where l is the lattice translation between atoms labelled 0 and l. In this instance, there are in general six force constants between an atom pair. For each general value of q_j there are three frequencies and three quantities required to specify the eigenvectors. Thus, the relation $n_f = n_\omega + n_e$ is again satisfied, in the sense implied by this discussion. Of course, not all $6N$ force constants are independent; the number of independent force constants is reduced by symmetry to $\frac{1}{48}$ of the total, at least when the range is large, which was noted by Leigh et al. (1971). However, approximately the same factor applies to n_ω and to n_e.

By analogy with the one-dimensional example which we considered in more detail above, it is clear that when the eigenvectors have not been determined, no solution can be unique. In the absence of other physical information, any unitary matrix $e'(q)$ which satisfies the symmetry conditions (and there are no conditions for a general value of q) is acceptable, subject to considerations of continuity. While it seems improbable in practice that there will ever be an equivalent set of force constants having a shorter range than the correct set, there must always be an infinite number of equivalent sets of greater range.

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The Streaking of X-ray Diffraction Spots in Platelet-Shaped Polytypic Crystals

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The c-axis oscillation X-ray diffraction photographs of platelet-shaped polytypic crystals exhibit 10.l, 20.l, etc. rows which are sharply divided into two zones, one having streaked diffraction spots and the other having sharp spots. Evidence and arguments have been advanced to show that this behaviour is due to shape-effect on the diffraction, and the observed streaking is not representative of any real disorder in the stacking of the layers in the crystal.

Introduction

The streaking of X-ray diffraction spots in the case of polytypic crystals has special significance since it directly indicates the disorder, in the stacking of close-packed layers, in the polytype. The polytypic crystals have trigonal lattices, the close-packed layers being stacked along the c axis; often, the stacking is not ordered and thus a streaking along c^* reciprocal-lattice rows, characteristic of stacking disorder, is observed in the disordered crystals. All the spots in the 10.l, 20.l, etc. rows of the disordered crystals are connected through streaks, and the amount of streaking is directly related to the amount of disorder, i.e. the greater the disorder the more pronounced the streaking. Many polytypic crystals, however, exhibit a curious type of disorder in which 10.l and other similar rows consist of two parts; one part comprises reflexions that show

streaking indicative of disorder; the other part is perfectly sharp, as observed in crystals exhibiting no disorder. It is the purpose of this paper to point out that the existence of partly streaked and partly unstreaked reciprocal-lattice rows is due to shape-effect and does not represent any lattice disorder that results from random arrangement of stacked layers in the polytype.

c-axis oscillation photographs of cadmium iodide polytype

The polytypic crystals, like SiC, CdI_2, ZnS, PbI_2 etc. grow in the shape of platelets with flat faces parallel to the (0001) plane and often have hexagonal shapes. The lateral extent of the platelets is a few millimetres while the thickness of the crystals ranges from 10 to 100μ. Since the various polytypic modifications of a polytypic substance differ in the number and arrange-

ments of layers along the c axis, it is most useful to take c axis oscillation photographs that record 10.*l*, 20.*l*, etc. rows. These rows are situated at equal ξ reciprocal-lattice coordinates from the centre because the a lattice constant of the various polytypes of a substance is the same. The study of the arrangement and intensities of various spots in the 10.*l* row suffices for the identification and structure determination of polytypes (Verma & Krishna, 1966). Since the polytypic crystals grow as platelets with faces parallel to the (0001) plane, c-axis oscillation photographs are obtained by mounting the crystals about the axis perpendicular to the flat faces. Fig. 1 shows a typical c axis oscillation photograph (oscillation range 15°) from the 4H basic structure of cadmium iodide polytype, the crystal being in the form of a hexagonal platelet. The 10.*l* row above the zero layer consists of sharp spots; the part of the row below the zero layer is not like the upper one: the streaking and arcing of spots in this part of the 10.*l* row is clearly visible. All the c-axis oscillation photographs of cadmium iodide exhibit this streaking and arcing feature of the 10.*l* row and other similar parallel rows. The streaking behaviour of this type has been noticed earlier (Trigunayat, 1961, 1966; Srivastava, 1964), but its cause up to now is not known.

Results and discussion

It has been argued that the streaking and arcing of spots, in general, may be due to translation and rotation of the crystal layers with respect to each other (Trigunayat, 1961). In cadmium iodide this is possible since it consists of molecular sheets of cadmium and iodine ions. The iodine layers are held together by van der Waals forces which are weak in nature; thus, translation and rotation between them can occur easily. The above mentioned explanation of streaking and arcing, however, does not seem to apply to the present case. It is known that in a layer lattice where the layers are displaced irregularly and parallel to each other, only the 00.*l* spots are sharp; all spots lying on a given row hk are streaked to the same extent (Guinier, 1963). The present observation does not agree with this since 10.*l* reflexions with *l* = −1, −2, −3 ... are streaked, but those with *l* = 1, 2, 3 ... are unstreaked, i.e. they are sharp. To decide unequivocally whether the streaking is due to mutual rotation and slippage of layers, we studied c-axis oscillation photographs of a hexagonal-shaped platelet crystal of silicon carbide whose thickness and lateral width were nearly identical with those of cadmium iodide. In silicon carbide crystals the layers are held together with covalent bonding; thus, mutual slippage and rotation between layers is not possible. Fig. 2 shows a c-axis oscillation photograph of a platelet-shaped basic 6H polytype of silicon carbide. This photograph shows streaking features similar to those observed for cadmium iodide. Unlike cadmium iodide, silicon carbide is a brittle material and can be broken into small pieces. Fig. 3 shows an oscillation photo-

graph of a small piece of silicon carbide that was nearly equidimensional; it is obvious from Fig. 3 that no streaking features are present. A comparison of Figs. 2 & 3 makes it evident that the streaking and arcing of a part of the 10.*l* rows owe their origin, in some way, to the shape of the crystal. In the case of cadmium iodide, small equidimensional crystals cannot be prepared since the crystals always grow in platelet form and any attempt to break or cut a crystal into small pieces results in severe deformation.

Let us now consider the effect of the shape of the crystal in the c-axis oscillation photographs. A noticeable feature of Figs. 1 & 2 is the presence of considerable scattering, producing intense background, for one half of the film below the zero layer. As is well known, all kinds of scattering other than Bragg scattering produce background, and it is obvious that this scattering is profuse for one half of the diffraction pattern while it is sparse for the other half. Another experimental observation with reference to the c-axis oscillation photograph is the fact that it is not possible to align the crystal correctly so that the c axis coincides with the oscillation axis; this implies that the crystal platelet is inclined with the X-ray beam which is perpendicular to the oscillation axis. This is apparent from Figs. 1 & 2 where the first-layer lines above and below the zero-layer line are not equidistant. The usual method of estimating crystal misalignment (Nuffield, 1966) showed that the c axis was inclined to the oscillation axis by about 5'. This small error in alignment could not be removed despite our best efforts. We discuss this point later on, but its significance is that the crystal platelet is not exactly parallel to the beam: it is somewhat inclined to it. Fig. 4(a) & (b) represent schematically the diffraction geometry for the two cases, one in which the platelet parallels the beam and the other when it does not. To make the geometry clear, the inclination of the platelet has been exaggerated; the actual inclination geometry described in Fig. 4(b) is obtained in the present case. Now consider the influence of the shape on the diffraction spots in the case of silicon carbide. The X-ray beam of the collimator has a much larger vertical extent than the thickness of the crystal; thus, the whole vertical width AB of the crystal is completely bathed in the X-ray beam. The horizontal extent of the crystal platelet is about 4 mm and the linear absorption coefficient for Cu Kα radiation for SiC is approximately 141 cm⁻¹; thus, the beam can penetrate horizontally to an extent of about 70μ. Consequently, the beam sees only portion ABCD of the crystal which is nearly equidimensional, and this portion will diffract in almost similar ways in the two cases depicted in Fig. 4(a) & (b). The symmetrical Bragg diffracted beams travelling upwards and downwards encounter almost the same amount of crystal material; thus, they undergo similar absorption. [In Fig. 4(a) & (b), the extreme diffracted beams outlined by dashed lines will get absorbed since these travel longer distances than those outlined by full lines.] The diffraction spots produced by the equidimen-
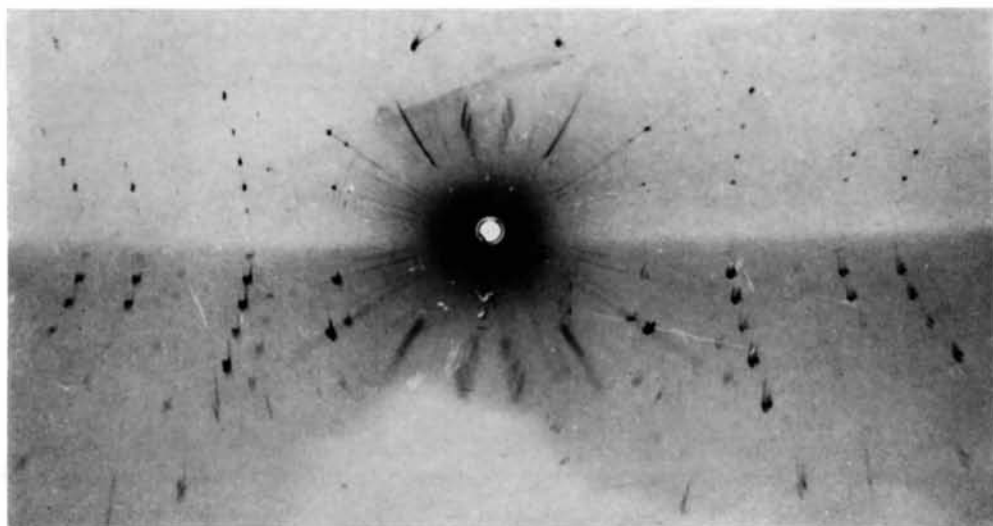
Fig. 1. Cadmium iodide *c*-axis oscillation photograph. One half of the spots above the zero layer are sharp and the other half below the zero layer contain streaking and arcing.
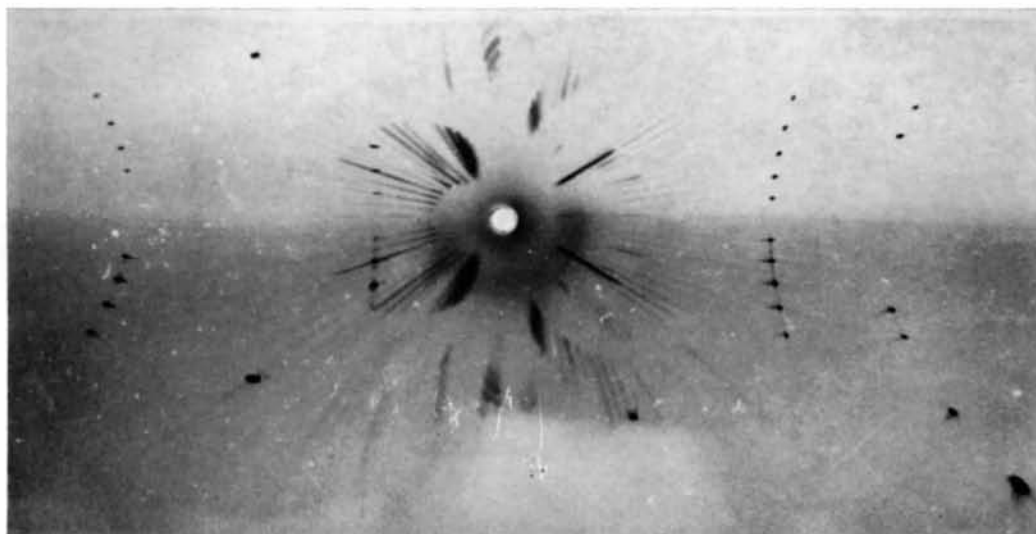

Fig. 2. Silicon carbide *c*-axis oscillation photograph in which crystal dimensions are similar to those of CdI$_2$ crystal corresponding to Fig. 1.
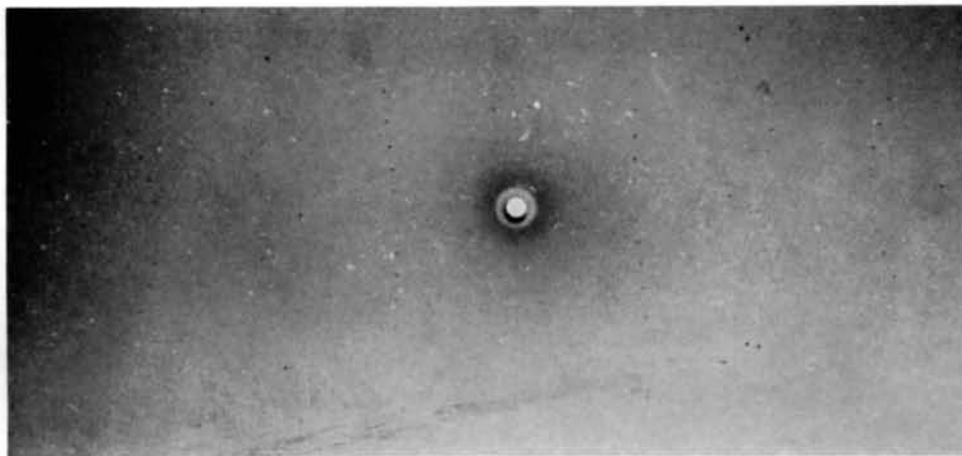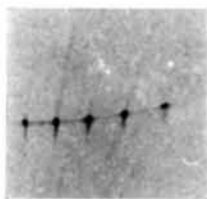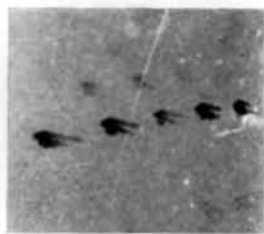
Fig. 3. Silicon carbide c-axis oscillation photograph in which the crystal is in the form of an equidimensional small piece.

(a)

(b)

Fig. 6. Magnifications showing the displacement characteristic
of the streaked and sharp spots for (a) silicon carbide and
(b) cadmium iodide.

sional crystal region *ABCD* will evidently be sharp and will form the usual spots in the 10.*l* type rows, both above and below the zero-layer line. Another region, *DEFG*, is also illuminated by the X-ray beam in the diffraction geometry obtained in the present case [Fig. 4(*b*)] and this will also diffract. Fig. 4(*c*) shows the diffraction geometry for the region *DEFG*. This region will diffract non-symmetrically since the upward beams will travel a longer distance and will get absorbed. In contrast, the downward beams will hardly be absorbed; therefore, they will be recorded on the film. Unlike region *ABCD*, crystal region *DEFG* will be non-equidimensional; it will consist of a thin strip whose dimensions will depend on the inclination of the crystal plate with the beam, the lateral extent of the crystal, the width of the X-ray beam and the linear absorption
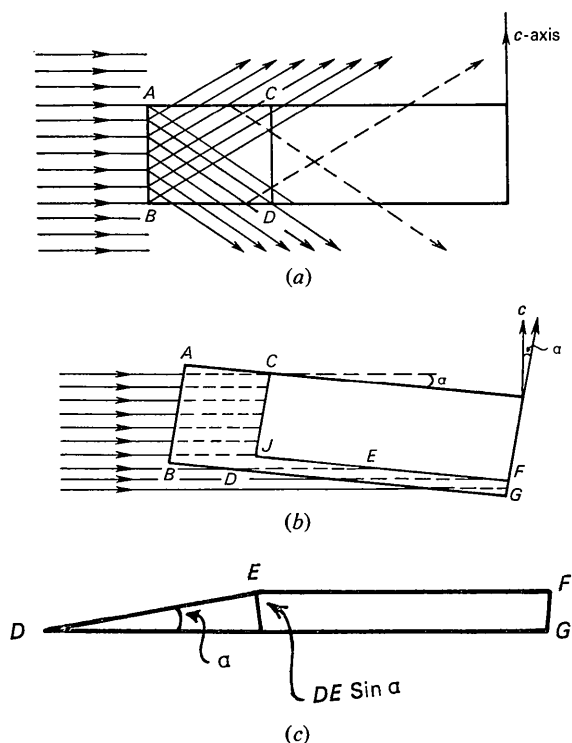

(a)

(b)

(c)

Fig. 4. Schematic representation of the diffraction geometry of X-rays from the crystal platelet when (a) the platelet is parallel to the X-ray beam and (b) when it is not. Portion of the crystal due to which streaking and arcing arise is shown in (c).
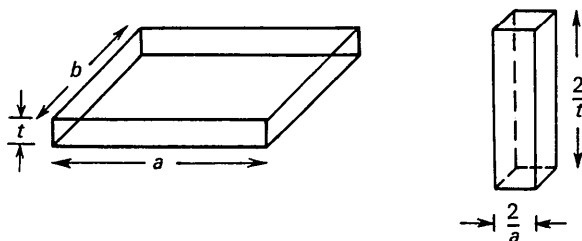

Fig. 5. Schematic of the crystal shape and corresponding reciprocal space.

coefficient of the crystal. The thin strip, to a first order of approximation, will be in the form of a rectangular plate. The usual shape transforms show that for such a crystal shape the reciprocal-lattice space, *i.e.* the reflexion domain, is in the form of rods perpendicular to the plate.

Fig. 5 shows schematically the crystal shape and the corresponding reciprocal space. The *a* and *b* dimensions of the reciprocal space will depend on the lateral extent of the crystal and the width of the X-ray beam; these two dimensions will, however, be much larger than the thickness *t*; also *a* and *b* can be considered nearly equal. The crystal region will then be in the form of a square-shaped thin plate, and the reciprocal space will consist of rods whose individual length will be $2/t$. The rods will be perpendicular to the plate and somewhat inclined to the oscillation axis since c^* is not coincident with the axis. The shape of the curve in which these rods will intersect the Ewald sphere during crystal oscillation will depend on the initial position of the rods and the curvature of the sphere at the point of intersection. Thus, the diffraction spots produced by crystal region *DEFG*, will not appear as sharp spots but will be spread. It can be conjectured that the main streaking due to the rod-shaped reciprocal space will be in directions nearly parallel to c^*; there will also be streaking in directions nearly parallel to a^*, because of the cross section of the reciprocal-lattice rod. The streaked and arced reflexion produced from crystal region *DEFG* will be confined to the film region below the zero layers as described previously; the corresponding beams travelling upwards are absorbed and are not recorded.

It is worth while to obtain an estimate of the thickness of the plate-shaped crystal region *DEFG*. As shown in Fig. 4(*c*), this equals $DE \sin \alpha$, where DE can be considered equal to the extent to which the beam penetrates and α is the angle through which the *c* axis is misaligned. In the present case, as discussed previously, $\alpha \simeq 5'$ and $DE \simeq 10^{-2}$ cm; thus, $t \simeq 10^{-5}$ cm and this size is small enough for the reflexion domain to have an appreciable size which can lead to appreciable streaking of spots (Guinier, 1963).

The streaking and arcing of spots shown in Fig. 2 are in keeping with the above explanation; the row above the zero layer consists of sharp spots produced from crystal region *ABCD* and the 10.*l* row below the zero layer consists of streaked reflexions from region *DEFG*. The arcing of streaked reflexions is nearly parallel to the a^* and c^* axes. The streaking along c^* is more spread than along a^*. Also, since the beam strikes the two crystal regions *ABCD* and *DEFG* at slightly different places, the origin of the reciprocal lattice corresponding to the two regions will be slightly displaced; therefore, the streaked reflexions from *DEFG* will be slightly displaced from the sharp spots produced from *ABCD*. Fig. 6(*a*), which is a magnified view of a 10.*l* type reflexion, clearly shows the displacement characteristics. It is apparent from the diffraction geometries

depicted in Fig. 4 that in the downward region a large number of beams is present compared with the upward region; this results in increased general scattering in this region. Clearly, the presence of intense background in the region below the zero layer is due to this increased general scattering. Thus, the simultaneous presence of the streaked and sharp reflexions in the *c*-axis oscillation photograph, shown in Fig. 2, is clearly due to the shape-effect on the diffraction. The above mentioned features also explain the previously stated observation that it is not possible to align the crystal platelet accurately so that its *c* axis coincides with the oscillation axis, *i.e.* the platelet is parallel to the beam. Based on the standard procedure adopted for mounting a crystal (Nuffield, 1966) so that its *c* axis coincides with the oscillation axis, two oscillation photographs taken on the same film for two crystal positions (one obtained after rotating the crystal through 180° from the initial position) will show that the positions of the streaked and the sharp reflexions in the same 10.*l* row will interchange. Thus, the streaked portion of the 10.*l* row will go above the zero layer if it was below the zero layer in the initial position. This is evident from the geometry shown in Fig. 4; also, as result of rotation the sense of inclination will change. The superimposed oscillation photographs will contain both sharp and streaked reflexions all along the 10.*l* row, and it will be difficult to select proper corresponding spots for applying corrections. This explains the fact that it is not possible to align the crystal accurately.

In the case of cadmium iodide crystals, the same streaking features as outlined above will be observed; however, some details will be different. The linear absorption coefficient of cadmium iodide for Cu $K\alpha$ radiation is 1642 cm^{-1}, which is about 10 times higher than in silicon carbide, so that the lateral width of region *ABCD* will be smaller in CdI$_2$; but this will not affect the sharp reflexions since region *ABCD* still remains nearly equidimensional and is larger than the dimension when shape-effects become visible. Because of the increased absorption, the diffracted beams emanating from the middle region of the crystal portion *ABCD* will be absorbed much more than those from the surrounding regions; thus, the sharp spots from region *ABCD* may be split into two closely spaced spots. This splitting will depend on the thickness of the crystal and is like the splitting observed in powder diffraction photographs from thick specimens (Henry, Lipson & Wooster, 1951). The *a* lattice constant of CdI$_2$ is different from that of SiC. Consequently, the 10·*l* row will be situated at a different ξ reciprocal-lattice coordinate from the centre so that the reflexion

domain corresponding to the *DEFG* crystal region will meet at a different curvature of the Ewald sphere; this will mean that the curve in which a plate- or disc-shaped reflexion domain will cut the sphere, will have a different shape than in SiC. As described earlier the thickness of the plate-shaped crystal *DEFG* is given by $DE \sin \alpha$. In the case of cadmium iodide the linear absorption coefficient is 1642 cm^{-1}, and thus the cross section equals $10^{-4} \sin 5'$, *i.e.* ·01μ. This size is 10 times smaller than that for SiC; thus, the reflexion domain will be 10 times larger than in case of silicon carbide. Also, the cadmium iodide spots in crystal region *DEFG* will be, streaked and arced to a greater extent than in silicon carbide. All these described characteristics for cadmium iodide are observed in the *c*-axis oscillation photograph shown in Fig. 1. The sharp spots are somewhat split, the arcing of streaked reflexion is different from that observed in silicon carbide and the extent of arcing for the streaked reflexions is greater than in silicon carbide; this is obvious from Fig. 6(*b*), which shows the magnified view of a 10·*l* type streaked spot.

Our analysis clearly shows that the streaking and arcing of spots in *c*-axis oscillation photographs of platelet-shaped polytypic crystals are due to the size and shape-effect. The resultant disorder observed in X-ray diffraction spots is not representative of any disorder present in the lattice. Thus, the streaking and arcing caused by the shape-effect must be accounted for in analysing the disorder in X-ray diffraction spots due to lattice disorder; this is particularly important in the case of polytypic crystals like CdI$_2$ and PbI$_2$ where small equidimensional crystals cannot be prepared and the crystals are always in platelet form. Although the results derived here refer to polytypic crystals, any crystal having a shape similar to the shape of the crystals we have investigated will show streaking and arcing characteristics of the present type.

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