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Causes of Birefringence in Diamond

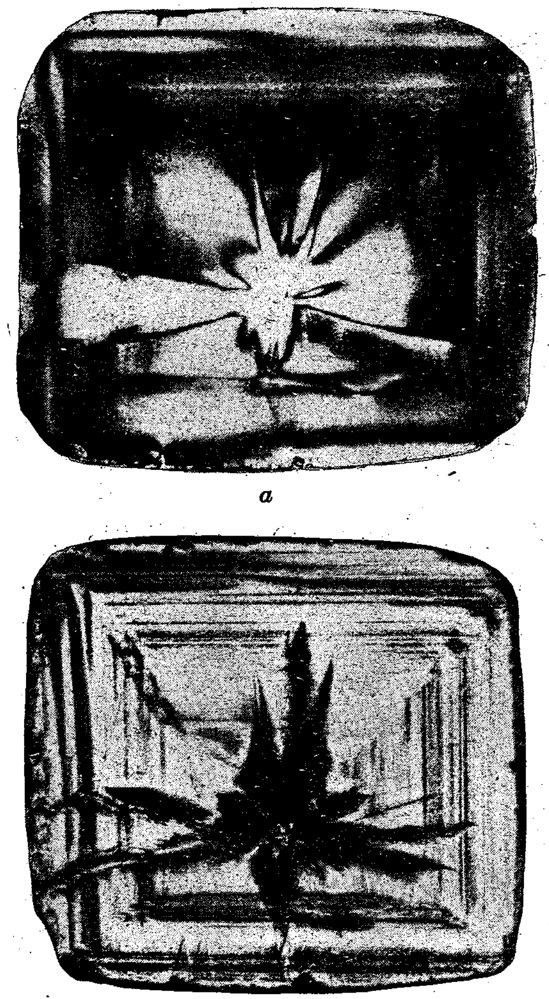
by
A. R. LANG
H. H. Wills Physics Laboratory,
University of Bristol

By optical and X-ray techniques many different causes of strain birefringence in diamond can be distinguished. The perfect diamond, free from strain, is an elusive ideal

In a recent paper, Tolansky[1] reports that of 5,000 good quality diamonds he examined, not one was found free from birefringence. Any strain except uniform dilatation will produce birefringence in diamond. Tolansky's observations become less surprising when viewed against the evidence accumulated in the last couple of decades both for the diversity of strain-producing defects in diamond and for their inhomogeneity of distribution in any stone. The "perfect" diamond becomes ever more elusive as it is pursued with increasingly sensitive tests for imperfection. This article attempts to describe some characteristic patterns of birefringence in diamond and to explain them in terms of the distribution of the particular strain-producing defects responsible for them. The types of defect causing strain have been classified, for convenience, into five groups: (i) dislocations, (ii) lattice parameter variations, (iii) precipitates and inclusions, (iv) fractures and (v) plastic deformation.

(i) *Dislocations*. Many diamonds show a concentration of strain birefringence near their geometric centre. Birefringent regions sometimes extend outwards from this centre, like rays. An association of such patterns with dislocations radiating from the crystal nucleus was first suggested by Frank, Puttick and Wilks[2]. Correctly interpreting as etch pits the pyramidal pits which form one class of the equiangular-triangle-bounded pits known as "trigons" commonly observed on natural octahedral faces, they noted that in a specimen possessing a cluster of trigons on every face, each cluster lay roughly at the foot of the perpendicular dropped from the central strain nodulus to the face concerned. Such a disposition of pits would be expected if they were the outcrops of "grown-in" dislocations generated at the imperfect nucleus and subsequently entrained in the crystal along lines radiating outwards to the growing faces. The association suggested by Frank *et al.* was confirmed by X-ray topography[3]. Further X-ray topographic studies, in which the correspondence of dislocation outcrops with apices of pyramidal trigons was demonstrated[4], and also more recent investigations on both whole stones and sections, have shown that there are many specimens in which radiating bundles of dislocations were obviously the agencies responsible for the major manifestations of birefringence in the specimen.

Fig. 1*a* shows a birefringence topograph of a polished slice of clear white diamond cut from the girdle region of an octahedron. The print is a positive: black means extinction between crossed polarizers; light is failure to extinguish, that is birefringence. The contrast of the print has been enhanced so as to display better the set of rectangular "frames" of relatively weakly birefringent lamellae which cover most of the section, and which arise from variations in lattice parameter (ii). Visual observation shows that the birefringence is strongest at the centre of the "star" and decreases somewhat outwards along its rays. From the X-ray topograph (Fig. 1*b*) it appears that this slice has included the nucleus of the crystal, and that it is dense bundles of dislocations radiating from the nucleus that produce the birefringence star. The greater sensitivity and topographic resolution of the X-ray technique enable the bundles to be resolved into individual dislocations where they are less dense, and disclose in various parts of the slice many individuals which escape detection by birefringence. A uniaxial strain of only one part in 10^6 should produce measurable birefringence in a diamond plate 1 mm thick. Such high sensitivity to strain can be realized with simple optical apparatus when the field observed contains strains differing by this amount or more; for then, with strong illumination and careful exclusion of scattered light, the small variations in extinction over the area of the specimen can be recorded directly by high contrast photography. The X-ray diffraction method requires strain gradients for the production of contrast:



a

b

Fig. 1. Diamond slice cut parallel to (001), edge length 6 mm, thickness 1 mm. *a*, Birefringence topograph. *b*, X-ray topograph, 400 reflexion, molybdenum $K\alpha$ radiation.

only inhomogeneous strains can be detected, but with a sensitivity that surpasses that of the optical method. An earlier report[4], dealing with observations on complete natural octahedra, stated that "possibly some hundreds of dislocations are required to produce noticeable birefringence". With polished slices, which are free from strains due to surface damage, it appears possible to detect by birefringence small bundles of dislocations the resultant Burgers vector of which is perhaps only 3 or 4 unit Burgers vectors.

(ii) *Lattice parameter variations.* The concentric rectangular "frames" which appear in Figs. 1*a* and, better resolved, in Fig. 1*b* are traces of octahedral planes. Such patterns, together with those produced by etching polished slices[5,6], give a valuable stratigraphic record of the growth history of the stone. They testify to non-uniform conditions of growth, with consequent non-uniform concentrations of incorporated impurity. The record in Figs. 1*a* and *b* is unusually simple for diamond: it suggests growth with unchanging regular octahedral habit. A more complicated history, involving a change from rounded to octahedral habit, is indicated by the birefringence, X-ray diffraction and ultra-violet absorption topographs of one of the specimens investigated by Takagi and Lang[7], and is displayed in striking form in the etch patterns of Tolansky[1,6] and some of those of Seal[5]. (A straightforward explanation of the geometry of Seal's and Tolansky's etch patterns has recently been put forward by Frank[8].) The chemical nature of the impurities whose non-uniform incorporation produces strain in Fig. 1 cannot be discovered from birefringence and diffraction topographs. Neither can it be stated whether they are incorporated on an atomic or coarser scale, except that the state of division must be finer than about 1μ. Larger aggregates would probably produce strain fields which could be individually resolved by both the X-ray and optical techniques. It is pertinent to recall the pioneer birefringence topographs of Raman and Rendall[9] and the X-ray topographs of Ramachandran[10]. Raman and Rendall's specimen *D*179 (shown in their Fig. 1) contains a central concentration of birefringence like that shown in Fig. 1*a* here. Ramachandran's X-ray topograph of *D*179 shows a corresponding central region of strong diffraction contrast, but does not resolve dislocations. Raman and Rendall's specimens *D*174, 178 and 179 show growth stratifications parallel to octahedral faces, forming concentric octahedral shells. Ramachandran's careful determination of the sign of the uniaxial birefringence of individual lamellae interspersed in diamonds (Type I) opaque to ultra-violet showed that some lamellae are in a state of tension and some in compression[11]. This certainly suggests that more than one type of impurity is responsible for the differences in mean lattice parameter of adjacent layers of diamond, from which differences the coherency strains arise. Mismatch of this sort can be accommodated by arrays of dislocations lying in the surface separating regions of different lattice parameter. An array probably performing this function is seen in plan in Fig. 7 of the article by Takagi and Lang[7]. Others, seen edge-on, appear in Fig 2*c*. The slice of which the birefringence, ultra-violet transmission and X-ray diffraction topographs appear in Figs. 2*a*, *b* and *c*, respectively, had the same thickness and orientation as the slice shown in Fig. 1, but was somewhat larger. It was also much more imperfect, containing cracks and large inclusions whose strainfields dominate the birefringence pattern Fig. 2*a* and which, as seen in the X-ray topograph Fig. 2*c*, cause either strong diffraction contrast or, in some regions, a misorientation sufficient to tilt the region away from the Bragg reflecting position altogether. The one impurity known to be present in variable concentration is nitrogen, since its presence, when precipitated in platelet form[7,12], is associated with ultra-violet absorption[13]. The ultra-violet transmission topograph Fig. 2*b* (kindly provided by Dr. W. Kaiser) shows a roughly square band of relatively highly transmitting material. This appears because the slice cuts through an octahedral

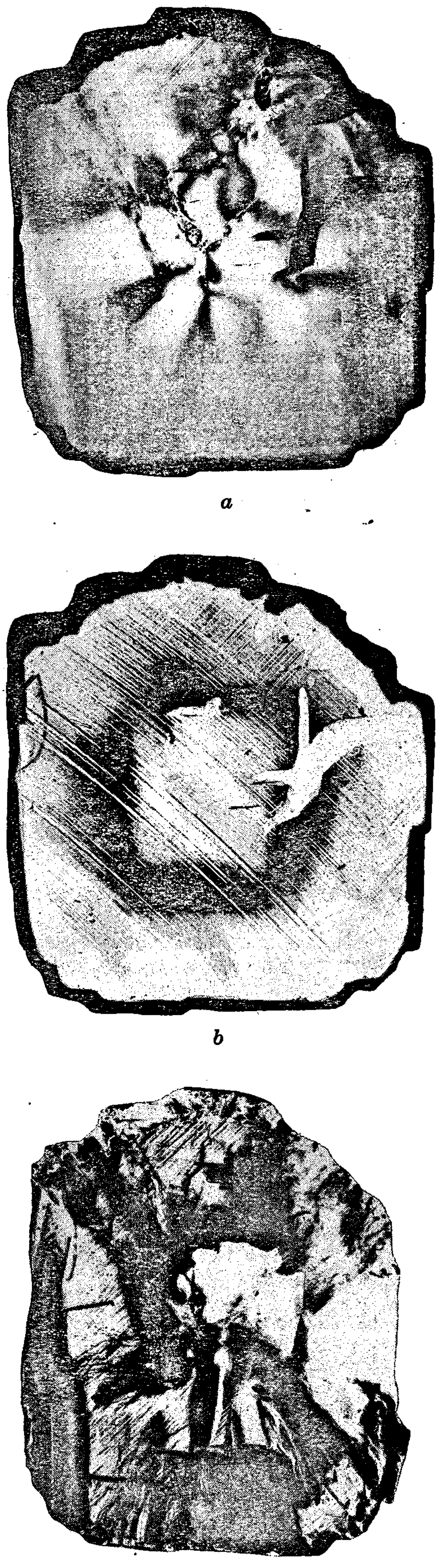


Fig. 2. Diamond slice roughly parallel to (001), edge length 9 mm, thickness 1 mm. *a*, Birefringence topograph. *b*, Ultra-violet transmission topograph. (Blackening on image corresponds to high transmission.) *c*, X-ray topograph, 220 reflexion, silver $K\alpha$ radiation.

shell, roughly 1 mm thick, in which the nitrogen concentration is about 2×10^{19} atoms/c.c., which is about a fifth of that ($\sim 10^{20}$ atoms/c.c.) in the more absorbing central and outer parts of the slice. (Diagonal striae on Fig. 2*b* are to be ignored: they arise from refraction at saw-cut grooves on the specimen faces.) A relatively steep nitrogen concentration gradient appears to be present at the lower, horizontal outer boundary of the band. This boundary correlates with the innermost of three horizontal bands of blackening on the X-ray topograph. From this and other topographs it appears that these bands contain arrays of dislocations; some of the dislocations in each band become entrained in the growing crystal and form the "cascade" of dislocations seen in the lower part of Fig. 2*c*. The regions of high gradient of nitrogen concentration, that is the inner and outer boundaries of the transmitting octahedral shell cut in Fig. 2*b*, have no manifest correlation with any feature on the birefringence topograph Fig. 2*a*, though the strains due to cracks and inclusions may be masking small birefringence variations. It is clear, on the other hand, that the bands of strongest diffraction contrast (note especially the bands running vertically near the left margin of Fig. 2*c*) and which correlate well with bands of birefringence on Fig. 2*a*, have no corresponding feature on Fig. 2*b*. If they are associated with abrupt changes in nitrogen concentration, then such changes must be confined within layers not more than about 10μ thick in order to escape detection in the ultra-violet transmission topograph (Fig. 2*b*) assuming that the layers are parallel to octahedral planes and hence make 35° with the specimen normal.

(iii) *Precipitates and inclusions*. The strains arising from incorporation of inclusions large enough to be easily visible optically are an obvious cause of birefringence. Such inclusions may or may not be the source of dislocations generated by lattice closure errors arising as the foreign body is enveloped by growing crystal: this question will be answered by X-ray rather than birefringence topography. Generation of dislocations at inclusions is very common. Small bodies in the micron range of size are a cause of birefringence less readily identified optically. These small bodies may be inclusions mechanically incorporated at the growing crystal surface, or precipitates formed after growth: the distinction can probably be made if dislocations are present. Inclusions often are a source of grown-in dislocations, as already mentioned, whereas precipitates are observed strung along previously grown-in dislocations, like beads on a thread[14]. In general only the larger strain centres visible on X-ray topographs can be correlated individually with those detected by birefringence[7,14].

(iv) *Fractures*. Strains associated with internal cracks produce both X-ray diffraction contrast and visible birefringence. Cracking is frequently found in the otherwise rather perfect cores of coated diamonds[15]. Natural diamonds have suffered much surface damage: edges are burred and faces bear many percussion marks in the form of partial or complete ring cracks. On X-ray topographs of such surfaces, it is only too evident that all faces are peppered with images of ring cracks. It is found that ring cracks the diffraction images of which spread 25μ or more wide on topographs taken with molybdenum $K\alpha$ or silver $K\alpha$ radiation produce, individually, clearly visible birefringence figures. Cracks of such magnitude occur with a density around 10/mm² of surface. To the extent, then, that all natural diamonds have damaged surfaces, all are birefringent. (It may be noted that the birefringence generated by deliberately produced ring cracks with diameters of 100–200μ is extremely intense[16]; but the birefringence produced by the strainfields of micro-abrasions[17] is quite slight.) If cleavage occurs in an irregular fashion, as it does when diamond plates fail during bending experiments[18], strong birefringence and diffraction contrast are generated by strains associated with subsidiary cracks accompanying the fracture[19]. It is thus not unexpected that a high incidence of birefringence is found among diamond chips (that is, cleavage fragments)[1].

(v) *Plastic deformation*. A type of birefringence found in many Type II (nitrogen-poor) stones[9,11,20] is exemplified in Fig. 3. Such specimens were called "laminated diamonds" by Ramachandran. A descriptive term proposed[7] for this pattern which avoids any suggestion of connexion with growth layers is "tatami"—after the Japanese rice straw mat. The birefringence is very strong. In Fig. 3 it occurs in lamellae dominantly parallel to one octahedral plane. In other specimens equally well developed intersecting birefringent lamellae parallel to more than one octahedral plane can occur. Ramachandran reported that lamellae occasionally occur parallel to dodecahedral planes. Significant features of the tatami pattern are that lamellae parallel to different crystallographic planes intersect each other and also that they cut right through growth stratifications. The latter occurrence could be demonstrated with the specimen of Fig. 3 which was found by M. Takagi to contain some growth layers with a sufficient nitrogen platelet content to show up in ultra-violet transmission topographs. They formed a series of roughly concentric shells centred about a point slightly to the right of the centre of Fig. 3. The similarity of the tatami birefringence patterns to those produced by slip-bands in plastically deformed transparent crystals[21] is so close that its explanation, proposed by Frank, as due to varying amounts of slip, on one or more slip planes, at some stage after growth, appears irresistible. The lower plastic yield stress of nitrogen-poor diamonds (which often show tatami patterns) compared with nitrogen-rich diamonds[18] could account for the greater probability of finding plastic deformation in the former.

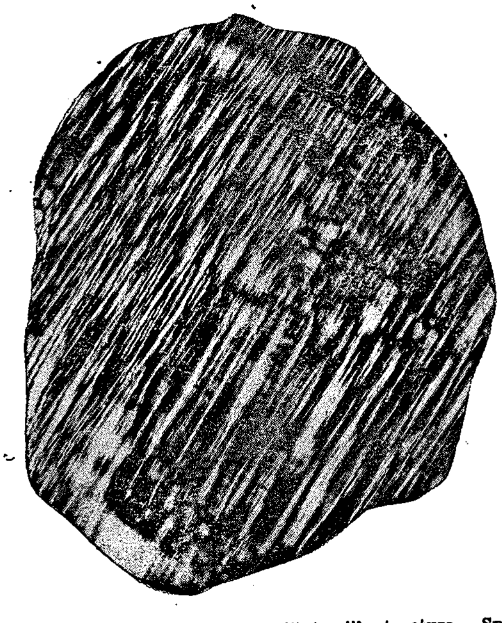


Fig. 3. Birefringence topograph: "tatami" structure. Specimen width 8 mm, thickness 1 mm.

Another type of birefringence pattern found in Type II diamonds is shown in Fig. 4. This is very weak: an exposure forty times that of Fig. 3 was needed to record the pattern, and it could easily escape notice. It was the highly imperfect crystal lattice, found by X-ray topography to approach the ideal "mosaic", that first attracted attention[19]. The X-ray and birefringence topographs look rather alike. There is some overall long range warping, but the characteristic feature is the division of the whole specimen into cells ($\sim 10\mu$ diameter) in the walls

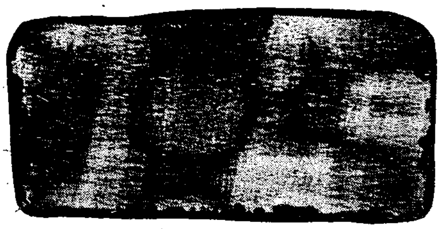


Fig. 4. Birefringence topograph: "annealed" structure. Specimen width 4 mm, thickness 0·5 mm.

of which reside strains, and, presumably, dense, unresolvable dislocation networks. It is believed that this pattern represents an annealed plastically deformed crystal: strains have been greatly reduced compared with those seen in Fig. 3, and the dislocations have been largely re-arranged to lie in cell walls which bear no obvious relation to the original slip planes.

The foregoing account has indicated the variety of causes of birefringence of diamond. Tolansky's[1] invocation of an ever present intermixing of Type I and Type II layers is unnecessary. Indeed there is evidence that it is not generally present. Growth in layers alternately poor and rich in nitrogen platelets, repeating with a period of 5μ or less, would be detected by electron microscopy[12]; and if such occurred with a larger period, and was accompanied by strains sufficient to produce birefringence, it would be detected by X-ray topography. Sharp gradients of platelet concentration do, however, exist at particular growth horizons[7,12] and a single such gradient in the specimen should produce observable birefringence unless dislocation arrays exactly compensate the dimensional mismatch across the boundary where a given number of unit cells of pure diamond meets the same number of cells of a mixture including some cells of platelet[22] structure with those of pure diamond. But birefringence demonstrably arising from other causes is usually observed.

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