X-ray topography of natural tetrahedral diamonds

A. YACOOT* AND M. MOORE

Dept. of Physics, Royal Holloway, University of London, Egham, Surrey TW20 0EX

Abstract

The symmetry of diamond is still sometimes questioned. Most people agree that diamond belongs to the space group $Fd\bar{3}m$ and therefore to point group $\frac{4}{m}\bar{3}\frac{2}{m}$. Some however, on account of the existence of a few natural tetrahedral diamonds, have assigned diamond to the point group $\bar{4}3m$. We report here on an X-ray topographic investigation, using both conventional and synchrotron sources, of eleven natural tetrahedral diamonds. Two large specimens (from the Alpheus Williams' collection) were studied and found to consist of two portions, unequal in size, that were twinned on a (111) plane. Another diamond (from Professor R. A. Howie's collection) was found to contain two non-parallel {111} twin planes with the diamond filling the space between them, giving the crystal a tetrahedral morphology. Four tetrahedral diamonds (selected by Tolansky) were shown to be either twinned on a (111) plane, or cleavage fragments consisting of one component of a macle or single crystals that had been plastically deformed. Similar results were found for some diamonds from the Argyle Mine. Our findings are consistent with diamond belonging to the holosymmetric class ($\frac{4}{m}\bar{3}\frac{2}{m}$) rather than to the hemihedral class ($\bar{4}3m$).

KEYWORDS: diamond, X-ray topography, synchrotron source.

Introduction

OCCASIONALLY diamonds are found which have the appearance of tetrahedra (Seager, 1979). Illustrations of such diamonds may be found in the classic works of Fersmann and Goldschmidt (1911), Sutton (1928) and Williams (1932). Many natural diamonds have complicated unrecognisable shapes; but octahedra, cubes, rounded dodecahedra and triangular twins (macles) are of common occurrence and other shapes, such as interpenetrant cubes, are also found.

Until Bragg and Bragg (1913) showed that diamond possesses full cubic symmetry and belongs to the point group $\frac{4}{m}\bar{3}\frac{2}{m}$ and space group $Fd\bar{3}m$ some crystallographers assigned diamond to the point group $\bar{4}3m$. Their argument rested upon the assumption that such tetrahedra result from unimpeded growth from a centre and were thus true growth forms. It is surprising that so long after the Braggs' publication, the point group of diamond is still called into question, for example, by Donnay and Donnay (1981). We have used high-resolution X-ray topography to probe non-destructively the interiors of eleven tetrahedral diamonds and to deduce their modes of growth. All the specimens have had their morphologies modified by twinning and/or cleavage or by plastic deformation.

* Now at National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK.

X-ray topography

X-ray diffraction topography is a non-destructive technique, developed by Lang (1957, 1958), for imaging crystal imperfections such as dislocations, precipitates, inclusions, strain and growth banding. The ability to image growth banding non-destructively makes topography ideally suited for the elucidation of crystal growth mechanisms. For a review of the various topographic techniques see Lang (1978) and for reviews of X-ray topographic studies of diamond, see Frank and Lang (1965), Lang (1979) and Moore (1988).

When examining a crystal by X-ray topography it is important to use radiation of sufficient energy to penetrate the whole crystal. The absorption coefficients (μ) for copper $K\alpha_1$ radiation, synchrotron radiation of wavelength 1 Å and molybdenum $K\alpha_1$ radiation in diamond are 16.1 cm^{-1}, 4.9 cm^{-1} and 2.2 cm^{-1} respectively. Two of the specimens described in this paper had edge lengths of about 4 mm making them unsuitable for examination with copper $K\alpha_1$ radiation since the attenuation factor, (given by $I/I_0 = \exp(-\mu t)$), would be 0.0016 compared with 0.14 and 0.42 for the other two radiations.

Diamonds from the Williams' Collection

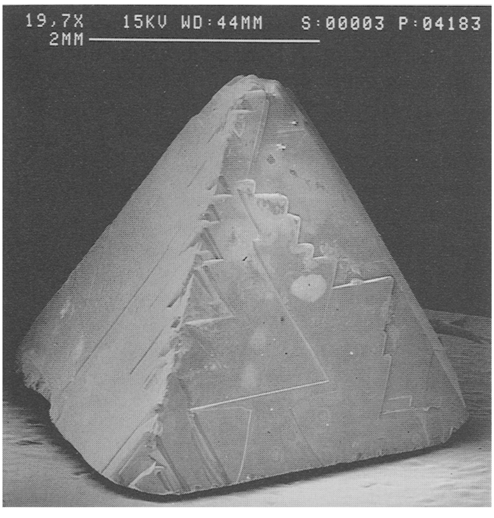
Two tetrahedral diamonds from the Alpheus Williams' Collection (Williams, 1932), on display at the Kimberley Open Mine Museum, were lent to us for examination. Both specimens were large (edge length 4 mm), clear and colourless.

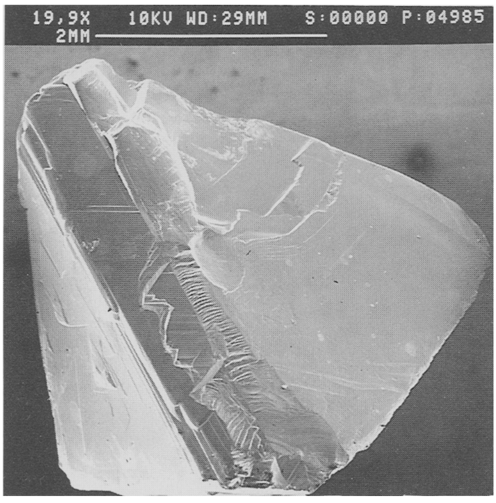
Sharp-edged tetrahedron. This specimen (0.385 cts) is shown in Fig. 1. Let the left-hand face be $(\bar{1}11)$ and the right-hand face be $(11\bar{1})$. The face on which the specimen is resting is the $(1\bar{1}1)$ and the small triangular face at the front, which intersects these three faces, is (111).

The specimen was initially examined using synchrotron radiation at the SERC Daresbury Laboratory (Cheshire, England). The spectrum of this synchrotron radiation (from the 'wiggler line' (station 9.4)) is continuous and is of high intensity at X-ray wavelengths as short as 0.2 Å. With the specimen's $[0\bar{1}1]$ axis approximately parallel to the goniometer's axis and its [011] axis parallel to the X-ray beam, the whole specimen was illuminated with synchrotron radiation. A forward reflexion Laue picture was taken which showed that this diamond had only one twin plane and that one component of the twin was much larger than the other.

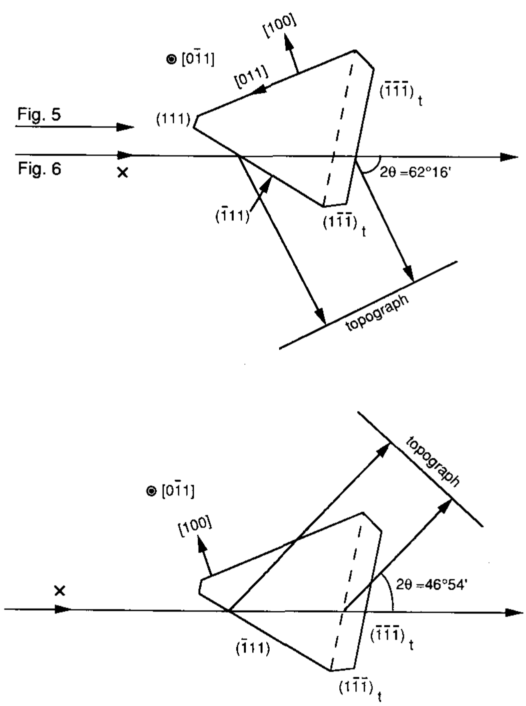
Fig. 2 is another scanning electron micrograph of the specimen. The right-hand face (which appears to have been cleaved) is the $(1\bar{1}1)$ and the diagonal line running between this face and the trapezoidal face $(\bar{1}1\bar{1})_t$ is the intersection of the composition plane with the crystal surface. The composition plane is parallel to the left-most face $(\bar{1}\bar{1}1)_t$. That trapezoidal face has a trigon (etch pit) on it confirms that it is of the type {111}. Similarly shaped faces were observed between the $(\bar{1}1\bar{1})_t$ face and the $(11\bar{1})$ and $(\bar{1}11)$ faces. At the top of the intersection of the composition plane with the crystal surface one can see two very small re-entrant faces which have almost grown out of the crystal. (Note that we have regarded twinning as a rotation of one half of the crystal by 180° about the [111] axis.)

The specimen was topographed with molybdenum $K\alpha_1$ radiation (λ = 0.71 Å) using a $\bar{3}33$ reflexion (θ_B = 31°8′) and a 400 reflexion (θ_B = 23°27′). The geometries of these reflexions are shown in Figs. 3 and 4, the dotted lines representing the composition plane. The $\bar{3}33$ reflexion images both components of the twin since rotating the $\bar{3}33$ planes by 180° about the [111] axis makes them coincident with the $5\bar{1}\bar{1}$ planes in the smaller component of the twin. The 400 reflexion images only the larger component. In each case the horizontal width of the crystal imaged is





FIGS. 1 and 2. FIG. 1 (*left*). Scanning electron micrograph of the sharp-edged tetrahedron showing the large $(\bar{1}11)$ and $(11\bar{1})$ faces and the small (111) face (at the front). Scale mark 2 mm. FIG. 2 (*right*). SEM of the sharp-edged tetrahedron showing the $(1\bar{1}1)$ face. Scale mark 2 mm.



FIGS. 3 and 4. FIG. 3 (top). Schematic diagram showing the geometry of the $\bar{3}33$ reflexion using Mo$K\alpha_1$ radiation (λ = 0.71 Å, θ_B = 31°8′). *Fig.* 4 (*bottom*). Schematic diagram showing the geometry of the 400 reflexion using Mo$K\alpha_1$ radiation (λ = 0.71 Å, θ_B = 23°27′).

compressed by a factor of sin $2\theta_B$ (0.89 and 0.73 respectively) on the topograph.

Two $\bar{3}33$ section topographs which image parts of the crystal separated by 500 µm are shown in Figs. 5 and 6. (The projection of the diffraction vector, **g**, is to the left). They image the specimen's composition plane around which there is a high degree of strain together with a few dislocations. Some growth banding can be seen that is approximately parallel to the ($\bar{1}$11) and (11$\bar{1}$) faces of the tetrahedron. The angle on the topographs between the sets of bands is 106° ± 1° which corresponds to 108° ± 1° in the crystal. Since the angle between two {111} planes is 109°28′ one may infer that growth has occurred in these octahedral directions.

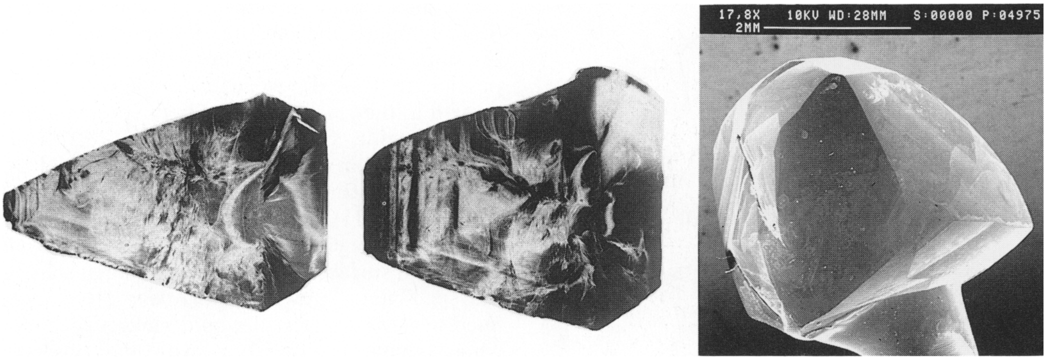
Discussion. The growth banding in the $\bar{3}33$ section topographs suggests that growth occurred on {111} planes and that the crystal must have twinned soon after the first few atoms nucleated, since growth occurred in directions leading away from the composition plane. Usually both components of a twin are of the same size; in this case one component is much larger than the other. Since temperature and pressure must have been the same for each component during growth, it is possible that the difference in size may be due to growth in the $[\bar{1}\bar{1}\bar{1}]_t$ direction being prevented by an obstruction. Growth in the [111] direction did not suffer from any such disadvantage and the (111) face continued to grow, being delineated by the ($\bar{1}$11), (1$\bar{1}$1) and (11$\bar{1}$) faces until it almost grew out of the crystal. The presence of trigons on the crystal surface indicates that the final stage in the specimen's growth history was dissolution. Such a mode of growth would yield a specimen whose shape is consistent with the observed topographs and morphology.

Rounded tetrahedron. An electron micrograph of this diamond (0.585 cts) is shown in Fig. 7. Unlike the sharp-edged tetrahedron, this specimen has suffered severe dissolution: all its surfaces are rounded and terracing can be seen around some of the triad axes, which is similar to that seen on rhombic dodecahedral diamonds (Moore and Lang, 1974). The protuberance from the lower part of the diamond is the glue which was used to adhere the diamond to the supporting rod. Fig. 8 is an indexed sketch which labels directions in Fig. 7.

The specimen was mounted in an identical orientation to the previous specimen and a synchrotron forward-reflexion Laue photograph was taken which illuminated the whole specimen. It showed that, like the previous specimen, this diamond had only one twin plane, the (111) plane. The diamond was then topographed using $\bar{3}33$ and 400 reflexions. The $\bar{3}33$ mid-section topograph (Fig. 9) shows that the diamond is strained, particularly near the composition plane (vertical line). Just above the mid-point of the composition plane there is a dark round area overlapping both components of the twin. Out of this area two fans of dislocations radiate. In the area between them there are two fringe systems indicating that there were areas of high perfection within this crystal. The diamond's surface has twelve edges of the form {*hhl*} in keeping with the surface being the result of dissolution of {111} surfaces (cf. the surfaces of rhombic dodecahedral diamonds; Moore, 1973).

As is the case for many twins, this specimen's composition plane is not planar; some intergrowth can be seen between the two members.

Two 400 section topographs that image only the larger component of the twin are shown in Figs. 10 and 11; they image crystal sections separated by 1 mm. (The concave surface at the bottom of Fig. 10 is due to the diffracted beam being shadowed by the brass screw on which the



FIGS. 5–7. FIG. 5 (*left*). $\bar{3}33$ section topograph of the sharp-edged tetrahedron intersecting the small (111) face (as indicated by the arrow in Fig. 3). Image width 3.9 mm, (←**g**). FIG. 6 (*centre*). $\bar{3}33$ section topograph of the sharp-edged tetrahedron displaced 500 μm from the section shown in Fig. 5, (in the direction sketched in Fig. 3). Image width 3.6 mm, (←**g**). FIG. 7 (*right*). SEM of the rounded tetrahedron showing the $(\overline{111})_t$ face. Scale mark 2 mm.

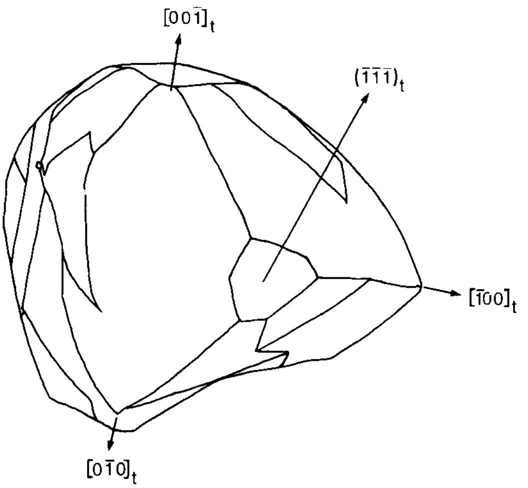


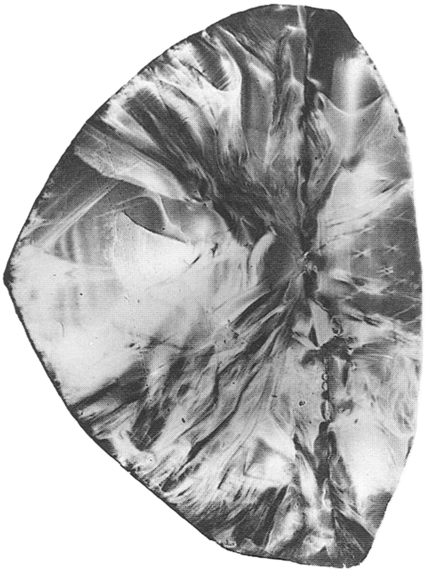
FIG. 8. Indexed sketch of previous scanning electron micrograph.

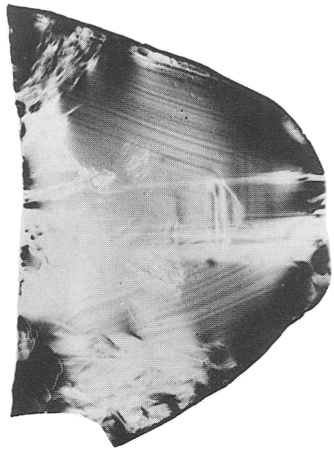
specimen was mounted.) Fig. 10 shows some growth banding which is approximately parallel to the crystal faces, $(1\bar{1}1)$ and $(11\bar{1})$, (upper and lower respectively). Growth banding in the (111) plane is also visible. The angle between the bands is 116° which reduces to 109° when the horizontal compression factor sin $2\theta_B$ is taken into account and thus confirms that growth has occurred on {111} planes. Fig. 11 shows more growth banding: the (111) growth banding not being intersected by the X-ray beam.

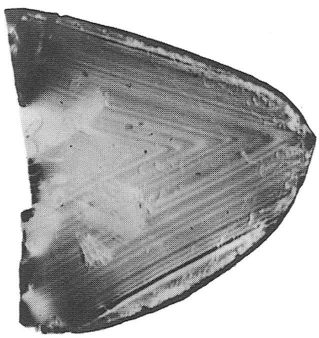
Discussion. Unlike the previous specimen, this diamond has a high dislocation content, particularly in the larger component. Since the Burgers vectors for diamond are usually of the form $\frac{1}{2}$<110> (Hornstra, 1958), all dislocations other than those for which the Burgers vector is parallel to $[01\bar{1}]$ should have been imaged by either the $\bar{3}33$ or $\bar{4}00$ reflexion, i.e. five sixths of all possible dislocations should have been imaged. Frank (1949, 1958) described how screw dislocations could promote crystal growth. Since the larger component has a much higher dislocation density than the smaller it is reasonable to suggest that its growth was enhanced by the dislocations. These would cause the face parallel to the twin plane in one component of the twin to grow more rapidly than the other. It would become smaller in area, being delineated by the adjacent octahedral facets. Eventually this face would grow out of the crystal, giving this part of the crystal a tetrahedral morphology. The overall shape of the crystal would then consist of a tetrahedron together with a thinner region in a twinned orientation. The final stage in this specimen's growth history was dissolution which caused a rounding of the facets and gave the specimen its rounded morphology.

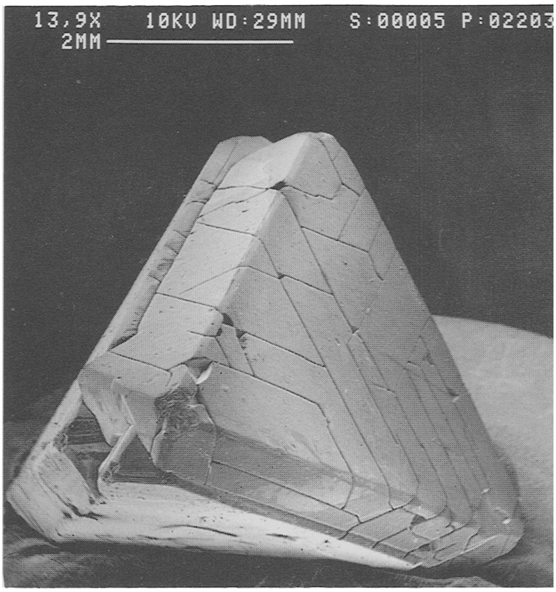
Howies's diamond: a tetrahedral diamond with two twin planes

This large (edge length 6 mm, 1.03 cts) yellow opaque diamond, originally from Sierra Leone, is shown in Fig. 12 and has the general appearance of a tetrahedron to the unaided eye. The diamond consisted of four large triangular {111} faces between which there were six trapezoidal {111} faces and some smaller triangular {111} faces. The edge on which the specimen is resting in Fig. 12 was the only sharp edge; the others all had a {110} bevel between adjacent {111} faces. This edge was the only edge formed by the intersection









FIGS. 9–12. FIG. 9 (*top left*). $\bar{3}33$ mid-section topograph of the rounded tetrahedron. Image width 3.2 mm (←g). FIG. 10 (*top right*). 400 mid-section topograph of rounded tetrahedron. Image width 2.4 mm, (g→). FIG. 11 (*bottom left*). 400 section topograph 800 μm from the mid-section. Image width 2.4 mm, (g→). FIG. 12 (*bottom right*). SEM of Howie's tetrahedron. Scale mark 2 mm.

of two large triangular {111} faces. We will show that this diamond had two twin planes, (111) and $(11\bar{1})$, inclined at 70°32′. The faces parallel to the twin planes were surrounded by trapezoidal {111} faces. The sharp edge was opposite and perpendicular to the line of intersection of the two twin planes. In Fig. 12 the octahedral growth of one twinned component can be seen; note the cube axis pointing out of the picture. Several surface cracks can be seen parallel to the edges of the crystal's faces. Where two of these intersect, near the cube axis mentioned earlier, a small tetrahedral shaped chip of diamond has fallen away. It is possible that some of the small tetrahedral diamonds described later in this paper could have formed in this way.

A synchrotron Laue picture of this specimen was taken with its [00$\bar{1}$] axis parallel to the goniometer's and its [110] axis parallel to the X-ray beam. The Laue picture showed that this

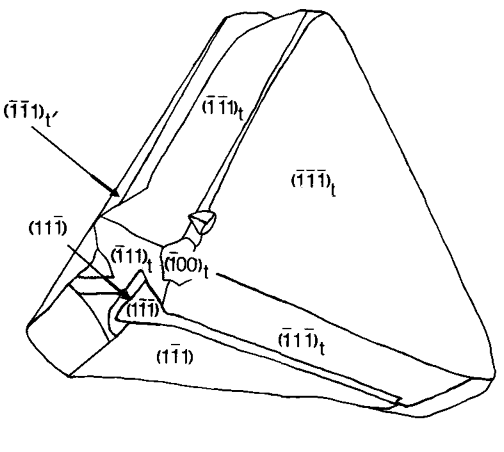
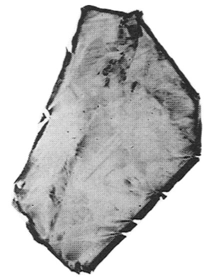
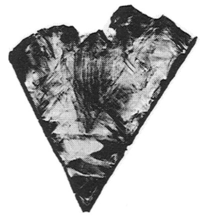


FIG. 13. Miller indices of faces shown in previous SEM picture.





FIGS. 14 and 15. FIG. 14 (*top*). $\bar2\bar20$ section topograph of Howie's tetrahedron, imaging crystal 1.5 mm from $(\bar111)$ vertex. Image width 3.6 mm, (g→). FIG. 15 (*bottom*). 040 mid-section topograph of Howie's tetrahedron. Image width 3.6 mm, (←g).

diamond had two non-parallel {111} twin planes. Fig. 13 is a sketch of the diamond showing Miller indices assigned to its faces.

The crystal was topographed using synchrotron radiation of wavelength 1 Å and a $\bar2\bar20$ reflexion (θ_B = 23°22′). A rotation of the $\bar2\bar20$ planes in the main body of the crystal by 180° about the [111] and [11$\bar1$] axes (the twin axes *t* and *t′*) makes them coincident with the (2$\bar2$8) and ($\bar2$28) planes in the two smaller twinned components. Since both of these planes will reflect X-rays of wavelength 0.34 Å with a Bragg angle of 23°22′ all three components of the diamond were imaged. Fig. 14 shows the mid-section topograph of the series taken.

The diagonal line running from the intersection of the two re-entrant faces at the top of the topograph to the lower left of the topograph is parallel to the $(\bar1\bar11)_t$ face. this line is intersected by another line which is parallel to the $(\bar1\bar11)_{t'}$ face. The angle between these two lines is 55° which, once the compression factor of sin $2\theta_B$ is taken into account corresponds to 71° in the crystal. Consequently one may infer that these two lines are traces of the (111) and (11$\bar1$) composition planes.

This topograph showed that the specimen's surface is highly strained with surface cracking which is about 80 μm deep. The strain and cracking are caused by impurities that have adhered to the diamond's surface during growth. As the diamond cooled they caused a non-uniform contraction of the surface which gave rise to the stresses that caused the surface cracking.

An 040 reflexion using molybdenum radiation (λ = 0.71 Å, θ_B = 23°27′) was used to image the central component of the stone; the other two parts being in a non-reflecting orientation. Fig. 15 shows the mid-section topograph, the lower left hand edge of the topograph being ($\bar1$11) and the lower right being (1$\bar1$1). Growth banding can be seen parallel to these two faces. The two upper edges are both irregular since they are the composition planes of the specimen and the material above them is in non-reflecting orientation.

Discussion. Fig. 14 shows that growth started from near the top of the crystal, where the two composition planes appear to intersect. Twinning occurred on both the (111) and (11$\bar1$) planes after the first few atoms had nucleated. These two planes grew at an angle of 70°32′ to each other. The growth banding in the [$\bar1$11] and [1$\bar1$1] directions indicates growth occurred on the corresponding planes. This would have filled up the space between the (111) and (11$\bar1$) planes, thereby giving the diamond a tetrahedral morphology.

Tetrahedral diamonds selected by Tolansky

Four very small (<1 mm^3) natural diamonds selected by Tolansky (1971), (two from the Finsch Mine, one from Premier and one from De Beers) have been examined by Yacoot (1990). A synchrotron Laue picture of each specimen was taken: these showed that two of the specimens were twinned. Scanning electron micrographs of the diamonds showed that their surfaces had striations which were indicative of all the diamonds having suffered mild dissolution. Two of the specimens had suffered severe plastic deformation; X-ray topography, with conventional and synchrotron sources, produced no useful results. Synchrotron topography of one of the specimens suggested that growth started from its (111) face. It is more likely however that the specimen had originally been a twin which was cleaved on the (111) composition plane. Such a cleavage, followed by dissolution would be consistent with the features revealed in the X-ray topographs. Surface dissolution has then enhanced its pseudo-tetrahedral appearance.

Tetrahedral diamonds from the Argyle Mine

The Argyle diamond mine, situated in the remote north of Western Australia, started producing diamonds in 1983 and in 1986 over six tonnes of diamond (30 million carats) were mined from Argyle, accounting for 30% of world natural production (Chadwick, 1987). When examining the lattice distortion in a batch of two hundred diamonds from the Argyle Mine, Clackson (1989) found four diamonds that roughly resembled tetrahedra, three of which were twinned. Synchrotron Laue photographs showed that these diamonds had suffered severe plastic deformation having a polycrystalline structure and were unsuitable for topographic investigation even with synchrotron radiation.

Conclusions

Eleven natural tetrahedral diamonds from different mines have been examined. With the exception of Williams (1932), this is the largest number of tetrahedral diamonds examined in any study and it is certainly the first time X-ray topography has been used to elucidate their modes of growth. All specimens have been shown to possess full cubic symmetry, their tetrahedral appearance being the result of modified octahedral growth which often involved twinning. Their various possible modes of formation are summarised below.

1. The diamond has one twin plane and one half of the twin grows more rapidly than the other: the whole diamond then approximates to a tetrahedron. This difference in growth rates may be due either to one component of the twin containing growth-enhancing dislocations or one component of the twin being prevented from further growth by an obstruction. The two specimens from the Williams' collection described in this paper are examples of these modes of growth. The morphology of these specimens was similar to that described by Shrafranovskii *et al.* (1966).
2. The diamond twins on two non-parallel {111} planes and space between them is filled out by growth in the other <111> directions.
3. The specimen, either a single or twinned crystal, has suffered severe plastic deformation and by chance roughly resembles a tetrahedron.
4. The specimen is a cleavage fragment from a larger specimen, e.g. the tetrahedral shaped chip missing from Howie's diamond. Seager (1979) examined also a tetrahedral diamond which he concluded was a cleavage fragment from a larger stone.
5. A theoretical possibility may be for the crystal to grow outwards from a single face rather than from the centre. If this face was the (111) say, then growth may occur preferentially on the $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$ faces, since these form re-entrant angles with the obstructing surface in contact with the (111) face. These $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$ faces would therefore become smaller in area (and even grow out of the crystal). The $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$ and $(\bar{1}\bar{1}1)$ faces would become relatively large, and delineate a small $(\bar{1}\bar{1}\bar{1})$ facet. The overall morphology would therefore be a truncated tetrahedron (or octahedron with alternately large and small faces). We have not observed a diamond which has grown by this mechamism.

No specimens have been found that grew as flat-faced tetrahedra. Various accidents during crystal growth can account for the existence of tetrahedral diamonds in the point group $\frac{4}{m}\bar{3}\frac{2}{m}$, suggesting that the arguments for assigning diamond to the point group $\bar{4}3m$ are unnecessary.

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