On the Variation of X-ray Diffraction Contrast with Wavelength: A Study with Synchrotron Radiation

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Abstract

Diffraction contrast phenomena on X-ray topographs taken with continuous-spectrum synchrotron radiation have been studied at wavelengths of 0.057, 0.064, 0.071, 0.100, 0.154, 0.206 and 0.250 nm. The specimen was a polished plate of natural diamond with surfaces parallel to (110), ½ mm thick. Using the 111 reflection and a stored electron beam energy of 1.8 GeV all topographs (except that taken with \( \lambda = 0.25 \) nm) were harmonic free. The specimen exhibited mixed-habit growth, containing sectors of normal faceted \{111\} growth and sectors of non-faceted 'cuboid' growth in which growth-surface orientation was variable and only approximately parallel to \{100\}. Prior to X-ray topography the specimen had received localized damage from implantation with fluorine ions of 17 MeV energy. Features whose variation with wavelength was studied included (1) the relative strengths of integrated reflections from \{111\} and 'cuboid' growth sectors, (2) the intensity of 'spike' disorder diffuse reflections relative to sharp Bragg reflections, (3) contrast from inclusions, polishing striae and fracture damage and (4) lattice bending and diffraction contrast at the sites of fluorine ion implantation. Theoretical predictions of the wavelength variation of the intensity of the diffuse reflection images and of contrast due to resolved defects showed good agreement with the observations.

1. Introduction

The application of synchrotron X-ray sources in X-ray topography is now an established practice. In one of the earliest series of synchrotron-radiation topographic experiments, Hart (1975) demonstrated that a resolution at least matching that obtained with conventional X-ray sources and topograph cameras could be realized. Consideration of resolution capabilities and of other attributes and advantages of the method have been discussed in reviews of continuous-spectrum synchrotron-radiation topography (Tanner, 1977; Miltat, 1980).

The freedom of choice of wavelength, within quite wide limits, evokes a question that the experimenter must answer: what wavelength will be most informative in the topographic problem at hand? Clearly, there can be no universal answer; and indeed in many situations the particular circumstances of the experiment (such as high absorption in the case of transmission specimens) greatly circumscribe the choice. Nevertheless, case studies of imaging of common lattice defects, comparing results obtained with as wide a range of wavelengths as possible, will provide useful guidance. The availability of a set of reference topographs can facilitate the interpretation of unfamiliar diffraction contrast patterns. To generate a set of such reference topographs, and to try and account for the differences between them, were the aims of the series of experiments described here.

A well-recognized complication in the interpretation of white-radiation topographs produced by synchrotron sources arises from the overlapping of several orders of reflection in each image. A straightforward way of lessening this complication is to study the 111 reflection from a crystal possessing the diamond structure, for then the second order is forbidden. Having decided on this approach, there remains the choice of crystal species. Diamond itself has the advantage over silicon or germanium in that a relatively thick crystal can be used in transmission by virtue of its low X-ray absorption. Diamond is also of proven robustness and insensitivity to X-radiation damage. Specimen stability is imperative when com-
parability, and, as its prerequisite, reproducibility, of
topographs must be maintained. There are also ad-
vantages in employing a specimen whose imperfec-
tions can be characterized by methods other than
X-ray topography, i.e. by birefringence and optical
absorption spectroscopy. The specimen used in the
present work had been previously studied by several
techniques. It was exemplary in its rich variety of
imperfections, internal and superficial, natural and
laboratory-induced. These characteristics are listed in
§ 2, and the topographic features they generated are
described in § 4. Some quantitative discussion of the
diffraction contrast is presented in § 5.

2. The specimen

The polished plate of natural diamond used for the
topographic experiments was roughly oval in shape,
its maximum dimension overall being 7.4 mm, its least
diameter 4.8 mm, and it was 0.55 mm thick. Its faces
were polished accurately parallel to (110). The original
shape of the entire crystal had been a slightly
elongated rounded rhombic dodecahedron. It was one
of a suite of 13 specimens which had been studied in
the uncut state by X-ray topography (Suzuki & Lang,
1976a) for the purpose of delineating the relative
development of normal, faceted octahedral and of
abnormal, non-faceted growth of approximate cube
orientation. The latter habit was termed 'cuboid' as a
shorthand description (Lang, 1974). These mixed-
habit diamonds manifest (in greater or lesser degree)
two features of special interest in the present context.
Firstly, within the cuboid growth sectors (mainly in
their inner regions) they contain a population of
microscopic and sub-microscopic non-diamond
bodies (whose mineralogy is still the subject of conjec-
ture). These bodies are detectable optically by light-
scattering, and X-ray topographically by the strain
they produce in the relatively perfect diamond matrix
surrounding them. Secondly, there is a growth-
sectorial dependence of the amount and state of
aggregation of nitrogen impurity in these crystals.
[Nitrogen is the major identified, and certainly the
most studied, impurity in diamonds. For an introduc-
tion to the study of nitrogen in diamond, see the
review by Evans (1976).] In mixed-habit diamonds
one finds more nitrogen in the {111} growth sectors
than in the cuboid sectors. Also, one finds a greater
population of the {100} platelet defects in the former
sectors, as indicated both by the 7.3 μm infrared
absorption peak which correlates with platelets and
by the strength of the 'spike' diffuse X-ray reflections
which the platelets produce. [These spike reflections,
known in the X-ray diffraction patterns of diamonds
since 1940, have recently been studied also in the
electron diffraction patterns of diamonds by Sumida
& Lang (1982), and their report gives a summary of the

history of observations and explanations of spike
reflections.] Regions of diamond which contain a
population of relatively large platelets, i.e. platelets
having a major diameter of, say, 40 nm or more, give a
significantly higher integrated reflection than platelet-
free regions. However, it is only when the platelets are
exceptionally large (≥1 μm diameter) and well spaced
apart (≥5 to 10 μm mutual separation) that they can
be individually resolved X-ray topographically (Lang,
1977). An excess reflectivity produced by the platelet
population was strongly evident in the {111} growth
sectors of the crystal (specimen GDO2) used in the
present experiments. This crystal, which combined a
display of individual diffraction-contrast images of the
non-diamond particles in the cuboid growth sectors
with the above-mentioned heightened integrated in-
tensity from {111} sectors, was thus admirably suited
to be a test specimen for studying the wavelength
dependence of contrast from both individually re-
olved defects and from those not so resolved.

Slices parallel to (110) cut from crystal GDO2 have
been used for X-ray, optical, cathodoluminescence,
transmission electron microscopy and other studies.
X-ray topographs of a near central slice (specimen
GDO2/1) taken when its surfaces were in a well-
polished and almost damage-free state have been
published in connection with two investigations. The
first described {111} faceted re-entrants at some
cuboid–cuboid growth-sector boundaries (Suzuki &
Lang, 1976b). The second included experiments on
this specimen concerning the correlation of electrosta-
tic charging patterns with internal structure (Adam,
Bielicki & Lang, 1981). Other experiments were per-
formed on this specimen subsequently. It has been
bombarded locally with 19F ions with the aim of
estimating hydrogen content by the in situ reaction
1H+19F, εα16O (Sellschop, Madiba & Annegarn, 1980).
Later it had been repolished (rather imperfectly) and
then bombarded again. Consequently, in the state
in which it existed during the present experiments it
exhibited both man-made and natural defects in
juxtaposition. Fig. 1 is a much simplified map of
specimen GDO2/1. The orientations of important
crystallographic directions are given, and the location
of features alluded to in § 4 are shown in this figure.

3. Topographic experiments

The rough periphery of the specimen slice represents
the intersection of the polished (110) surfaces with the
original external surface of the crystal. This external
surface was a rounded solution form, without facets.
Thus correct orientation of the specimen, both for
the accurate polishing of the (110) faces and for most
X-ray topographic experiments, was performed by
X-ray methods. In the case of the topographs here
discussed, those taken with the 111 reflection in
symmetrical transmission, alignment was performed on a conventional topograph camera set up on a laboratory X-ray source. The specimen, mounted by two thin Araldite pillars within a light frame attached to a standard goniometer head, was then transported to the white-radiation topograph camera installed at the SERC Storage Ring at Daresbury, Cheshire (Bowen, Davies, Clark, Nicholson, Tanner, Roberts & Sherwood, 1981, 1982). The incident-beam collimator consisted of a pair of coaxial circular apertures trepanned in discs of X-ray-absorbing glass. Each disc was 6 mm thick and their separation was 50 mm. The apertures were each of 8.3 mm diameter, a suitable size for producing a beam that just comfortably covered the whole specimen. Topographs were taken with the plane of incidence vertical (i.e. normal to the plane of the storage ring). Hence the patterns represented diffraction with a single polarization mode, the σ mode. Zero setting of the Bragg-angle scale was done optically, taking advantage of the (110) polished faces of the specimen, but the true Bragg angles could have been about $\pm \theta$ off the nominal values of $\theta_b$ listed in Table 1. A corresponding uncertainty attaches to the wavelengths tabulated, but it is not significant.

Three series of topographs were taken. The principal series, which provided the most data, was the set of $\{111\}$ transmission topographs taken with the wavelengths listed in Table 1, and these topographs are exhibited in Figs. 2–5 and 7–9. In this series, a fixed specimen-to-plate distance of 118 mm was employed, the stored beam energy was 1.8 GeV and the stored current was between 133 and 123 mA. The second series used symmetrical surface reflection from the (110) specimen surface with $\theta_b = 45^\circ$, and specimen-to-plate distances of 20, 40, 80 and 160 mm. The third series repeated the $\{111\}$ symmetrical transmission with $\theta_b = 22^\circ$ but used specimen-to-plate distances of 20, 40, 80 and 160 mm. The second and third series were taken with a stored beam energy of 1.9 GeV. Ilford L4 nuclear plates, emulsion thickness 25 μm, constituted the principal recording medium in all cases. One Agfa Strukturix Type D2 X-ray film was placed on the specimen side of the L4 plate. (One sheet of this double-coated film transmits the fraction 0.87 of Mo $K\alpha$ radiation, $\lambda = 0.071$ nm, and 0.54 of Cu $K\alpha$, $\lambda = 0.154$ nm.) The nuclear plates were processed in diluted D19 developer (1 part D19 to 3 parts water) for 5 min at room temperature. Exposure times ranged from 5 to 100 s, the times being chosen so as to produce photographic densities not greatly dissimilar in the topograph images to be compared.

### 4. Observations

#### 4.1. General remarks

Table 1 includes parameters of importance in determining the leading characteristics of the type of diffraction contrast exhibited by the topographs. The parameters are the absorption and the extinction distance. A reasonable measure of absorption is the transmission ratio ($I/I_0$) of the primary beam calculated from $I/I_0 = \exp(-\mu t \sec \theta_b)$, where $\mu$ is the normal linear absorption coefficient and $t$ is the thickness of the specimen plate. This simple expression disregards anomalous transmission (which is consi-
dered later). The values of $I/I_0$ show that with the four lowest wavelengths in Table 1 one expects patterns not significantly differing from the ‘zero-absorption’ case, but conditions for the pattern with $\lambda=0.25$ nm are tending towards the ‘high-absorption’ case. With a stored electron beam energy not higher than 1.8 GeV it is only at the greatest Bragg angle that one would expect a noticeable contribution from the harmonic radiation giving the 333 reflection. Hence parameters relating to the 333 reflection are included in the table only for $\theta_B=37^\circ$ (in parentheses). Indications of the presence of a harmonic contribution in the pattern recorded at $\theta_B=37^\circ$ are described below in §§ 4.2 and 4.4.

The extinction distance, $\xi$, is given by

$$\xi^{-1} = r_0|F|/\lambda\pi V \cos \theta_B,$$

in which $r_0$ is the classical radius of the electron, 2.818 fm, $F$ is the structure factor and $V$ the volume of the unit cell. Expression (1) omits the polarization factor which is unity in the present experiments. The structure factors used for Table 1 adopt the atomic scattering factors of Dawson (1967). The measure of reflection width, $\Delta\psi_0$, is the full width at half-maximum intensity, in the symmetrical Laue geometry (disregarding anomalous transmission), for the reflection of monochromatic radiation, and is

$$\Delta\psi_0 = 2d\xi^{-1},$$

where $d$ is the interplanar spacing.

A glance at the topographs in Figs. 2–9 shows that the pattern of distribution of octahedral and cuboid growth sectors is the dominant natural feature detected in the specimen at all wavelengths. Its contribution to the image has two major components, that from the growth-sector boundaries, and that from the differing intensities registered from the volumes of octahedral growth compared with those of cuboid growth. The greater intensity from the octahedral sectors is seen to have two components, that which is generated within a range of angular reflection comparable in order of magnitude with $\Delta\psi_0$, and that which arises from the diffuse spike reflections. The latter may spread over an angular range several orders of magnitude greater than $\Delta\psi_0$. The contribution of the diffuse reflections is considered further in §§ 4.3 and 5.2 below. The most striking man-made features imaged in the topographs are the patches of ion-bombardment damage. Their contrast characteristics show a strong variation with wavelength; description of them follows in § 4.5, with more discussion in § 5.3.

4.2. Contrast from internal lattice defects

It was suspected that the diffuse reflections would be leading features of interest in these experiments. To maximize their visibility the unusually long specimen-

![Fig. 2. Synchrotron-radiation topograph of specimen GDO2/1, $\lambda=0.057$ nm. Direction of 111 $g$ vector is shown in Fig. 1. Topograph viewed looking towards X-ray source. (Similar diffraction conditions in Figs. 3–5 and 7–9 except for change of wavelength.)](image1)

![Fig. 3. Synchrotron-radiation topograph, $\lambda=0.064$ nm.](image2)
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To-plate distance of 118 mm was chosen to ensure that background from Compton and other scattering was very low. The resulting loss of geometrical resolution was deemed tolerable especially since this specimen showed no individual dislocation images and (in the $\bar{1}11$ reflection) no fringes in the images of the growth-sector boundaries, for the observation of both of which the best resolution would have been desirable. In studying the thick dark lunes embracing the ion-bombarded patches indifferent topographic resolution was no great handicap. Indeed, in this instance the long specimen-to-plate distance was helpful in revealing the ‘caustics’ associated with the lunes (described in § 4.5). The probable source dimensions when the topographs were taken were about 0.5 mm in the vertical direction (i.e. parallel to the plane of incidence) and about 12 mm in the horizontal direction. With the ratio of specimen-to-plate distance to specimen-to-source distance employed ($1.5 \times 10^{-3}$), the predicted image spreads due to finite source size are 0.75 and 18 $\mu$m parallel to and normal to the plane of incidence, respectively. These predictions are consistent with the observations. A separation of the contributions of the spike diffuse reflection and of the sharp Bragg reflection to the intensity recorded from an extended crystal region cannot be achieved by any simple experimental device in the Laue projection topograph arrangement. In making estimates of the ratio of the integrated intensity from octahedral growth sectors to that from cuboid growth sectors, the spike contributions to the intensities could not be excluded. (This ratio is, of course, not only strongly specimen-dependent in general, but in most specimens it varies irregularly with distance from the crystal centre. Crystal GDO2 is unusually free from the latter variation.) In specimen GDO2/1 the ratio is found to be about 3, a value arrived at by image matching with neutral density filters. It shows no clear-cut dependence upon wavelength.

The images of growth-sector boundaries do vary markedly with wavelength. The diffraction-contrast phenomena at the growth-sector boundaries in this crystal are complex, and only their leading features will be commented upon. As a generalization, the growth-sector-boundary contrast increases as the inclination of the boundary to the plane of incidence steepens. In the present symmetrical Laue-case geometry one would expect the contrast from a plane segment of sector boundary to vanish if the segment lies in the plane of incidence. No segments fulfil the latter condition in this specimen. In the topographs taken with the shorter wavelengths, all the boundaries show strong contrast at their outcrops at both surfaces of the specimen. Consider, as examples of strongly visible boundaries, the $(111)/(001)$ growth-sector boundary (which runs from the centre of the specimen towards the upper left edge of the specimen, in the orientation in which the topographs are reproduced), and the $(\bar{1}1\bar{1})/(00\bar{1})$ growth-sector boundary (seen running from the specimen centre to the lower right

Fig. 4. Synchrotron-radiation topograph, $\lambda = 0.071$ nm.

Fig. 5. Synchrotron-radiation topograph, $\lambda = 0.100$ nm.
edge). The large, relatively flat segments of these boundaries make an angle of about 78° with the specimen surface. In the case of the (111)/(001) sector boundary, the right-hand member of the pair of outcrop images represents the outcrop of the boundary at the X-ray entrance surface, and the same

![Image](image-url)

**Fig. 6.** Characteristic-radiation topograph, 111 reflection, Cu Kα₁, \(\lambda = 0.154\) nm. For comparison with Fig. 7.

**Fig. 7.** Synchrotron-radiation topograph, \(\lambda = 0.206\) nm.

**Fig. 8.** Synchrotron-radiation topograph, \(\lambda = 0.154\) nm.

**Fig. 9.** Synchrotron-radiation topograph, \(\lambda = 0.250\) nm.
situation applies with the \( \{1\bar{1}\}/(00\bar{1}) \) boundary. It follows that in a path parallel to the \( \{1\bar{1}\} \) Bragg planes (i.e. in the direction of energy flow under the exact Bragg condition) the X-rays pass from octahedral growth material to cuboid growth material in the case of the \( \{1\bar{1}\}/(00\bar{1}) \) boundary, and from cuboid to octahedral at the \( \{1\bar{1}\}/(00\bar{1}) \) boundary. With increasing wavelength, the narrowing of the images of sector-boundary outcrops and the reduction in the overall contrast of such outcrops is clearly evident. The visibility of the \( \{1\bar{1}\}/(00\bar{1}) \) boundary outcrops becomes greater than that of the \( \{1\bar{1}\}/(00\bar{1}) \) boundary outcrops at the longer wavelengths 0.154 and 0.206 nm. Regarding ‘area contrast’ from the boundaries, i.e. the contrast seen where the growth sectors overlap in projection, when such contrast is not masked by strong contrast from the outcrops, it is perceived that at the shorter wavelengths the area contrast from the \( \{1\bar{1}\}/(00\bar{1}) \) boundary is greater than from the \( \{1\bar{1}\}/(00\bar{1}) \) boundary. The above-mentioned variations are discussed in § 5.4. Caution is needed in dealing with the sector-boundary images in Fig. 9. It is likely that the broad dark images of the boundaries under discussion exhibited in that figure include appreciable contributions from the \( 2/3 \) harmonic. The strains associated with these boundaries will generate very broad and strong images in the 333 reflection as a consequence of the small value of \( \Delta \psi_0 \) (Table 1).

An intriguing feature in Fig. 9 is the narrow bright line following the course of the image of the X-ray entrance surface outcrop of the \( \{1\bar{1}\}/(00\bar{1}) \) boundary. This bright line (which of course represents a deficiency in the diffracted beam) can be traced from the edge of the crystal to close to the centre. One can also detect a narrow dark line running from the centre in the opposite direction, along a line corresponding to the X-ray exit surface outcrop of the \( \{1\bar{1}\}/(00\bar{1}) \) sector boundary: this dark line can be seen near the crystal centre but is difficult to follow further than about halfway to the specimen edge. The width of the bright line is about 5 \( \mu \)m. These light and dark lines have all the characteristics of the X-ray refraction effects such as quite often appear on high-resolution topographs of sharp-edged, flat-faceted, polyhedral crystals when images of the face edges (or of re-entrants of large steps) cross the projection topograph image. However, no significant surface steps or grooves are associated with the growth-sector boundary outcrops on the polished surfaces of this specimen. The lines are considered again in § 5.4.

Regarding the contrast from the microscopic non-diamond bodies in the cuboid sectors, there is difficulty in judging how its variation with wavelength compares with that of other strain-gradient-producing defects because of much obscuration by the contrast arising from the polishing striae. This problem is evident in the \( \text{Cu \text{K}_\alpha} \) topograph, Fig. 6, and is exacerbated by the lesser geometrical resolution of the synchrotron-radiation topographs. However, individual images of some of the larger bodies in the inner regions of the specimen can be distinguished in the topographs taken with the three shortest wavelengths.

4.3. Disorder diffuse scattering

The platelet defects lying on the \( \{100\} \) planes in diamond constitute a static lattice disorder which generates rod-like extensions of reflecting power in reciprocal space, the so-called 'spikes', parallel to \( \langle 100 \rangle \) and centred on the reciprocal-lattice points. Details of the theory and of the experimental recording of spikes relevant to the present work have been given by Suzuki & Lang (1976c) and Moore & Lang (1977). When a small crystal is set up on an X-ray camera with a characteristic radiation source it is in general a straightforward matter to effect a complete spatial separation of the spike reflections (produced by the characteristic radiation) away from each other and also from the sharp, Bragg reflection of (weak) continuous radiation) simply by mis-setting the crystal a degree or so off the Bragg angle for the characteristic radiation employed. Clearly, when only a continuous spectrum is present, no unique Ewald sphere is available with which to make a single chosen intersection with each spike, and some overlap between the spike reflections themselves, and between them and the sharp Laue reflection, is unavoidable (as mentioned above in § 4.2). The consequence of this on a continuous-spectrum synchrotron-radiation topograph is to add a diffuse haloation to the sharp Bragg-reflection image of a spike-producing region.

The strength of a spike parallel to a given cube direction (say parallel to \( \{100\} \)) varies systematically with the corresponding index of the reciprocal-lattice point with which the spike is associated (in this example the 'h' in \( hkl \) ) (Hoerni & Wooster, 1955). At the \( \{111\} \) point, that of present concern, spikes in all three cube directions are equally strong. The diffuse reflecting power (which the spike represents) falls off inversely as the square of the distance from the reciprocal-lattice point. Despite the fact that with very platelet-rich diamonds spike diffuse reflecting power can be detected over distances from the reciprocal-lattice point comparable with the reciprocal of the unit cell, it is only unusually strong and sharp spikes that retain an easily recordable intensity above the Compton background scattering at mis-settings greater than 2 or 3° off the Bragg angle (in a conventional characteristic-radiation experiment with \( \text{Cu K}_\alpha \)). Crystal GDO2 produces unusually strong and sharp spikes from its octahedral growth sectors. At the \( \{111\} \) reciprocal-lattice points, the strength of the spikes from octahedral growth sectors is several times that from the cuboid growth sectors. Thus, as can be
seen in the figures, it is the octahedral growth sectors which show noticeable halation in the synchrotron-radiation topographic images. These topographs register an integration of the diffuse reflecting power along each spike (to a good approximation). Thus with all three spikes being equivalent at 111 reflections, all will make the same contribution to the total diffuse intensity. The spatial extent of diffuse streaking produced by a spike on a continuous-radiation topograph depends upon the spike orientation in a way which can be calculated as follows. Consider scattering from a point in reciprocal space distant \( R \) from the reciprocal-lattice point of the Bragg reflection concerned. Let the Cartesian components of \( R \) be: \( R_1 \) parallel to the reciprocal-lattice vector \( \mathbf{g} \), \( R_2 \) normal to the plane of incidence, and \( R_3 \) normal to \( \mathbf{g} \) and lying in the plane of incidence. With continuous radiation it is easily seen that \( R_1 \) produces no deviation of the direction of scattering away from that of the sharp Bragg reflection (whose diffracted wave vector is \( \mathbf{K}_0 \)), that \( R_2 \) causes a rotation of the direction of the scattered wave by an angle \( R_2/|\mathbf{K}| \) normal to the plane of incidence, and that \( R_3 \) deviates the scattered wave away from \( \mathbf{K}_0 \) and in the plane of incidence by the angle \( 2R_3/|\mathbf{g}| \). For a spike oriented to give equal components \( R_2 \) and \( R_3 \), streaking in the plane of incidence will exceed that normal to the plane of incidence by the factor \( 2|\mathbf{K}|/|\mathbf{g}| = 2d/\lambda \). This factor is 2.7 for the 111 reflection and \( \lambda = 0.154 \) nm; and in all specimen settings for this reflection the streaking parallel to the plane of incidence will significantly exceed that normal to the plane of incidence.

There is clearly evident wavelength dependence of the visibility of the halation on the synchrotron-radiation topographs. The strength of diffuse reflection relative to sharp Bragg reflection appears to go through a maximum at a wavelength around 0.15 nm.

4.4. Abrasion and fracture damage

Specimen surface abrasion damage of two types is seen on the topographs. The type producing the more important topographic features consists of the polishing striæ which run in two directions rotated 10° clockwise and anticlockwise from the [001] direction, respectively, and which cover most of the area of the specimen. The other manifestation is the population of black flecks of various sizes which represent a peppering of percussion damage on the natural surfaces of the diamond that surround the plate. There can also be seen a delineation of the edges of the plate by diffraction contrast. The last-mentioned has two origins. Firstly, there is some additional damage around the edges, small-scale chipping and cracking produced in the polishing process. Secondly, there is local lattice curvature at the edges arising because of the unsupported edge a relaxation of the state of compressive stress existing in the polished surfaces can take place. All the above-described contrast features progressively diminish with increase in wavelength. However, Fig. 9 again presents an anomaly. This is the wide and relatively strong image of the segment of the edge of the X-ray entrance surface that appears in the lower left of the topograph. The similarity of this image to that of the same segment as recorded by the shortest wavelengths will be noticed, and there can be little doubt that the harmonic radiation contributes to the images of edges registered in Fig. 9.

The fracture damage covers a roughly circular area, diameter about 1 mm, lying just below the top apex of the specimen. This is where some fragments flaked away from the (110) surface when pressure was applied to the apex by a clamping screw holding the specimen in a frame used in the ion-bombardment experiments. The fracture has a rough conchoidal surface. The diffraction contrast from the fracture surface decreases progressively with increase in wavelength. The striking feature revealed by the synchrotron-radiation topographs is the large angular range of misorientation with the contrast producing material in the fracture surface. Observe the displacements in the pattern of blackening on Fig. 7 relative to that on Fig. 6. In particular, note the plume of blackening which has spread across the image a short distance above the topmost ion-bombarded patch in Fig. 7. These displacements increase linearly with increasing specimen-to-plate distance, as shown by the series of topographs taken at \( \theta_s = 22° \) with specimen-to-plate distances increasing from 20 to 160 mm. The maximum rotation of fracture-damaged material relative to the substrate, as exemplified in the plume just mentioned, is about 0.15°.

4.5. Contrast from ion-implantation damage

The five ion-beam-damaged patches, each of diameter \( \sim 0.5 \) mm, all lie on the X-ray exit surface of the specimen. At patches 1 and 5 about \( 8 \times 10^{14} \) fluorine ions per mm² were implanted at an energy of 17 MeV, and half that number at each of the other three patches. The penetration depth of these ions is 5 \( \mu \)m. The dilatation within the lenticle of radiation damage introduced at this depth causes a local uplift of the adjacent specimen surface which is detectable by several optical methods. Three diffraction-contrast features are noteworthy: (1) the strong contrast from the periphery of the patches, giving the lunes so strongly visible in most of the topographs, (2) the much more weakly visible reflection caustics associated with the peripheries, and (3) a possible X-ray interference effect.

The displacement normal to the specimen surface within the area of the patch is accompanied by a lattice rotation at the periphery of the patch. This rotation generates the strong contrast represented in the lunes. Since the rotation axis is tangential to the
periphery its contrast-producing effect is minimal when the tangent to the periphery is parallel to \( g \). Thus the familiar phenomenon of a diametrical 'line of zero contrast' normal to \( g \) is produced. In the present case this pattern is complicated by kinks in the boundary of the patch arising from an imperfectly circular cross section of the pinhole-collimated ion beam. The thickness of the lunes, and their overall intensity, decrease progressively with increasing wavelength through the series of topographs, from the shortest wavelengths up to the wavelength 0.2 nm. The difference between the images of the ion implantation damage recorded with \( \lambda = 0.2 \) nm and with \( \lambda = 0.25 \) nm is not properly understood, but harmonic contribution to the latter pattern is believed to be significant.

Outside the very dark lunes there is an elliptical area of faint extra darkening bounded by a narrow dark elliptical ring. (See sketch in Fig. 1.) The major diameter of the ring lies in the plane of incidence. It is the same for patches 1 and 5, and at these patches its separation from the outer margins of the dark lunes is twice that seen at patches 2, 3 and 4. The ellipses are recognizable at all wavelengths except 0.25 nm, and are seen best on the topographs taken with \( \lambda = 0.154 \) nm. The diameters are independent of wavelength. The rings are explicable in simple geometrical optical terms as reflection caustics, and they correspond to Bragg reflections at the extrema of lattice rotation within material in the vicinity of the boundary of the patches of ion implantation. This interpretation is confirmed by measurements of the major diameter of the ring on topographs with specimen-to-plate distances of 40, 80, 118 and 160 mm, and by absence of the caustic on the characteristic radiation topograph, Fig. 6. The direction of rotation is that expected. At patches 1 and 5 the extremum of lattice rotation has the surprisingly high value of 2.1 mrad (0.12°).

Lastly, on Fig. 7 one can see some finely-spaced oscillations of intensity at the outer boundary of the left-hand lune of patches 3 and 4. They extend round the boundary over a range of about 30° above and below the plane of incidence. Fig. 10 is an enlargement of part of the left-hand lune of patch 3 where the oscillations are seen best. There are two, possibly three maxima. The spacing is about 8 \( \mu \)m. These oscillations hardly justify designation as a 'fringe system', but a type of 'Lloyd's mirror in transmission' interference is not impossible when a plane incident wave of given wavelength passes in succession through two layers, slightly mutually misoriented, and is partially reflected by both of them. In this case, with \( \lambda = 0.154 \) nm, the calculated misorientation is 0.02 mrad. These 'fringes' are absent at the more heavily irradiated patch 5, they are detectable only on the synchrotron-radiation topograph taken with \( \lambda = 0.154 \) nm, and only on the plate taken with a specimen-to-plate distance of 118 mm. If these features were moiré fringes then their visibility should not depend strongly upon the specimen-to-plate distance. Whether or not they be a true interference pattern, it is evident that the conditions for their observation are quite critical.

5. Discussion

5.1. Wavelength dependence of perfect-crystal reflectivity

Consider the relations between the intensities recorded from perfect regions of the crystal on synchrotron-radiation topographs and the familiar formulae of dynamical diffraction theory. The theory gives expressions for the ratio of diffracted intensity, \( P(\theta - \theta_B) \), to incident intensity \( I_0 \), as a function of departure of the glancing angle \( \theta \) from the exact Bragg angle \( \theta_B \) corresponding to the wavelength \( \lambda_0 \) when the incident beam is ideally monochromatic (of wavelength \( \lambda_0 \)) and monodirectional. The integrated reflection on the glancing-angle scale, \( R^\theta \), is given by

\[
R^\theta = I_0^{-1} \int P(\theta - \theta_B) d\theta.
\]

In the case of symmetrical transmission (symmetrical Laue case), zero absorption, and \( \sigma \) polarization state the ratio \( P(\theta - \theta_B)/I_0 \) takes a very simple form when expressed in terms of \( \Delta \psi \) [given by (2)] and the parameter \( y = (\delta A \omega_0)/(\theta_g - \theta_B) \). Then \( P(y)/I_0 = 1/4(1 + y^2)^{-1} \) and \( R^\theta = (\pi/4) \Delta \psi \). In all the following discussion, attention will be confined to one particular Bragg reflection, so that \( F \) and \( d \) are fixed, and the only variable affecting \( \Delta \psi \) is the wavelength. Then one can write (in the zero-absorption symmetrical Laue case)
$R^0 = \left( \frac{\pi}{2} \right) A \frac{\lambda}{\cos \theta_B},$  \hspace{1cm} (4)

where the constant $A = r_0 F d / \pi V$.

In work with synchrotron radiation, the X-ray beam intensity at wavelength $\lambda$, $P(\lambda)$, can be stated as photon flux per steradian per unit bandwidth. Then the intensity recorded on a synchrotron-radiation topograph by a perfect-crystal region will be proportional to $R^0(d\lambda/d\Omega)P(\lambda)$ (Hart, 1975; Miltat, 1980). Introduce $R^1 = R^0(d\lambda/d\Omega)$ to denote the expression for the integrated reflection now relevant. One then finds (under the conditions of the experiment previously stated) a simple proportionality with wavelength

$$R^1 = (\pi/2) A \int \frac{\lambda}{\cos \theta_B} d\lambda, \hspace{1cm} (5)$$

with $A = 2dA = 2r_0 F d^2 / \pi V$. In order to include absorption in the perfect-crystal case one needs to know $\varepsilon$, the ratio of the imaginary part of $F(hkl)$ to the imaginary part of $F(000)$. For odd-index reflections in diamond $\varepsilon$ will be slightly less than $2^{-1/2}$; here the value $\varepsilon = 0.7$ is adopted for the 111 reflection. Batterman & Cole (1964) present a convenient expression for $R^0$ for an absorbing crystal in the symmetrical Laue case, and the corresponding expression for $R^1$ is

$$R^1 = A_s (I/I_0) D \cosh B, \hspace{1cm} (6)$$

where $(I/I_0)$ is the normal absorption factor $\exp(-\mu t \sec \theta_B)$ (as listed in Table 1), $B = \varepsilon \mu t \sec \theta_B$ and the integral $D$ is

$$D = \int_0^\infty \frac{\cosh \{B(1+y^2)^{-1/2}\}}{(1+y^2) \cosh B} \, dy. \hspace{1cm} (7)$$

With magnitudes of $B$ large enough to cause the integral to fall significantly below $\pi/2$, the values of $D$ tabulated by Batterman (1962) can be used. Table 2 lists several values of $R^1$ for each wavelength in order to illustrate the effect of different absorption properties: all crystal parameters except $\mu$ and $\varepsilon$ are the same in these calculations, and are those for the diamond 111 reflection. The four columns of values of $R^1$ represent, respectively, the case of zero absorption, the case of $\mu$ appropriate to diamond but $\varepsilon = 0$, $\varepsilon = 0.7$ and $\varepsilon = 0.95$. The situation $\varepsilon = 0$ could apply in a structure containing two or more elements with judicious choice of wavelength relative to absorption edges of the elements. The value $\varepsilon = 0.95$ is roughly that which applies to even-index reflections from elements with the diamond structure at room temperature. The wavelength dependence of the four values of $R^1$ is illustrated in Fig. 11.

5.2. Wavelength dependence of diffuse reflectivity

The synchrotron-radiation topographs show quite dramatically how much stronger is the spike diffuse reflection component in their intensity compared to that in characteristic-radiation topographs taken with similar wavelengths. In the characteristic-radiation case the combination of narrow incident-beam divergence with a small effective wavelength range determines that only short segments of spikes immediately adjacent to the reciprocal-lattice point satisfy the diffraction conditions for contributing to the intensity when the Bragg reflection is recorded. (If, on the other hand, the crystal were rocked through several degrees about the Bragg-peak angle during the course of exposure, then the characteristic-radiation topograph would register as strong a contribution from spike reflections relative to Bragg reflection as do the synchrotron-radiation topographs.) The scattering

![Fig. 11. Calculated intensity on synchrotron-radiation topographs as a function of wavelength. The integrated reflection, $R^1$, for a perfect diamond crystal, 111 reflection, is plotted for absorption conditions $\mu t = 0$ in (a), and with $\mu$ appropriate to diamond, $t = 0.55$ mm, and $\varepsilon = 0$, $\varepsilon = 0.7$ and $\varepsilon = 0.95$ in (b), (c) and (d) respectively. The interrupted line shows the ratio, $C_1$, of integrated diffuse spike reflection to $R^1$ under the conditions applying in the present experiments. ($C_1$ ordinate scale is arbitrary.)](image)
power represented in the spikes can be calculated with 
the kinematical diffraction theory (Caticha-Ellis & 
Cochran, 1958). The integrated scattering intensity 
represented by the whole spike pattern surrounding a 
given reciprocal-lattice point is equivalent to that of a 
weakly scattering 'ideally imperfect' crystal whose 
lattice interference function is much spread out in 
reciprocal space. Thus the wavelength dependence of 
the strength of the spike reflections integrated over the 
whole region surrounding the reciprocal-lattice point 
within which appreciable spike intensity can be 
recorded is similar to that of the integrated reflection 
from an ideally imperfect crystal. The integrated 
reflection of the latter can be expressed as \( \rho^o \) on 
the glancing-angle scale, or as \( \rho^s \) on the wavelength scale 
appropriate for a Laue photograph. The familiar 
expression for the integrated reflection from a volume 
\( \Delta V \) of non-absorbing imperfect crystal, with the \( \sigma \) 
polarization state, is (James, 1954) \( \rho^o = QAV \) with 
\( Q = r_0^2 F^2 \lambda^4/V^2 \sin 2\theta_b \). Introducing the constant \( A \) 
from § 5.1, the integrated reflection per unit volume of 
imperfect crystal becomes 
\[ \rho^o = \pi^2 A^2 \lambda^2 / d \cos \theta_b. \] (8a)

The corresponding expression for \( \rho^s \) is obtained by 
multiplying by \( (d \lambda/d\theta) \) and is 
\[ \rho^s = 2\pi^2 A^2 \lambda^2. \] (8b)

To allow for absorption, these expressions should 
be multiplied by \( (I/I_0) \) in the case of symmetrical 
transmission. If one now makes the simplifying assumption 
that in the synchrotron-radiation topograph the range 
of wavelengths involved in recording the whole of the 
spike intensity is not so great that the effective average 
of \( \lambda^2 P(\lambda) \) differs much from its value for the sharp 
Bragg reflection, then the ratio \( C_1 = \rho^s / R^s \) (or its 
equal, \( \rho^o / R^o \)) will provide a measure of the relative 
contribution of diffuse reflection to sharp Bragg reflection 
on the synchrotron-radiation topographs as a 
function of wavelength. Taking absorption into 
account, one finds from (6) and (8b), 
\[ C_1 = \frac{\text{constant} \times \lambda}{D \cosh B}. \] (9)

A set of relative values of \( C_1 \) is included in Table 2, and 
their wavelength dependence is plotted in Fig. 11. 
There appears to be good general agreement between 
the calculated and observed trends of \( C_1 \).

5.3. Wavelength dependence of defect contrast

This simple analysis applies to diffraction contrast 
generated by the lattice rotation within the strain field 
of an individual X-ray topographically resolved defect. 
Attention is restricted to situations which can be 
treated as cases of plane strain. These are represented 
in the present specimen by (1) the displacements 
associated with the surface outcrops of growth-sector 
boundaries, where the displacements are in a plane 
perpendicular to the line of outcrop, (2) the displacements 
associated with the ion-bombarded patches in the 
plane normal to the specimen surface and containing 
a diameter of the patch, and (3) displacements in the 
plane normal to a polishing scratch. (In the last-
mentioned case, it should be recognized that 
the scratches consist microscopically of a chain of partial 
ring cracks. However, if the diameters of the ring 
 cracks and the spacing between cracks are both much 
smaller than the X-ray extinction distance, then the 
displacements will average out to a resultant displacement 
in the plane normal to the scratch at distances 
from the scratch greater than a certain distance which 
is still small compared with the extinction distance.) 
The analysis is a simplified version of that applied by 
Authier (1967) and others to calculate the width of the 
'direct image' of straight dislocation segments on X-
ray topographs. (Dislocation images are absent in 
topographs of the present specimen.) Firstly, assume 
that the characteristics of the defect strain field are 
such that the lattice rotations it contains are inversely 
proportional to distance, \( r \), from an axis defined by 
the geometry of the defect, and take place about that 
axis or one parallel to it. In the three cases considered, 
\( r \) is measured from, respectively, (1) the outcrop of 
the growth-sector boundary, (2) the tangent to the 
origin of \( r \). Its radius, \( r_k \), is inversely proportional to 
the plane normal to the specimen surface and contain-
ing a diameter of the patch, and (3) the centre line of the 
scratch. Assume too, for simplicity, that the diffraction 
vector is chosen so that the rotation axis is normal 
to the plane of incidence: this condition will give 
maximum contrast. Next, assume that the crystal 
volume within which the lattice rotation exceeds \( \Delta \psi_0 \) 
behaves as a kinematically reflecting 'ideally imperfect' 
crystal whose integrated reflection is given by (8a) or 
(8b). As a crude approximation, this volume can be 
taken as equivalent to a cylinder whose axis is the 
origin of \( r \). Its radius, \( r_k \), is inversely proportional to 
\( \Delta \psi_0 \), and the volume, \( V_k \), of kinematically reflecting 
crystal per unit length of defect will be proportional to 
\( \Delta \psi_0^{-2} \). It is thus given by 
\[ V_k = \text{constant} \times A^{-2} \lambda^{-2} \cos^2 \theta_b. \] (10)
The integrated intensity per unit length of image of the 
defect, \( \rho_k \), is given by \( V_k \rho^o \) or \( V_k \rho^s \), according to 
whichever expression for integrated intensity per unit 
volume of imperfect crystal is appropriate. Adopting 
\( \rho^s \), and allowing for specimen absorption by multiplying 
(8b) by \( (I/I_0) \), gives 
\[ \rho_k^s = \text{constant} \times (I/I_0) \cos^2 \theta_b, \] (11)
in which the absence of explicit wavelength dependence 
is noteworthy. One may then define, as a measure of 
defect contrast on the topograph, the ratio \( C_2 \) given by 
\[ C_2 = \rho_k^s / R^s = \frac{\text{constant} \times \cos^2 \theta_b}{\lambda D \cosh B}. \] (12)
Values of $C_2$ are listed in Table 2, taking $C_2 = 1$ for $\lambda = 0.057$ nm. The monotonic decrease in $C_2$ as wavelength increases is clearly in qualitative accord with the observations, and the rate of decrease suggested does not seem to be manifestly incorrect quantitatively.

5.4. Contrast from growth-sector boundaries

The contrast at growth-sector boundaries is prima facie evidence that octahedral and cuboid growth material have different lattice parameters. The variation with wavelength of the contrast of outcrops of the $(111)/(001)$ boundary compared with outcrops of the $(111)/(001)$ boundary (as described in § 4.2) indicates that $a_0$(octahedral) > $a_0$(cuboid), as explained below, but none of the contrast phenomena recorded shows directly the magnitude of this excess. It must be remembered that continuous-radiation topographs are insensitive to changes in the length of $g$ unaccompanied by any rotation of $g$. Thus the white line described in § 4.2 that is associated with the image of the X-ray entrance-surface outcrop of the $(111)/(001)$ boundary cannot arise from image displacement due to different lengths of $g$ on either side of the boundary. On the other hand, if it were due to a rotation of $g$ then it should appear at all wavelengths. The fact that the white line [and the dark line associated with the $(111)/(001)$ sector boundary outcrop on the X-ray exit surface] appears only at the longest wavelength (except for a very faint trace of the white line detectable with $\lambda = 0.2$ nm) suggests that anomalous transmission and/or an X-ray refraction effect associated with wave-matching requirements at the boundary are involved, but no plausible explanation in these terms has been developed so far.

Regarding the magnitude of the difference $\Delta a_0 = a_0$(octahedral) − $a_0$(cuboid), one may tentatively assume that this mixed-habit crystal behaves similarly to the specimens in the suite of diamonds of varying nitrogen content whose infrared absorption at 7-8 $\mu$m and lattice parameters were studied by Kaiser & Bond (1959). Then, from the excess absorption in the octahedral compared with the cuboid sectors of the present specimen (Suzuki & Lang, unpublished), one would predict $\Delta a_0/a_0 = 1.4 \times 10^{-5}$. Expressing this relative change in terms of the change, $\Delta \theta_0$, of Bragg angle at a given wavelength one finds that $\Delta \theta_0 \approx 0.2 \Delta \psi_0$ for all the wavelengths listed in Table 1. In § 4.2 it was pointed out that there is stronger area contrast from the $(111)/(0001)$ boundary than from the $(111)/(0001)$ boundary at wavelengths of 0.1 nm and lower. At these shorter wavelengths absorption is negligible and no simple explanation is forthcoming from dynamical theory for this disparity in contrast. Perhaps one may invoke the presence of more distortion associated with the former boundary having characteristics that would lead to wavelength dependence of contrast varying similarly to the ratio $C_2$ (see § 5.2 and Table 2).

Finally, to explain the contrast at the outcrops of these growth-sector boundaries, one must look at the curvature of the Bragg planes in the vicinity of the outcrops which results from the coherency strains involved in connecting two plates of crystal having a lattice-parameter difference such that $a_0$(octahedral) > $a_0$(cuboid). One sees that at the $(111)/(001)$ boundary outcrops the sense of Bragg-plane curvature is such that the direction of the radius drawn towards the centre of curvature is similar to the direction of $g$, whereas at the $(111)/(001)$ boundary the curvature has the opposite sense. This curvature reversal provides the dynamical diffraction conditions (see, e.g. Kato, 1974) under which, when anomalous transmission becomes significant, i.e. at wavelengths of 0.15 nm and greater, the diffracted beams from the $(111)/(001)$ outcrop images will be relatively enhanced, and those from the $(111)/(001)$ outcrop images relatively diminished. This behaviour is exhibited clearly in Figs. 7 and 8, but the state of affairs in Fig. 9 is more complex.

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References


