss cannot be explained on the basis of the evaporation of water adsorbed on the surface only, the dehydration results from loss of water from the entire crystal. Second, when the initial stage of crystal formation (the growth stage prior to the formation of a uniform thick layer of the crystal) was directly observed by electron microscope, it was noticed that the initial stage in the formation of the crystal was the development of a large number of tiny crystal domains which were incoherent in their alignment.

The above-mentioned type of paracrystallinity is shown in Fig. 1. We take here paracrystallinity of a simple type, namely the one where deviation from the ideal lattice is confined to only one of the basal lattice directions. It should be noted in passing that the distortions produced by the said type of paracrystallinity (Fig. 1) are markedly different from the distortions corresponding to the strain field of an array of edge

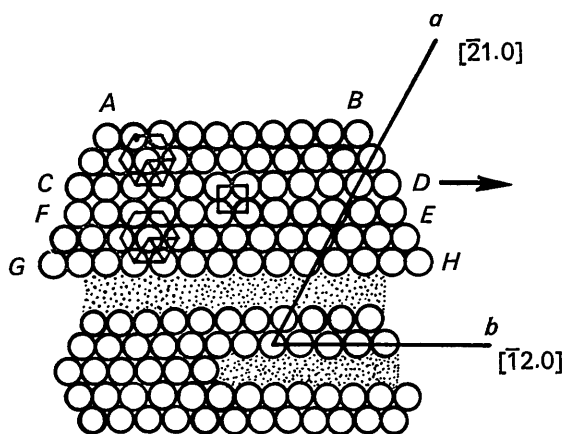


Fig. 1. Possible mode of creation of paracrystallinity in cadmium iodide crystals. The dotted regions represent the place where water molecules have been adsorbed. Regions *ABCD* and *EFGH* represent two perfect nuclei (domains). The regions *CDEF* (where the two domains came in contact) represent the misfit regions. In the perfect regions the nearest-neighbour atoms lie on a triangular (or a hexagonal) grid, in the region where misfit exists these lie on a nearly square grid.

dislocations, *i.e.* a tilt boundary. It is thus apparent that the diffraction effects from the present distortions are different from those described previously from tilt boundaries. Paracrystallinity is characterized by coordination statistics $H_k(r)$. The distribution function $Z(r)$ in general, has three components H_1 , H_2 and H_3 which give the distribution of the first neighbours along the three coordinate axes. The parameters of each are the mean square fluctuations Δ_{ik} which are the measure of statistical fluctuations in distances between first neighbours; they can be calculated if H_i is given a specific form. In Δ_{ik} the first subscript i implies that the quantity is characteristic of H_i and the second implies the coordinate axis along which the fluctuation Δ_i occurs.

The usual way of recording the shape of X-ray diffraction spots is to obtain a Laue diffraction pattern from the crystals. Since the CdI_2 crystals are hexagonal platelet shaped, the Laue photograph is taken with the c axis, which is normal to the flat face of the crystal, along the X-ray beam. Fig. 2 shows a typical Laue photograph taken from a polytypic crystal on a cylindrical camera of 3 cm radius. The arced spots can be explained on the basis of the simple type of paracrystallinity (see Fig. 1) where deviation from the ideal structure consists of fluctuations predominantly along one basal direction, *e.g.* $[2\bar{1}0]$ *i.e.* the a basal direction. Following the usual methods (Vainshtein, 1966), for this type of paracrystallinity, the fluctuation in parameter a can be thought of as having two components: (a) a radial component Δ_{11} and (b) a tangential component Δ_{12} . It is known that the radial and tangential components influence the diffraction pattern in similar ways although the radial components have a greater tendency to cause distortion in the reciprocal lattice rows (Vainshtein, 1966). In polytypic crystals because of the large c dimension most of the X-ray diffraction spots are confined to rows of the type $h0.l$, *e.g.* $10.l$ $20.l$ rows *etc.* Therefore, we retain the radial component only, in other words we consider the influence of Δ_{11} only and take Δ_{12} as zero. In this situation, only H_1 retains its form, the others, H_2 and H_3 , become δ functions. The function $H(r)$ and its Fourier transform are described by the following expressions (Vainshtein, 1966):

$$H_1(xyz) = \delta(z) \delta(y) \frac{1}{\sqrt{2\pi\Delta_{11}}} \exp \left[-\frac{1}{2} \frac{(x - \langle a \rangle)^2}{\Delta_{11}^2} \right]$$

$$H_2(xyz) = \delta(r - b)$$

$$H_3(xyz) = \delta(r - c).$$

$\langle a \rangle$ corresponds to the mean distance between nearest neighbours along the x , *i.e.* $[2\bar{1}0]$ axis and is defined as

$$\langle a \rangle = \int x H_1(x) dx,$$

where b and c are nearest-neighbour distances along y and z axes. The Fourier transform of the distribution function $Z_1(r)$ (described previously) of which H_1

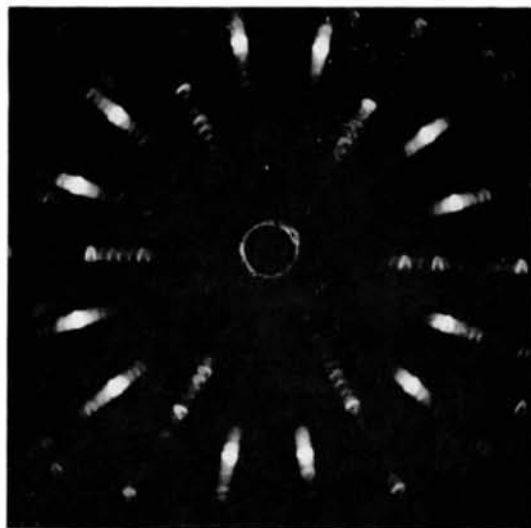


Fig. 2. A Laue photograph of a CdI_2 crystal taken with the X-ray beam along the c axis. Notice the arcing of spots.

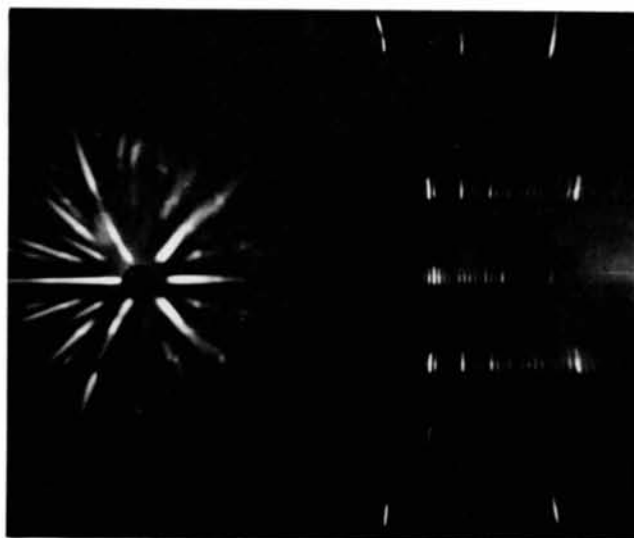


Fig. 4. a -Axis 15° oscillation photograph of a cadmium iodide crystal showing the change in width of the $h0.l$ rows.

is a component, is given by $Z_1(s)$ which is given by the following expression:

$$Z_1(s) = \frac{1 + F_1(s)}{1 - F_1(s)}$$

where, $F_1(s) = \mathcal{F}[H(r)]$ is the transform of H_1 . Fig. 3 shows the form of the interference function $Z_1(s)$. Function $H_2(r)$ and $H_3(r)$ would give the factors $Z_2 = L_2(s)$ and $Z_3 = L_3(s)$ which would correspond to one-dimensional Laue functions. As is obvious from Fig. 3 the intensity distribution corresponding to $Z_1(s)$ is such that hk rows are in the form of flat strips extending along the z direction and having their planes parallel to the x direction. The shape of the curve of intersection of these strips with the Ewald sphere would be in the form of an arc and thus the resulting X-ray diffraction spots would be arc shaped. The exact shape of the strip with respect to the X-ray beam. Fig. 1 is in keeping with the above description of the shape of spots. It should be pointed out that the width of the strips shown in Fig. 3 increases outwards from the origin with successive values of h , for example the $20.l$ row has a greater width of strips than the $10.l$. The extension of spot is not clearly brought out in Laue photographs since in most of the closely spaced spots the l value changes. The said extension can be best brought out on a -axis oscillation photographs. Fig. 4 shows an a -axis oscillation photograph obtained from a polytypic crystal showing arcing similar to that shown in Fig. 2. On a -axis oscillation photographs the zero and first layer records $10.l$ or equivalent rows and the second layer records $20.l$ or equivalent rows. Fig. 4 clearly shows that the $20.l$ type spots have a greater extension than the $10.l$ type. In oscillation photographs the intersection of the strips with the Ewald sphere would produce nearly linear curves. The observed extension for $20.l$ spots in Fig. 4 is too large to be understood as the usual extension due to divergence of the diffracted X-ray beams. Thus the observed extension can be safely ascribed to the extension expected from the interference function shown in Fig. 3. We therefore conclude that arcing of spots exhibited by Fig. 2 can be understood on the basis of paracrystalline distortion of the said type (see Fig. 1). It is worth mentioning that in the present case we have taken a simple form of paracrystalline distortion, the deviation introduced during growth of the crystals may introduce more

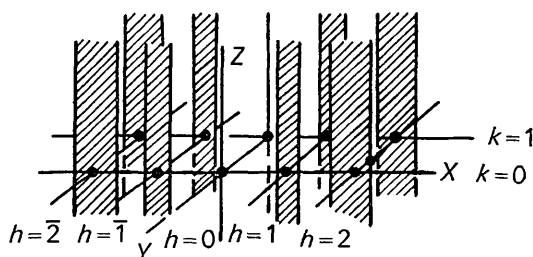


Fig. 3. hk strips in reciprocal space as a result of radial distortion in the x (or a direction) (after Vainshtein, 1966).

complex types of paracrystalline distortions. These would show different types of arcing which would presumably be more complex than those shown in Fig. 2. An analysis of other types of arcing, including a complex type, is at present being undertaken and results will be published shortly.

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