Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

A reply to Agrawal's comments on the papers: (a) The streaking of X-ray diffraction spots in the platelet-shaped polytypic crystals and (b) Arcing of X-ray diffraction spots in the X-ray photographs of cadmium iodide crystals.

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The *c*-axis oscillation photographs of platelet-shaped crystals exhibit curious disorder features on X-ray diffraction photographs. These disorders are shown to be shape-dependent and are not caused by any real disorder in the stacking of layers. Another type of disorder which appears on X-ray diffraction photographs of cadmium iodide polytypic crystals is the 'arcing' disorder. It is shown that in view of the paucity of experimental evidence, the 'arcing' cannot be understood on the basis of the occurrence of manifold tilt boundaries.

Recently, Agrawal (1973) has criticised our explanation of shape-dependent disorder on X-ray diffraction photographs from platelet-shaped polytypic crystals. We have reanalysed the proposed explanation for the above type of disorder in the light of the criticism. Agrawal has argued that the above disorder is produced by stacking faults. However, he fails to realize that the stacking faults would not affect all the $h0.l$ rows. As is well known, in hexagonal close-packed structures those rows for which $h-k=3n$ would not show stacking-fault-induced disorder (Wilson, 1962). This is borne out by several X-ray diffraction photographs of polytypes which exhibit real lattice disorder due to random stacking faults. The shape-dependent disorder, on the other hand, affects all the $h0.l$ rows as is actually observed (see Fig. 1, Prasad & Srivastava, 1971). Another fact that Agrawal (1973) has failed to realize is that wherever the faults may be situated, whether in the upper or lower region of the crystal, these would affect all the spots whose structure factors are influenced by the presence of faults. Thus, when random stacking faults are present, the whole $10.l$ row (whether above or below the zero layer, *i.e.* whether l is positive or negative) would show disorder. However, in the disorder under question only half of the rows (above or below the zero layer) have disordered spots. This can only be explained by shape-dependent disorder. The disordered and ordered portions of the $h0.l$ rows are interchanged when the crystal is rotated through 180° because the thin-slice region of the crystal producing disordered spots changes its position on rotation [see Figs. 5–6 of Prasad & Srivastava (1971)]. The details of the shape-dependent disorder features, including the varying degree of the disorder and the somewhat intense background on half of the original film in heavily exposed photographs, have already been explained by Prasad & Srivastava (1971). Agrawal's argument that dislocations and vacancies are responsible for the intense background on half of the X-ray diffraction photographs is unreasonable. It is not clear how the dislocations and vacancies for a crystal (held at room temperature) would produce disorder on only half of the X-ray diffraction photograph. Agrawal (1973) is mistaken in stating that the *c*-axis oscillation photographs from CdI$_2$ crystals taken by Jain & Trigunayat

(1970) do not show any disorder effects. These photographs are nowhere near to the normal *c*-axis oxcillation photographs [see, for example, Krishna & Verma (1963)]. In fact all the *c*-axis oscillation photographs published by Jain & Trigunayat (1970), *e.g.* Figs. 1, 2, 8 (and the magnified version – Figs. 9 and 10) definitely exhibit shape-dependent disorder. The shape-dependent disorder is easily visible in these photographs.

Agrawal (1974) has pointed out that the 'arcing' disorder is due to the presence of manifold (twofold, threefold, fourfold *etc.*) macroscopic tilt boundaries extending throughout the crystals. Regarding this, it suffices to say that such configurations, if actually present, could be easily seen by the optical (decoration or etching) and electron microscope techniques. Extensive investigations employing these techniques (Prasad & Srivastava, 1969, 1975; Prasad, 1971) failed to reveal the presumed manifold tilt boundaries. It is surprising that Agrawal has not produced any experimental evidence for the occurrence of manifold tilt boundaries in cadmium iodide crystals. It may be mentioned that, while some splitting of spots is always expected from the crystal region containing tilt boundaries the arcing type of disorder may not be easily explained on the basis of the presumed existence of these boundaries. In order to have an unequivocal verification of this we looked into the diffraction patterns produced by tilt boundary configurations obtained in Er$_2$O$_3$ crystal films. This material, which has been studied in this laboratory (Singh & Srivastava, 1969), exhibits extensive tilt-boundary configurations during the recrystallization stage which are thought to be the result of subgrain coalescence. When a diffraction pattern is taken from such a tilt-boundary configuration, some splitting is usually obtained (see Figs. 1 and 2). This splitting in no way represents disorder embodied in 'arcing' (Agrawal & Trigunayat, 1969). The basis of our explanation of arcing based on paracrystalline disorder, namely the changes in the density of the crystal on heating and the presence of incoherent nuclei during growth, has been found to hold good on rechecking. It may be mentioned that the time-dependent change of arcing observed by Agrawal (1972) is easily understandable on the basis of paracrystallinity
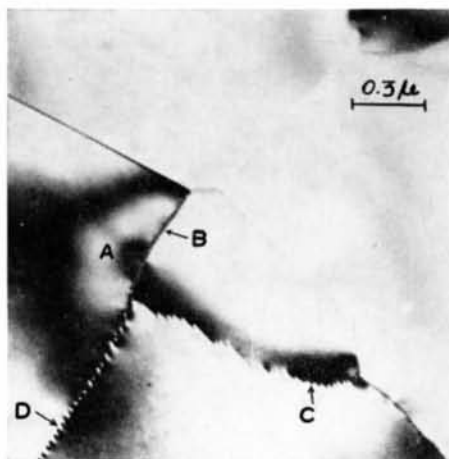
Fig. 1. Transmission electron micrograph of a thin Er_2O_3 single crystal. Notice the presence of the manifold tilt-boundary configuration as marked by arrows.
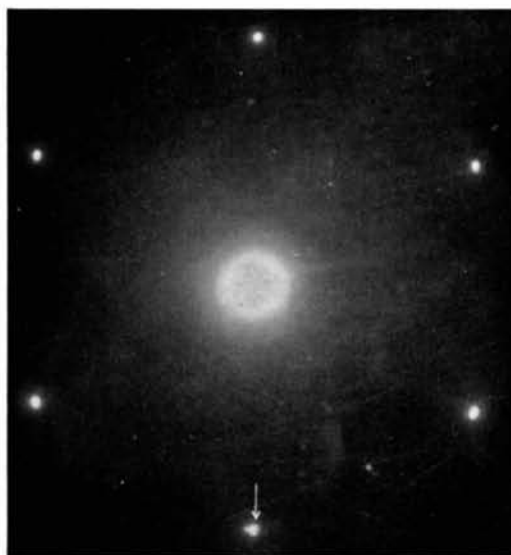

Fig. 2. Diffraction pattern corresponding to a region containing the tilt-boundary configuration shown in Fig. 1. Notice some splitting in spots (as marked by the arrow).

Water molecules and the incoherent nuclei within the crystal will change their distribution during a period of three to four years as a result of seasonal changes embodying a temperature variation of about 30°C. The argument advanced by Agrawal (1974) that paracrystallinity is shown only by fibrous crystals is incorrect in view of the fact that non-fibrous crystals have also been found to exhibit paracrystalline distortions (Urban & Hosemann, 1972). It can also be added that based on paracrystalline disorder the appearance of rounded and polygonal and other arbitrarily shaped spots can be easily explained, as indicated in our paper, by taking the fluctuations of a more involved type than that described in the said paper (Tiwari, Prasad & Srivastava, 1973).

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Precision lattice constant determination: erratum.

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A corrected version is given of equation (10) in Bond [Acta Cryst. (1960). 13, 814–818].

In the paper by Bond (1960), equation (10) should read

$$x = (\tfrac{1}{2}w)^2 \cot 2\theta \{(2 + \sin^2 2\theta)/(2 - \sin^2 2\theta)\}$$

where x and w are in radians.

This value should be added to the apparent Bragg angle.

For $\theta > 45°$, $\cot 2\theta$ is negative, so the correction is to be subtracted.

Reference

BOND, W. L. (1960). Acta Cryst. 13, 814–818.

Preliminary refinement of protein coordinates in real space.

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A simple unconstrained steepest-descent procedure is described for the preliminary refinement of protein coordinates in real space. The method is illustrated by application to ribonuclease S.

The typical procedure used to determine the atomic coordinates of proteins from single-crystal X-ray diffraction analysis makes use of the optical comparator described by Richards (1968) to build a skeletal model of the protein into the electron density map. The positions of the component atoms are then carefully measured from this model and transformed into a suitable reference frame for comparison with the Fourier map. The atomic coordinates are thus subject to systematic errors at each stage in this procedure.

These errors might, for example, arise from a misplaced reference origin, rotational shifts, shears and non-orthogonality of the reference axes. The random errors related to the difficulty in fitting the skeletal model in the poorly defined regions of the electron density map and the exact disposition of the bond angles and dihedral angles within the skeletal model are exceedingly difficult problems and will not be considered here, as they have been treated by Diamond (1971).

The systematic errors are, however, amenable to treatment by a simple unconstrained steepest-descent procedure which is outlined below. The results of this analysis are presented for ribonuclease S.

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