

## SELECTED PROPERTIES OF NEUTRON IRRADIATED DIAMOND<sup>1</sup>

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### ABSTRACT

An investigation of the grinding hardness of large single crystal diamonds in selected crystallographic directions as a function of the amount of fast neutron irradiation up to  $10^{18}$  nvt (fast) has been made. Further studies of other physical properties include cleavage, density, x-ray diffraction, piezobirefringence and index of refraction, and optical absorption. In each phase of the work, studies have been made of irradiated and non-irradiated diamonds, and in some cases, of annealed diamonds. It is concluded that displaced carbon atoms accumulate in the interstitial zones of amorphous carbon between mosaic blocks of diamond which contain randomly distributed vacancies and some interstitial carbon atoms. Annealing to  $600^\circ$  permits at least some of the interstitial carbon atoms to return to normal structural sites, but the carbon in the amorphous intermosaic zones does not return to the vacancies.

### DIRECTIONAL GRINDING HARDNESS IN IRRADIATED, NON-IRRADIATED AND ANNEALED DIAMONDS

In 1958, Damask (1958) published the results of a study of the grinding hardness and density of neutron irradiated diamond. In view of the well-known anisotropy of grinding hardness in diamond (Bergheimer, 1938; Kraus and Slawson, 1939; Slawson and Kohn, 1950; Wilks, 1952; Denning, 1953), it seemed worthwhile to investigate the directional changes of the grinding hardness of diamond with neutron radiation damage.

Because of the great hardness of diamond, it is not practical to use indentation or scratch methods as a measure of its hardness. Consequently, grinding hardness, which has been defined as a dimensionless quantity whose numerical value is reciprocal to the abrasion rate on a cast iron wheel charged with diamond dust under carefully controlled conditions, is used (Denning, 1953). An alternative procedure is the microabrasion method of Grodzinsky and Stern as applied by Wilks (1952, 1962), in which the depth of cut, as determined by multiple beam interferometry (Tolansky, 1948), is used as a measure of the abrasion rate under specified conditions. Both methods give consistent results with respect to hardness maxima and minima. In the present study the former approach, grinding hardness, was used.

A grinding hardness comparator (Denning, 1953) was used so that a reference diamond could be ground simultaneously with the diamond

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being tested, in order to minimize uncontrollable changes in grinding conditions. The abrasion was carried out on a conventional diamond cutter's 12-inch diameter wheel or skeif of cast iron. Diamond powder ( $8\text{--}25\mu$ ) mixed with olive oil was the abrasive medium. Two diamonds were ground simultaneously in all tests. One stone was a non-irradiated diamond which was arbitrarily assigned a unit hardness. The non-irradiated diamond, used as a hardness reference, was oriented with the plane

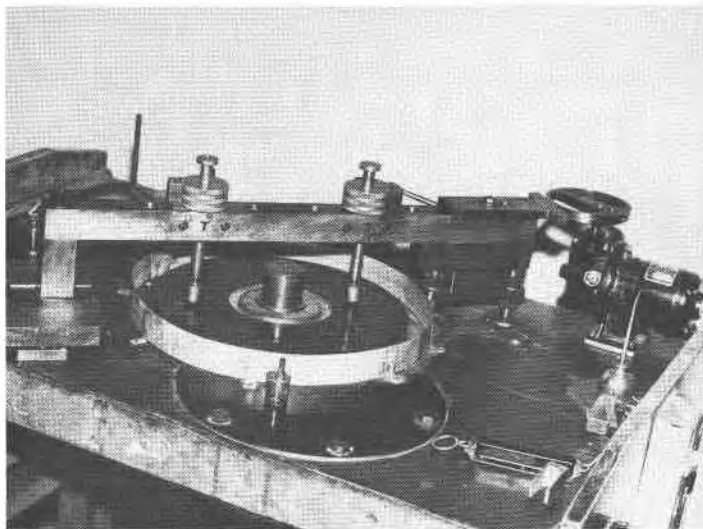


FIG. 1. Hardness comparator.

(101) parallel with the surface of the skeif and with the direction [010] normal to the radius of the skeif.

Figure 1 shows a general view of the hardness comparator. The horizontal bar was placed over a diameter of the skeif. During grinding the bar oscillated parallel to its length to distribute wheel wear. The two diamonds were mounted on the ends of the spindles which were free to move perpendicular to the surface of the skeif. Prior to measuring the grinding rate, facets were prepared on the stones and bevels were placed adjacent to the facets to be used for hardness measurements. In order to maintain self-consistent results during the entire study, three reference standards were prepared. In these non-irradiated standard reference stones, a (101) facet was prepared and the grinding direction within that plane was selected as [010]. A grinding hardness of unity was arbitrarily assigned to the reference standards. One standard was retained as a primary reference to check the secondary or working standards after the latter had been refaceted after prolonged use. Such a procedure was es-

sential, since small changes in the orientation and size of the facet might result in disproportionately large changes in the rate of abrasion.

The diamond to be studied and the reference diamond should present equal areas to the skeif and should be loaded to exert equal thrusts upon the skeif. It has been found that if the aspect ratio of the facets is kept below two and if the areas of the two facets are the same within a factor of two, the relative rate of abrasion of the two stones can be reduced to volume removed for constant force per unit area. The abrasion rate within these limits is directly proportional to the force normal to the skeif and inversely proportional to the area of the ground facet. If the aspect ratio of either facet or the areas of the two facets differ by a factor of much more than two, it has been found empirically that the linearity of the abrasion rate is seriously disturbed.

It is well known that the grinding rate in diamond is dependent, in a rather complicated way, upon orientation of the ground facet and the direction of grinding within the facet. Diamond is by no means unique in this regard; in fact, it seems certain that in all crystals a similar relation should be observed. In practice, such is not the case. The very large anisotropy of grinding hardness in diamond is due, not to a large anisotropy of any feature of the diamond structure, but to mechanical factors relating to the abrasion process. That this is true can be demonstrated by abrading diamond under different conditions from those used in the present experiments.

The extreme anisotropy of grinding hardness in non-irradiated diamond has been explained by Wilks and Wilks (1959; Wentorf, 1959) as being due to the fortuitous fact that the abrading grains are buttressed firmly against the cast iron skeif during the grinding of "soft directions," but the cast iron yields to the force of grinding in the hard directions. The presence of the hard and soft directions is explained in terms of cleavage. Another factor is the fact that the abrasive is diamond powder, whose hardness is very close to the extremes of hardness of the diamond under test. In considering the latter factor, it should be pointed out that it does not matter whether the abrasive diamond powder is randomly distributed on the skeif or whether it is oriented to present only the hardest directions of the particles to the diamond under test, since the grinding rate of a randomly oriented powder should be no less than half the rate of that of a preferentially oriented powder (Slawson and Denning, 1958).

The preparation of specimens for grinding tests must be carefully done, since in certain directions the orientation is quite critical. The most critical orientation in the present study is found in the case of a cube facet ground in the direction of a four-fold symmetry axis, *i.e.*, (001) [010]. The problem of orientation is greatly accentuated by the sense of the orienta-

tion error. If the plane is so oriented as to make an angle of 15 minutes with the [010] axis, then if the grinding is done toward the ideal cube plane, the hardness is greatly increased. If, on the other hand, the grinding is done in the opposite direction, *i.e.*, away from the ideal cube plane, then no appreciable hardness change is observed.

In the case of facet misorientation of 15 minutes of arc such that the facet remains parallel with the [010] axis, the effect upon grinding hardness is negligible. It is therefore essential that the grinding must not be performed toward the ideal cube plane. For this reason, it is not feasible to attempt to orient the cube facet exactly parallel with the ideal crystallographic cube, but it must be made certain that the orientation error is not one which will yield a markedly high hardness value.

Similar consideration should be applied to the dodecahedron plane. However, in this instance, the apparent hardness increase with misorientation is not so severe as in the case of the cube facet.

The diamonds used for the hardness tests were carefully selected by examination with a hand lens. The diamonds appeared to be nearly perfect octahedrons, were free of recognizable flaws, and showed no rounding of crystal faces. The stones were one-half carat (0.1 g) in weight and were slightly off color. They appeared practically colorless to casual inspection, but in the diamond trade, from the point of view of color, they would not be considered top quality stones. Because of the flatness of the faces, aside from the usual trigons and a few small steps, there was no difficulty in measuring the interfacial angles to within two minutes of arc on the optical goniometer.

The first step was the preparation of the desired facets for grinding tests. The facets were put on as accurately as possible (about 2° error) "by eye." Next the stones were placed on a two-circle goniometer and the poles of all the octahedral planes and the ground facet were located. The octahedral plane positions were self-consistent to within five minutes of arc. From the location of the poles of the octahedral planes, the most probable position of the reference axes was determined. Then (in the case of the cube plane) the two angular components needed to "move" the ground facet so as to be perpendicular to one of the reference axes were computed. After the measurements the stone was remounted. During the next operation only small angles need be measured. These angles are between the original ground facet and the corrected facet. The angle which the corrected facet made with the preliminary facet was determined by holding the stone in its dop close to the observer's eye so as to see a double image of a small light source reflected simultaneously from the two facets. Only a portion of the aperture of the observer's eye was covered during this operation so that he might simultaneously view a

scale on the opposite side of the room. Thus he was able to see two virtual images of the light source superposed upon the scale, which is graduated to 15 minute intervals of interfacet angle. With practice a precision of about five minutes of arc was attained quickly. After the proper correction had been made by the time-honored method of bending the copper rod which supports the dop, the corrected facet was enlarged by grinding until the preliminary facet was just eliminated. A final check was always made on the two-circle goniometer, but rarely was a further correction necessary.

The next operation was the cutting of four bevels around the edge of the facet. These made about a  $15^\circ$  angle to the plane of the facet. No great accuracy was needed as all of the bevels were subsequently measured on the goniometer. Finally, small identifying facets were placed on the stones to avoid any possible confusion during the study.

In order to abrade the diamonds for the actual hardness tests, they were mounted in small special solder dops which were attached to the spindles by means of a copper rod. The final adjustment of facet orientation was obtained by means of an optical back reflection apparatus. A nearly parallel beam of light from a ribbon filament lamp was incident on the diamond which was mounted on a spindle, resting in a V-block. A semi-cylindrical screen of 50 cm radius surrounded the diamond. A 3-mm opening in the screen allowed the light beam to impinge on the diamond. The light beam was parallel with the axis of the spindle. The facet on which the hardness measurement was to be made was adjusted so as to be made perpendicular to the spindle axis. The adjustment was made not only by means of reflections from the facet itself, but also by means of reflections from the bevel facets and the natural octahedron faces. An accuracy of five minutes of arc was attainable. The grinding azimuth on the facet was marked on the side of the dop.

Next the spindle was placed in the comparator and the surface was ground for a few seconds. The lightly ground surface was then examined under a microscope, and the correctness of facet orientation was confirmed. The azimuth of the grinding grooves was then compared with the desired direction, and thus the sense and the amount of spindle rotation needed to give the correct grinding azimuth were determined. The spindle was replaced in the comparator and the final azimuth was set from the graduated spindle circle.

The similar procedure was used to orient the reference standard. When both stones were in place, they were ground, usually with a 250 gram load, for three minutes. A series of three to twelve tests was made and the results were averaged. The measurements are summarized in Figs. 2-5. In common with previous experience in the measurement of grinding hard-

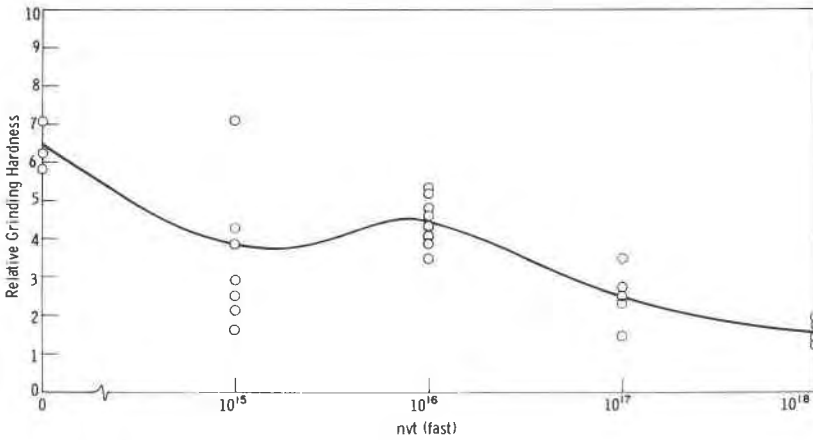


FIG. 2. Hardness vs. irradiation cube C-1.

ness on diamond, a major difficulty was found in the reproducibility of successive measurements. The principal causes of the variation in the measurements of grinding hardness on the diamonds are the result of changing conditions of the surface of the skeif during testing and the uncertainty of the measurement of facet size. The first effect is minimized by using the comparison of the cutting rates of two diamonds as described above. The average of a series of measurements has been found to be satisfactory in assessing relative grinding hardness of various directions within a diamond and in comparing the relative grinding hardness of

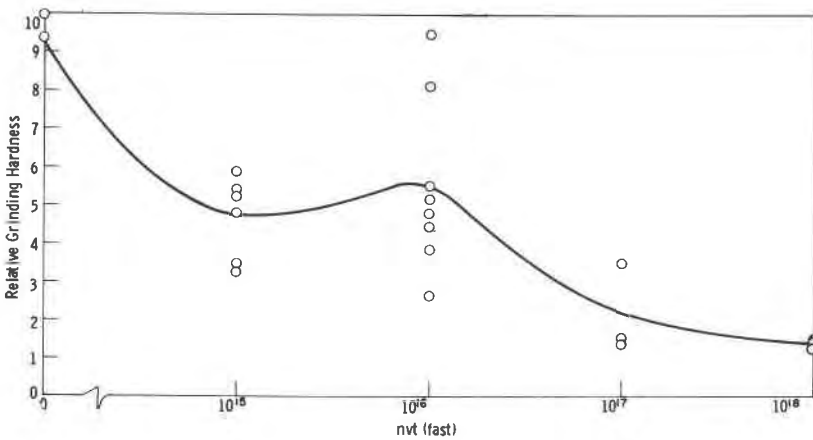


FIG. 3. Hardness vs. irradiation cube C-2.

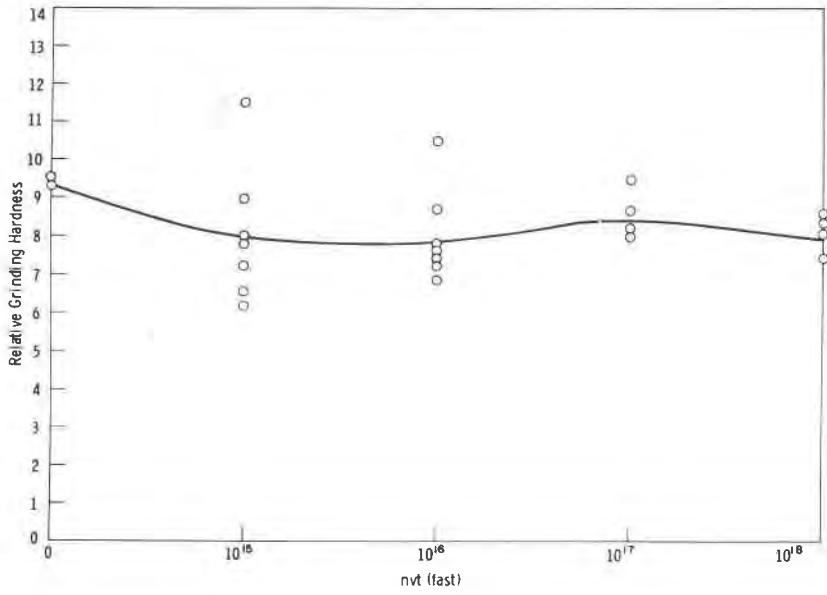


FIG. 4. Hardness vs. irradiation dodecahedron A-5.

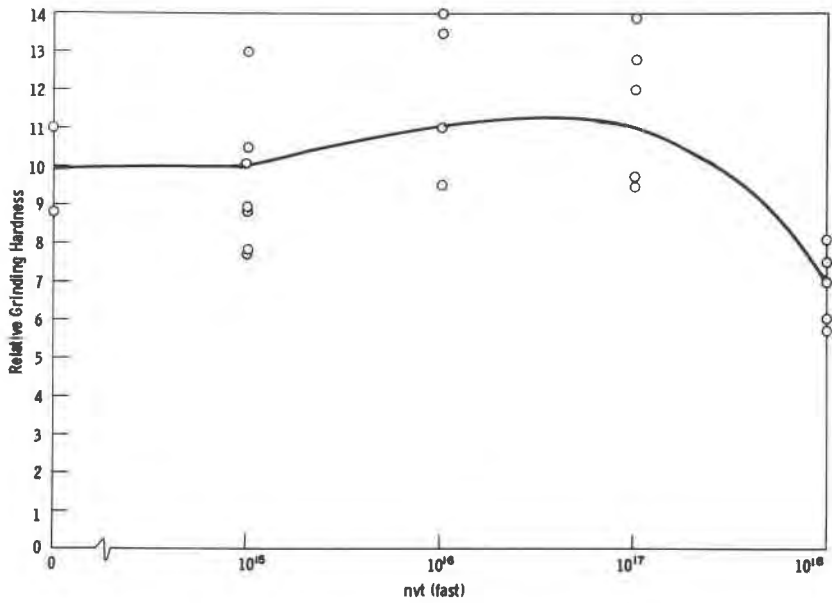


FIG. 5. Hardness vs. irradiation dodecahedron D-1.

different diamonds. Changing skeif conditions do not effect both stones in identical ways, but the use of two stones has been found to minimize the difference in behavior.

The deviation from the mean is large on the cube face of the diamonds irradiated to  $10^{16}$  nvt (fast). The cause can be readily traced to the unavoidable use of a filar micrometer which, because of the design of its reticule, did not permit so reproducible a setting during the measurement of the dimensions of the cut facets.

The decrease in hardness of the cube plane ground parallel to a four-fold symmetry axis is large and significant. While the spread of values is rather large, it is no larger than is to be expected in grinding hardness measurements. The curve drawn is based upon the average values for the hardness determinations represented by the points. The slight reversal of hardness decrease at  $10^{16}$  nvt (fast) may not be real. The uncertainty of the measurements is such that the reversal falls just within the 50% confidence limits of the measurements. Since corresponding reversals were not found in the properties other than hardness, it is believed that the inflection may not be significant.

The dodecahedron shows what is, within the accuracy of the measurement, an essentially constant hardness independent of the amount of radiation up to  $10^{17}$  nvt (fast) with a slight reduction at  $10^{18}$  nvt (fast). The fact that the grinding hardness on a dodecahedron plane ground parallel with the four-fold axis does not decrease with relatively low levels of fast neutron irradiation, while the grinding hardness of the cube face in such a direction does decrease markedly, indicates a reduction in the anisotropy of grinding hardness of diamond with respect to fast neutron irradiation.

Such a reduction immediately suggests the possibility that the octahedron plane (111) may be ground in such irradiated stones. It is generally recognized among practical diamond cutters that the octahedron plane can not be polished in any azimuth. In fact, the rate of removal of material on such a plane is very small. With prolonged grinding in non-irradiated stones and with the continued application of diamond abrasive on the skeif, it is possible to remove material from an octahedron plane; however, the surface remaining on the diamond undergoing such treatment is very rough and deeply grooved so that the surface is not what one would expect on a polished facet. It is generally considered impossible, or at least highly impractical, to polish a diamond facet closer than about two degrees to the octahedron (Slawson, 1957). Experiments in this laboratory confirm the diamond cutter's experience in attempting to grind octahedron planes.

Attempts were made to grind octahedron facets on diamonds which



had received fast neutron bombardment. The octahedron plane resisted abrasion in the usual manner through a total irradiation of  $10^{17}$  nvt (fast). After irradiation to  $10^{18}$  nvt, however, it was found that the diamond could be cut practically on an octahedron plane with an ease not found in the non-irradiated stones. The surfaces thus formed were not so smooth as on facets polished on-grain, but nonetheless the material could be cut very close to the octahedron without the addition of extra abrasive diamond dust to the skeif. Since it is not possible to orient a diamond exactly on the skeif, an attempt was made to place the stone as close as practically possible to the desired orientation. Recalling that the  $\rho$  angle from the cube plane to the octahedron plane in a cubic crystal is  $54^\circ 44'$ , tests were made at  $\rho$  angles which, when measured, were  $54^\circ 30'$ , and  $55^\circ$ . The uncertainty in these angular measurements does not exceed five minutes. On the facet  $\phi = 45^\circ$ ,  $\rho = 54^\circ 30'$ , the stone could be cut toward the nearest cube face, although this was the hardest of the directions observed in the octahedron tests. The surface left was rather rough. When the same facet was ground in the opposite direction, that is, away from the cube, and toward the very near octahedron plane, the stone was found to be softer, and it was cut without any particular difficulty. The other pair of measurements was made on a facet at  $\phi = 45^\circ$ ,  $\rho = 55^\circ$ . In this plane the grinding toward the near octahedron face was found to cut readily and also the direction toward the dodecahedron, which is  $180^\circ$  from the last mentioned direction, was also found to cut without difficulty. In general the relative grinding hardness decreases in the order in which these directions have been listed. In all of these octahedron tests, the sound of grinding was normal. This in itself indicates quite clearly that these normally extremely hard directions, encountered in non-irradiated diamonds, are considerably softer in the stones irradiated at  $10^{18}$  nvt. It is not possible to give quantitative measurements on these directions; however, there is no doubt that while the cutting rate is much more rapid than is normal for planes so close to the octahedron, it is still slower than the optimum cutting rates found on the cube and dodecahedron planes. Wilks (1962) found the relative depths of microabrasion cuts on octahedral planes of diamonds given a neutron irradiation of  $1.9 \times 10^{20}$  n/cm<sup>2</sup> to be 14.9, 7.3 and 6.9, in the direction toward the dodecahedron, parallel to an edge, and toward the cube, respectively. The results are compatible with those presented here, as also are the measurements on the cube and dodecahedron.

The demonstrated reduction in anisotropy of the grinding hardness with irradiation, is the most significant result of the specific hardness tests. It should be pointed out that there is no indication of an initial increase in hardness with low level radiation, which has been suggested

by some cutters who have worked with stones colored by neutron bombardment.

The annealing tests show that upon annealing to 600° in 200° steps with one hour of heating at each temperature, the hardness of the cube plane is partly restored, but the hardness of the dodecahedron plane, which was not effected appreciably, except slightly at the highest irradiation used, remains substantially unchanged during annealing. Since on the dodecahedron plane the reduction was so slight, the annealing was done only at 400 degrees. While there may be some recovery toward initial hardness on the octahedron plane, no obvious increase was observed during the annealing. Had reliable measurements been made on the octahedron, it might be found that some recovery toward initial hardness had occurred.

#### CLEAVAGE IN IRRADIATED, NON-IRRADIATED, AND ANNEALED DIAMONDS

Directional hardness in crystals has long been considered to be directly related to cleavage. Cleavage, used for over a century as a determinative property of minerals, has been described in qualitative terms, such as perfect, imperfect, easy, and difficult.

The principal cleavage of diamond is parallel with (111). In the qualitative scale of cleavage perfection in determinative mineralogy, diamond possesses a perfect cleavage. The essential meaning of the term, which could easily be misinterpreted, is that in diamond the tendency to break along the (111) plane is very strong, while the tendency to break along other surfaces, even those very close in angular position to (111) is slight. In other words, if cohesion, or surface energy, is plotted as a function of an angle, very sharp discontinuities appear in the directions normal to the (111) planes. In addition to the perfect (111) cleavage, diamond exhibits a rather poor (110) cleavage. If the cohesion is plotted as a function of direction, the minima found coincident with a normal to the (110) plane are not so deep and are much broader in zone  $[\bar{1}10]$  than are the practically discontinuous peaks of the octahedral cleavage. Other directions of cleavage have been reported in the literature (Ramaseshan, 1946). The difference between cleavage perfection in type I and type II diamonds (Wilks, 1958), while of considerable interest, is not germane to the present study since only type I diamonds were used.

The octahedral planes in diamond are those planes of greatest interatomic separation. Another means of expressing the same fact is that separation occurs along the planes of maximum reticular density. The perfect octahedral cleavage and [110] "microcleavage" of diamond have

been correlated with the covalent bonding of diamond (Wolff and Broder, 1959).

Since the hardness variation with respect to direction is related to cleavage (Bergheimer, 1938; Wilks and Wilks, 1959; Wentorf, 1959), then it would seem that the reduction in anisotropy could be interpreted as being dependent on the development of a larger number of cleavage planes. Since cleavage may be considered as anisotropy of cohesion, the increased number of cleavage planes suggests a reduction in anisotropy. The additional cleavage planes, or perhaps, a better nomenclature is fracture surfaces, need not be crystallographic planes in the usual sense.

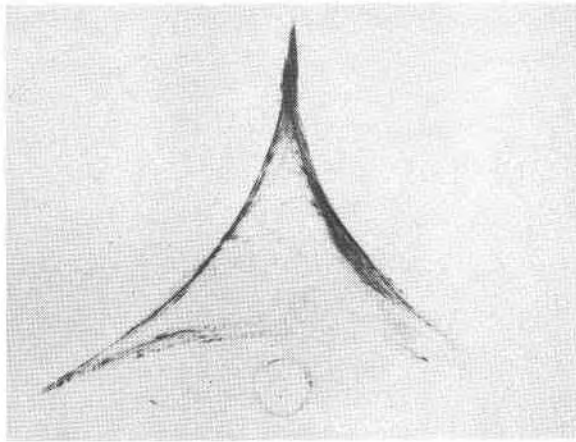


Fig. 6. Light figure, diamond irradiated to  $10^{18}$  nvt (fast).

In fact, there is no indication that these additional surfaces of weakness are crystallographically oriented in the irradiated diamonds. These virtual cleavage planes, or fracture surfaces, are probably quite randomly distributed with respect to crystallographic direction, and they may very well follow quite irregular surfaces which are controlled by the boundaries of the mosaic blocks which presumably constitute the large crystal. They may very well be related to initial defects or dislocations present in the diamond.

A serious attempt was made to examine the cleaved surfaces of the irradiated diamonds by multiple beam interferometry (Tolansky, 1948). It was found that the technique could not be applied for examination of minute details of surface topography because of the relatively irregular nature of the cleavage surfaces. The diamonds were cleaved by a professional cleaver so that an optimum technique was employed.

Figure 7 is a photomicrograph of a cleavage surface of diamond which

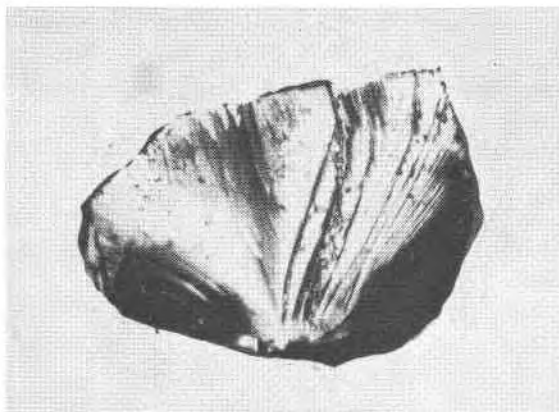


FIG. 7. Cleaved surface of diamond from which the light figure shown in Fig. 6 was obtained.

has been irradiated to  $10^{18}$  nvt fast prior to cleaving. The rather conchoidal nature of the surface is apparent. In order to obtain information on the angular distribution of all the small elements of the surface, an optical back reflection or light figure method was used (Fig. 6). The apparatus used to obtain the light figures is schematically shown in Fig. 8. The light source, lenses  $L_1$  and  $L_2$ , and the small aperture  $A$  produce a bright spot of light about 0.3 mm in diameter in the plane of the perforated photographic paper,  $P$ , at the focal point of a  $7\frac{1}{2}$  inch photographic objective,  $L_3$ .

The rays which pass through  $L_3$  to the diamond,  $D$ , are parallel to within 0.1 degree. In the diagrammatic representation, the diamond is drawn with two facets. Facet  $ox$  is shown normal to the optical axis of the instrument. The image representing plane direction  $ox$  then will lie at the focal point of  $L_3$ . Inclined facet  $oy$  is represented by a point  $z$ . In general all small elements of the surface of the crystal which are parallel to  $oy$  are also represented by the image at  $z$ . Facet inclinations up to about  $20^\circ$  can be recorded. Such a system provides an angular resolution of about  $\frac{1}{4}$  degree facet angle unless the individual reflecting element or facets are extremely small or few. The surfaces of the diamonds were aluminized by vacuum evaporation prior to obtaining the light figures. Such treatment

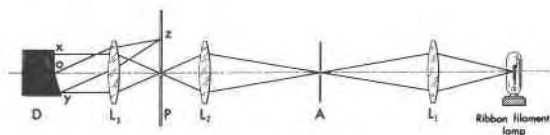


FIG. 8. Schematic diagrams of light figure apparatus.

removes the possibility of obtaining images from the rear surface of the diamond in the case of the transparent non-irradiated stones.

In the case of the octahedral cleavage surfaces of non-irradiated diamond, a small spot of threefold symmetry is produced which indicates that all of the reflecting elements are parallel within one degree. The surface must be skewed slightly so that it registers on the photographic paper.

The light figure from the irradiated diamond is striking in that no reflection is found at the center of the rather large triangular arcuate light figure. Thus the (111) cleavage has disappeared. In its place are three symmetrical sets of cleavage elements whose angular distributions are as the elements of three nearly hyperbolic cones. The planes closest to the pole of (111), that is, points at the centers of the arcs, have a  $\rho$  angle of  $56^\circ$ . The Miller indices were calculated as (36·36·35). The true values could lie between (31·31·30) and (41·41·40) if the maximum error of measurement is considered. The planes farthest from the pole of (111), the vertices of the triangular figure, have  $\rho$  equal to  $49^\circ 20'$  and indices near (33·33·40). Another noteworthy feature of the pattern is the concentration of the elements of the cleaved surface at discrete angular positions as revealed by the beaded appearance of the arcs. The lack of ideal symmetry of the light figures is attributed to the non-symmetrical arrangement used in cleaving the diamond. Such lack of ideal symmetry is less apparent in the non-irradiated stones. The non-irradiated stones are stronger as is revealed by the grinding tests and the bond distribution exerts a greater influence during the cleaving process.

The distribution of cleavage surface elements described above does not seem compatible with the diamond structure. In diamond the (111) cleavage planes are planes of separation which disrupt the least number of bonds per unit area (Winkler, 1955). A drastic change in structure would be necessary to produce the cleavage pattern observed. Such a change is incompatible with the observed x-ray patterns of irradiated diamonds. An alternative interpretation follows. Each reflection maximum observed is a reflection from a set of (111) planes in coherent blocks of diamond. The mosaic blocks have rotated as a result of the cleaving. In this way part of the strain energy acquired during radiation is liberated near the cleaved surface.

The regions separating the blocks consist of amorphous carbon, or, if diamond, a very poorly crystallized type. The light figure from a diamond cleaved after irradiation to  $10^{18}$  nvt fast and annealed at  $400^\circ$  for one hour, and again, at  $600^\circ$  for one hour, shows no significant difference from the light figure of irradiated non-annealed diamond. Thus annealing, as far as carried out, does not remove the amorphous regions. Recovery is

restricted to the minute single crystal mosaic units or to the amorphous layers, but these two essentially different phases are not reunited.

An electron micrograph of the cleavage surface of the irradiated diamond represented in Fig. 9 is shown. The deep cracks which appear in the photograph are interpreted as occurring in the intermosaic amorphous regions. The mosaic blocks are from  $0.1\mu$  to  $1\mu$  in diameter.

The reduction in grinding hardness and hardness anisotropy is explained by the development of additional surfaces of relative weakness produced during the radiation. These surfaces or regions are not highly

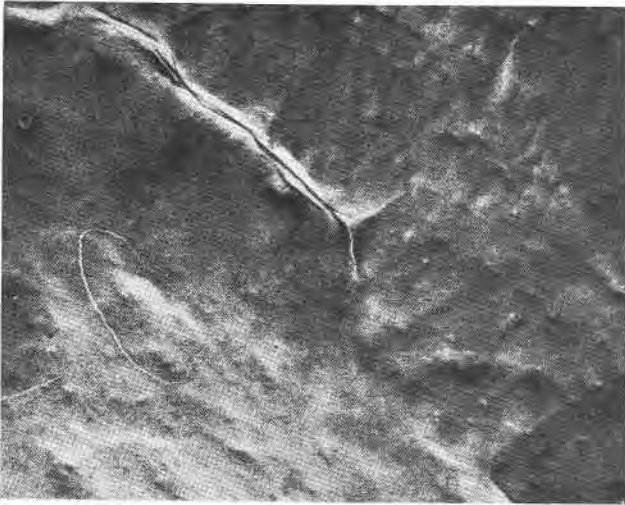


Fig. 9. Electron micrograph of cleaved surface of diamond irradiated to  $10^{18}$  nvt (fast).

oriented although they have the mechanical effect of greatly increasing the number of effective cleavage surfaces. The diamond as a whole is strained by such a gross change. The strain may be relieved at a surface by cleaving, but not by heat treatment as applied in the experiments. The threefold deep steep depressions are believed to represent voids which result from the rotation of the mosaic units.

The mosaic units originated during the growth of the diamond. Dislocations would be expected to accumulate along the boundaries and to contribute to the weakness of the gross structure. Giardini and Tydings (1962) note the existence of such units on a larger scale in the case of certain synthetic diamonds. It should be noted, however, that the synthetic diamond was crystallized in an environment quite different from that of the natural stones used in the present study.

DENSITY OF IRRADIATED, NON-IRRADIATED  
AND ANNEALED DIAMONDS

That neutron irradiation causes a decrease in the density of diamond is a well-known effect; nevertheless, because of the very small change at the radiation dosage employed, the determination of density in the present study required careful measurement.

The density was measured in two ways, both using Clerici solution as a suspension medium. The first method employs a meter long vertical column of liquid in which a linear thermal gradient with a higher temperature at the upper end of the tube is established. Five floats of known density were prepared. The vertical distribution of the floats and of the diamonds to be measured, read on a meter stick, enables the density to be determined to five significant figures. Since only relative density differences are important, no great attempt was made to attain a high absolute accuracy. The method has the advantage of very high sensitivity. Since an apparatus of improved design has since been described by Pelsmaekers and Amelinckx (1961), no further details of the construction are given. The graded density column is admirably suited to comparing nearly identical densities. The method was ultimately abandoned because the floats (platinum and glass) slowly reacted with the Clerici solution.

The second method involved the conventional pycnometer or specific gravity bottle. At room temperature the diamonds were placed in a specific gravity bottle containing Clerici solution of slightly greater density than the diamond. The bottle was placed in a water bath at 27° C. and the temperature of the latter was adjusted until the diamond showed no observable tendency to sink or float. The bottle was then stoppered, filled to the top of the capillary in the stopper, and removed, carefully dried, and weighed. As the bottle was cooled during weighing, the liquid retracted into the capillary. By filling the bottle with water at known temperature, the volume was computed and the rate of weight loss by evaporation was determined. The same weight loss correction was applied to the measurement with Clerici solution. Corrections for volume, for temperature, and for air buoyancy were made. The densities were thus determined to four significant figures.

The measurements usually required a full day. While the method is more time consuming than with the graded density column, it has the advantage of being straightforward. All density measurements were repeated several times during the course of the study.

In Fig. 10 the density of the diamonds is plotted as a function of the fast neutron irradiation. The points indicated are average values made on all of the stones as they were available. They are significant to four figures. The density change is not observed for radiation to  $10^{17}$  nvt (fast),

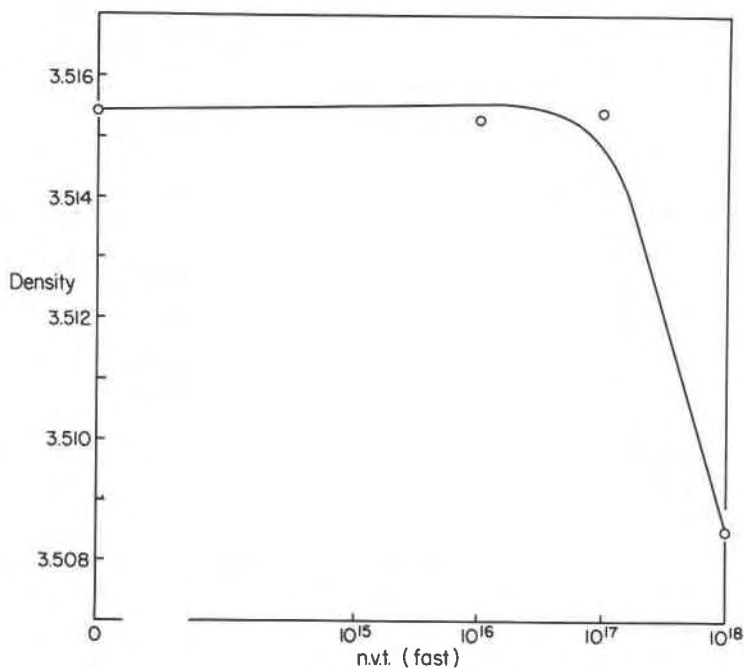


FIG. 10. Density of diamond as a function of neutron irradiation.

but a decided decrease (0.2%) in density is observed as a result of the last irradiation of  $10^{18}$ . The curve is continuous with that of Damask (1958) for radiation from  $10^{18}$  to  $6 \times 10^{20}$  nvt (fast). So far as measurable density changes are concerned, radiation damage does not occur until a radiation of  $10^{17}$  nvt (fast) is obtained.

In Fig. 11 the density of a stone annealed in  $200^\circ$  steps of one hour each is plotted as a function of the annealing temperature. The recovery to the last annealing at  $600^\circ$  is about 40%. In general, the measured density of irradiated diamond and subsequent annealing change is in accord with previous observations on density change (Crawford and Wittels, 1955; Primak, *et al.* 1956; Damask, 1958).

The maximum density change observed is 0.2%, which corresponds to an equal change in bulk specific volume. The corresponding change in cell edge to account for the density and volume change is 0.07%. Under the experimental conditions of the *x*-ray diffraction study, a very conservative figure for the least detectable cell edge change is 0.03%. The latter figure is based upon the recognition of a discontinuity of half of the line width across a diffraction line at  $\theta = 70^\circ 15'$ . Thus there is no doubt that at the very least, half of the density change observed in diamond irradi-



ated to  $10^{18}$  nvt (fast) is due to a mechanism other than a change of the cell dimensions.

X-RAY DIFFRACTION STUDIES OF IRRADIATED,  
NON-IRRADIATED AND ANNEALED DIAMONDS

Laue *x*-ray patterns have been made both on the non-irradiated and the irradiated diamonds up to  $10^{18}$  nvt (fast). No change of structural significance was observed in any of the patterns. For this reason, Laue photographs were not made of the annealed diamonds. The use of Laue

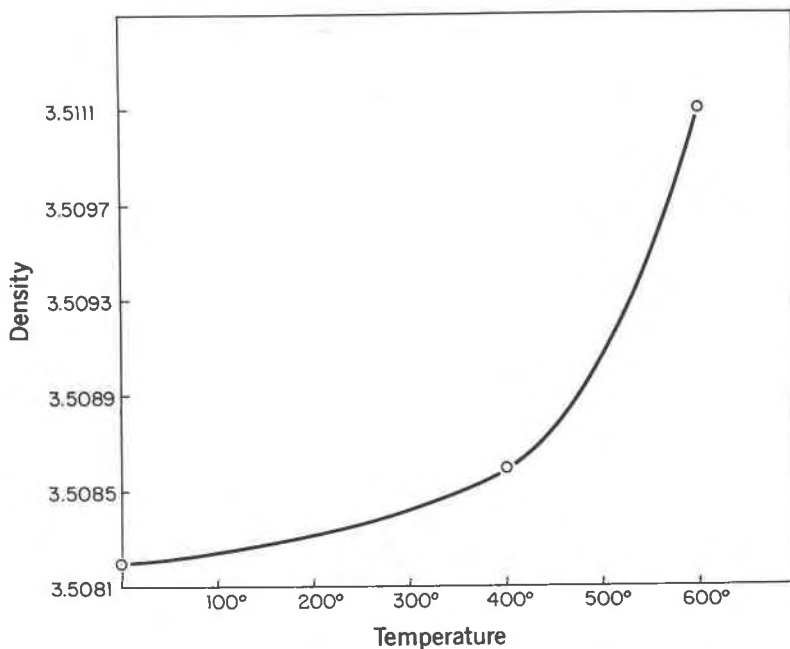


FIG. 11. Density of diamond irradiated to  $10^{18}$  nvt (fast) as a function of annealing temperature.

patterns is disadvantageous for two reasons: first, since the diamonds are quite large, the patterns do not exhibit sharply defined *x*-ray scattering maxima; second, the multiplicity of indices of the structural planes cannot be determined from Laue photographs. For example, maxima from (111) and (222) coincide in a Laue pattern.

Rotation photographs were essentially normal for diamond. Weak (222) reflections were observed in irradiated diamonds. No (200) reflections were observed. Because the spots are rather large, it was decided to use powder photographs for determining cell edge changes. The finely

powdered diamonds were allowed to settle in alcohol to remove the extremes of size. High purity silicon powder was similarly treated and spindles of equal amounts of diamond and silicon were prepared. Patterns of irradiated and non-irradiated diamonds were then made with a 114.6 mm camera. Careful measurements of the position of the diffraction lines of the diamond and of the silicon were made.

In order to attain a higher accuracy of measurement, another powder technique utilizing the non-irradiated and most heavily irradiated stones was employed. Separate spindles were made accordingly from a non-irradiated diamond and a diamond irradiated to  $10^{18}$  nvt (fast). A lead shield was made to cover half of the width of the film. The non-irradiated diamond powder sample was carefully centered and the film was exposed. Next, the sample was removed and replaced by the irradiated specimen and the lead strip was shifted to the other side of the film, care being taken to avoid moving the film. A second exposure was made. The two patterns can then be compared directly, both as to the interplanar spacing and line width without any complications due to dimensional changes of the film, differences in film processing, or measuring.

It was observed that the irradiated diamond pattern showed slight line broadening, but no difference in diffraction angle (thus interplanar spacing) could be detected. The line broadening indicates some disorder in the structure, as is to be expected (Dienes and Kleinman, 1953), but the lack of change in interplanar spacing indicates that the relative change in cell edge does not exceed  $10^{-4}$ . The latter figure is based upon the assumption that the least detectable mismatch of the two patterns is 0.1 mm at a  $\theta$  value of  $70^\circ 15'$  (331), which is the largest recorded with copper  $K\alpha$  radiation. If the observed density decrease of 0.2% were attributable entirely to a change in cell edge, then the cell edge should increase by  $7 \times 10^{-4}$ . It is therefore clear that the density change cannot be due primarily to a change in cell edge of the diamond. Another significant feature of the pattern of the irradiated diamond is the presence of diffuse forward scattering, which is enhanced in the irradiated diamond. The diffuse scattering is not changed by annealing to  $600^\circ$  for one hour. The results of the determination of the relation between measured density change and cell edge change is not in accord with that found by other investigators who have studied the effects of neutron irradiation to much higher levels (Crawford and Wittels, 1955; Levy and Kammer, 1955; Primak *et al.*, 1956). Whatever the degree of disorder produced during radiation, it has not been distributed in such a way as to produce cell edge changes greater than  $10^{-4}$ .

One possible explanation of the disagreement with previous work is that in the present investigation, relatively large single crystals were used

which were powdered for  $x$ -ray examination after irradiation. The crushing of the diamond may have largely annealed the disorder produced by irradiation.

If the diamond is considered to have been divided into domains of slightly disordered structure separated by shells of essentially amorphous carbon, the constancy of the cell edge is explained. It seems qualitatively reasonable that these domains need not be extensively reoriented during the radiation damage. In this way the density change may be accounted for by a general expansion of the mosaic-like crystal, while the interplanar spacing within the mosaic units is not appreciably changed. The position of the boundary regions of loosely packed amorphous carbon may be fixed by dislocations in the original crystal. Such zones of amorphous carbon can then behave in a gross way like a random collection of cleavage planes as discussed under grinding hardness. The reduction of anisotropy of grinding hardness that has been observed is compatible with such a concept.

Kolonysova and Zhestovskaya (1962) have reported an analogous behavior in the ionic crystal, lithium fluoride, irradiated with neutrons. They concluded, on the basis of  $x$ -ray scattering and etching studies, that lithium fluoride single crystals are separated into slightly reoriented mosaic fragments of 1 to 0.1 micron size. The separating regions are, in their case, parallel with the (100) planes. The effect is confined to the outer layers of the crystals. The boundary features shown by etching are believed to be due to the local accumulation of Frenkel defects.

#### PIEZOBIREFRINGENCE AND INDEX OF REFRACTION OF IRRADIATED AND NON-IRRADIATED DIAMONDS

The phenomenological theory of piezobirefringence in crystals was first developed by Pockels (1889). Corrections to his theory have been made independently by Bhagavantam (1942), Jahn (1949), Fume (1952) and Poindexter (1955). No satisfactory physical theory of piezobirefringence has been developed. Since the index of refraction of a crystal should be calculable from the Lorenz-Lorentz equation, it might seem reasonable, that if the latter equation is differentiated with respect to density, a relation of the index change with respect to stress and compressibility could be worked out. Since such a treatment neglects the mutual effects of polarization, it does not provide an even approximate relationship. More sophisticated treatments, as those of Banerjee (1927), Mueller (1935), Herzfeld (1928), and Herzfeld and Lee (1933) have not been notably satisfactory. Nonetheless, the measurements of piezobirefringence provide data which are potentially useful in relating the polarizability of

electron configurations to deformation of the crystal under stress. Since carbon atoms are believed to be displaced during neutron bombardment, the determination of piezobirefringence of neutron irradiated diamond is a worthwhile field of investigation. Ideally, the change of index of refraction with stress would be more informative, but the measurements are extremely difficult (Denning *et al.*, 1957). The theories of piezobirefringence do not permit quantitative predictions of the phenomenon in irradiated diamonds. Therefore, it seemed justifiable to measure the piezobirefringence constants to determine whether measurable differences between the stress optical behavior of non-irradiated and irradiated diamonds could be detected. It is not feasible to make piezobirefringence measurements on diamonds irradiated to  $10^{17}$  or  $10^{18}$  because they are opaque in sections thick enough to be used.

Prisms were prepared from two small diamonds, which received fast neutron radiation of  $2 \times 10^{13}$ ,  $2 \times 10^{14}$ , and  $2 \times 10^{15}$  nvt. Indices of refraction were measured for mercury 546 m $\mu$  light. The index of refraction of the prisms was measured by the minimum deviation method on a one-circle goniometer. The measured index of refraction of one prism was 2.4239; the other was 2.4237. The indices of refraction remained constant to  $\pm 0.0001$ . These measurements confirm the findings of Pelsmaekers and Schepers (1958), who found no index change in a prism so heavily irradiated that it became too opaque for measurement.

Two high quality gem diamonds from Sierra Leone of two and one-quarter carats each were used for the piezobirefringence measurements. They were selected on the basis of the perfection of their octahedral faces, their freedom from visible flaws and twinning, and their low birefringence. These two diamonds were faceted to form rectangular parallelepipeds bounded by (001), (00 $\bar{1}$ ), (110), ( $\bar{1}\bar{1}$ 0), ( $\bar{1}\bar{1}$ 0) and ( $\bar{1}$ 10). The dimensions of the specimens were  $3.18 \times 3.52 \times 3.58$  and  $3.35 \times 3.41 \times 3.94$  mm. The general method used was identical to that employed in preparing diamonds for hardness tests. High accuracy of orientation is not essential, but opposite faces must be as nearly parallel as possible, in order to secure uniform stress during compression.

After the diamonds were cut, a lamellar pattern of birefringence common in type I diamond was observed. Photographs of the birefringence patterns are shown in Figs. 12 and 13. It is believed that these lamellae are due to strain induced by structural misfit, due to compositional variation in successive adjacent lamellae (Denning, 1961). The maximum birefringence of the diamonds was about  $10^{-6}$ . The piezobirefringence constants are of the form  $Q = 2h\lambda/n^3Td$ , in which  $Q$  is the stress induced birefringence constant,  $n$  the initial index of refraction,  $d$  the path length, and  $T$  the stress per unit area. The units used are cm<sup>2</sup>/dyne. The relation

between stress and index of refraction is a fourth rank tensor property (Nye, 1957). The non-vanishing coefficients are, in crystals of symmetry  $m\bar{3}m$ ,  $q_{1111}$ ,  $q_{1122}$ ,  $q_{1212}$ . If birefringence, rather than absolute index change, is measured, then there remain two constants ( $q_{1111} - q_{1122}$ ) and  $2q_{1212}$ . The first of these constants is measured by measuring the birefringence in a direction normal to a fourfold symmetry axis  $[001]$  while the crystal is compressed along the fourfold axis. The second is determined by compressing the diamond along a twofold axis of symmetry  $[110]$  and measuring the birefringence along  $[001]$ . As a check for consistency of the data, the diamond may be stressed on  $(110)$  and examined in the direction  $[1\bar{1}0]$  which gives the redundant constant

$$1/2(q_{1111} - q_{1122} + 2q_{1212})$$

The diamond is compressed in an apparatus which is designed so that the load is increased linearly with respect to time to several hundred kilograms per square centimeter. Crossed or parallel linear polars are used and the light used is the  $546\text{ m}\mu$  mercury line. The light beam is chopped at 750 cps and impinges on a photocell whose output is recorded on a chart recorder after amplification. Great care must be taken to secure

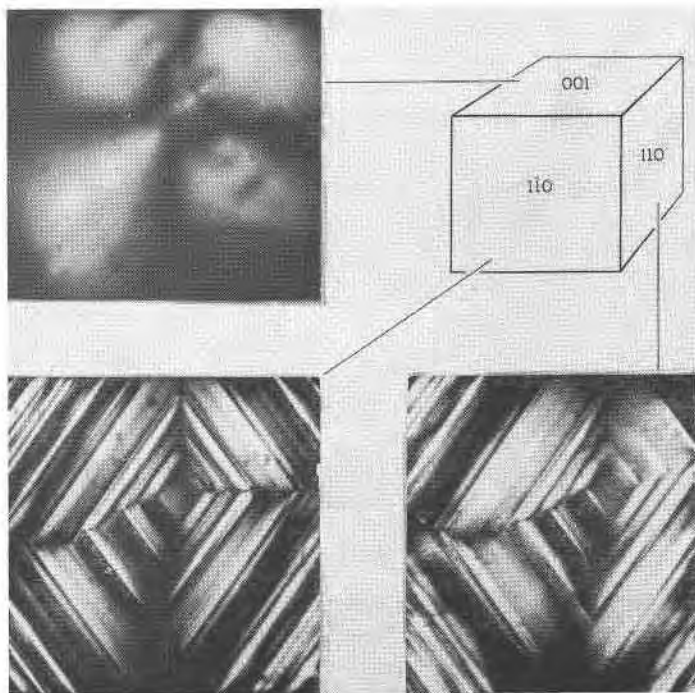


FIG. 12. Well defined birefringent lamellae in type I diamond.

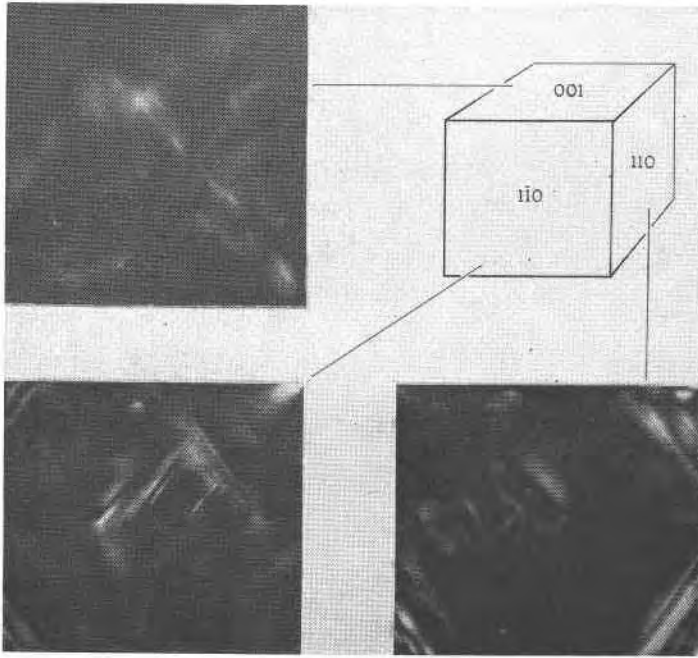


FIG. 13. Poorly defined birefringent lamellae in type I diamond.

uniform stress distribution. Uniformity of stress distribution was checked by observing the diamond in white light between crossed polars. The errors due to improper stress distribution are serious and are rather difficult to avoid.

The chart record is used to determine the maxima and minima of transmission of the polars and diamond as the load is increased. In the case of crossed polars, the maxima represent positions of phase difference of  $\pi$ ,  $3\pi$ ,  $5\pi$  . . . and minima represent phase differences of  $0$ ,  $2\pi$ ,  $4\pi$  . . . due to the birefringence of the diamond. If the polars are parallel (in either case their privileged directions make a  $45^\circ$  angle with the direction of compression stress), the maxima correspond to phase differences of  $0$ ,  $2\pi$ ,  $4\pi$  . . . and the minima correspond with  $\pi$ ,  $3\pi$ ,  $5\pi$  . . . .

These diamonds were irradiated at the Phoenix reactor at The University of Michigan. The dosages were  $2 \times 10^{13}$ ,  $2 \times 10^{14}$  and  $2 \times 10^{15}$  nvt (fast). The computed piezobirefringence constants are tabulated in Tables I and II.

The higher value of the anisotropy of the piezobirefringence of diamond number 2 is not understood. The lamellar initial birefringence of this diamond is less well developed than that of diamond number 1 and during

TABLE I. PIEZOBIREFRINGENCE CONSTANTS OF DIAMOND No. 1  
 ( $\lambda = 546 \text{ m}\mu$ )

Constant	Direction of		Radiation nvt (fast)	Value
	Compression	Observation		
$2q_{1212}$	[110]	[001]	0	$-2.9 \times 10^{-14} \text{ cm}^2/\text{dyne}$
			$2 \times 10^{13}$	-3.0
			$2 \times 10^{14}$	-3.2
			$2 \times 10^{15}$	-3.1
$(q_{1111} - q_{1122})$	[001]	[110]	0	-3.2
			$2 \times 10^{13}$	-3.1
			$2 \times 10^{14}$	-3.1
			$2 \times 10^{15}$	-3.1
$\frac{1}{2}(q_{1111} - q_{1122} + 2q_{1212})$	[110]	[110]	0	-3.1
			$2 \times 10^{13}$	-3.1
			$2 \times 10^{14}$	-3.2
			$2 \times 10^{15}$	-3.2

cutting, it did not seem so free of twinning. Whatever the cause, the difference is not a result of neutron irradiation, but is due to some inherent difference in the diamonds (both are type I). Conrad (1959) found similar values of piezobirefringence in the ultraviolet and visible spectral regions

 TABLE II. PIEZOBIREFRINGENCE CONSTANTS OF DIAMOND No. 2  
 ( $\lambda = 546 \text{ m}\mu$ )

Constant	Direction of		Radiation nvt (fast)	Value
	Compression	Observation		
$2q_{1212}$	[110]	[001]	0	$-2.8 + 10^{-14} \text{ cm}^2/\text{dyne}$
			$2 \times 10^{13}$	-2.8
			$2 \times 10^{14}$	-2.8
			$2 \times 10^{15}$	-2.9
$(q_{1111} - q_{1122})$	[001]	[110]	0	-3.3
			$2 \times 10^{13}$	-3.3
			$2 \times 10^{14}$	-3.4
			$2 \times 10^{15}$	-3.4
$\frac{1}{2}(q_{1111} - q_{1122} + 2q_{1212})$	[110]	[110]	0	-3.5
			$2 \times 10^{13}$	-3.6
			$2 \times 10^{14}$	-3.4
			$2 \times 10^{15}$	-3.6

of another non-irradiated diamond which showed well developed lamellar birefringence. Poindexter (1955) found values similar to those of diamond number 1 in a non-irradiated stone free of any visible initial birefringence.

The lack of change of piezobirefringence with neutron irradiation up to  $2 \times 10^{15}$  nvt (fast) is not so sensitive to broken covalent bonds as was anticipated. Potentially, it should be possible to relate the birefringence of irradiated diamond to the number of broken bonds, but the present state of the physical theory does not permit such a quantitative interpretation.

#### ABSORPTION IN THE VISIBLE REGION

The diamonds assume a green color after a radiation of  $2 \times 10^{13}$  nvt (fast), although at this low level, the color is very pale in a specimen 4.5 mm thick. At  $10^{17}$  nvt, the green color is very deep and can be recognized only on the thinnest edges. At  $10^{18}$ , the diamonds are black with no indication of color except in a finely powdered state. Absorption spectra were not obtained at this time in the whole visible spectrum, but the absorption as viewed in a spectroscope shows no well defined bands, but only a rather general absorption greatest at the ends of the visible spectrum. Absorption spectra from 300 to 600  $m\mu$  are plotted in Figs. 15 and 16 and are discussed under the section on ultraviolet absorption.

Transmission measurements in white light were made with a densitometer having a response roughly the same as the human eye. These measurements were made on the diamonds prepared for the piezobirefringence study. The measurements are accurate to 1% transmission. The data corrected for the large Fresnel loss are tabulated in Table III. The data are plotted in Fig. 14.

#### ULTRAVIOLET ABSORPTION

Ultraviolet absorption was first studied by measuring the position of the absorption edge. A D-C iron arc was used as a source since the relative intensity and wavelengths of the iron lines are well known. The diamond was mounted close to the slit of a Bausch and Lomb medium quartz

TABLE III. TRANSMISSION OF IRRADIATED DIAMOND IN VISIBLE SPECTRUM

	Diamond No. 1 (thickness 3.18 mm)	Diamond No. 2 (thickness 3.04 mm)
nvt (fast)	T	T
$2 \times 10^{13}$	99%	99%
$2 \times 10^{14}$	95%	95%
$2 \times 10^{15}$	77%	75%



spectrograph. The diamonds showed the usual absorption cut off at  $310\text{ m}\mu$  prior to irradiation. Irradiation to  $2 \times 10^{15}$  nvt (fast) shifts the absorption edge only slightly toward a longer wavelength.

Three type I diamonds of 3 mm thickness were examined on a Perkin-Elmer model 112 single beam spectrometer equipped with a quartz prism and photocell detector. Figures 15 and 16 show typical absorption spectra before and after neutron irradiation. All measurements were made at

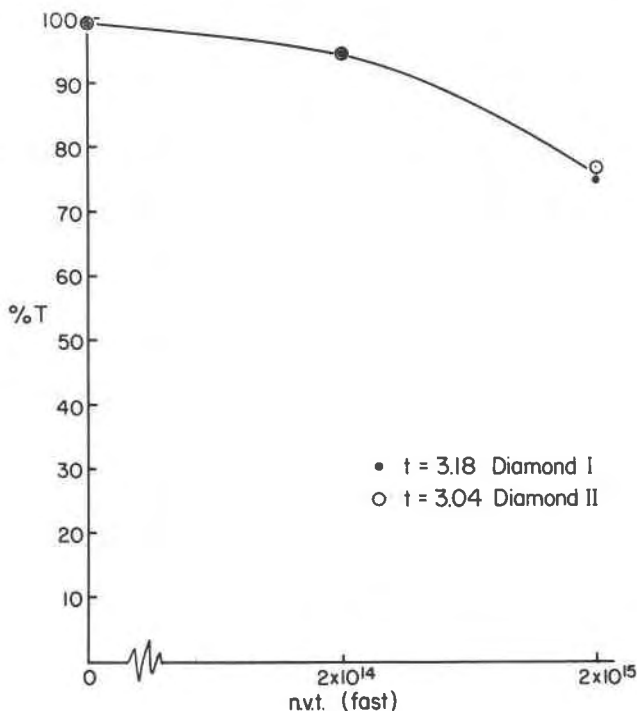


FIG. 14. Transmission of visible light in diamond as a function of neutron irradiation.

room temperature. The curves are not corrected for Fresnel losses. The absorption edge at  $310\text{ m}\mu$  is essentially unchanged by radiation up to  $2 \times 10^{15}$  nvt (fast) in all three of the diamonds examined. The transmission peak at  $550\text{ m}\mu$  remains after radiation, but the transmission is reduced by about half at this wavelength in C-1 and C-2 and is reduced very little in C-3, irradiated to  $3.6 \times 10^{14}$  nvt. The transmission peak at  $350\text{ m}\mu$  is completely lost in the three specimens at  $2 \times 10^{15}$  nvt. The identity of the rather broad absorption at  $400\text{ m}\mu$  is retained in varying degrees in the three specimens. The variation in the ultraviolet and visible absorption of the individual diamonds is no greater than has been ob-

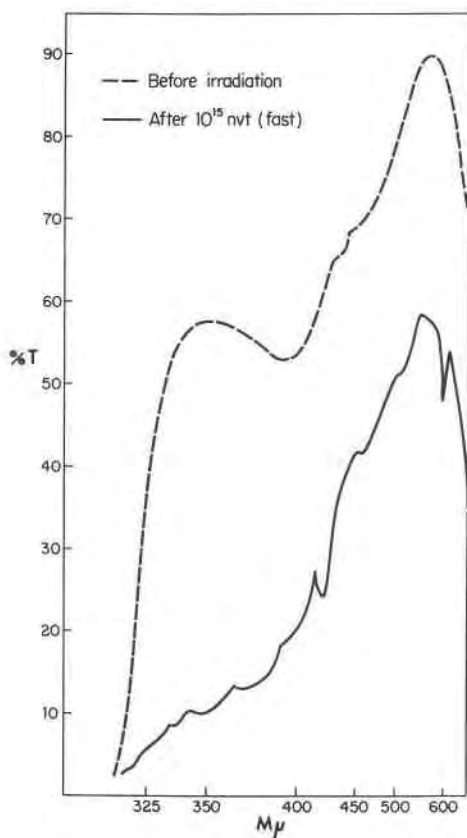


FIG. 15. Spectral transmission of irradiated diamond.

served by others. Whether the differences are due to impurity atoms in substitutional or interstitial sites is debatable. The specimens were not annealed, since they were retained for subsequent studies. Clark *et al.* (1956) have considered the nature of absorption in irradiated and annealed diamonds.

#### INFRARED ABSORPTION

Infrared absorption spectra were obtained on the diamonds before irradiation, after irradiation, and after annealing. These spectra were obtained on a Perkin-Elmer model 112 spectrometer with a sodium chloride prism. A special oscillating holder was made so that the diamond was inserted into and out of the beam at 5 cycles per minute. The beam with and without the diamond was confined to an aperture 2 mm in diameter

immediately in front of the slit. The amplified output of the spectrometer was fed to a Varian recorder. The spectrum was then scanned at slow speed through the region from 2 to 10 microns. These spectra are not reproduced since they are unavoidably complicated by atmospheric water vapor bands.

The spectra were obtained at room temperature on plane parallel sec-

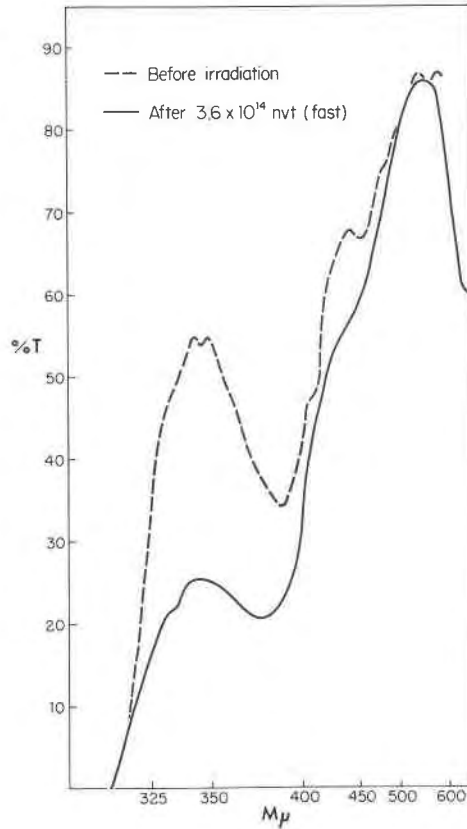


FIG. 16. Spectral transmission of irradiated diamond.

tions of the diamonds. The transmissions were not corrected for the surface reflection losses. All of the diamonds have the strong absorption at  $8\mu$  characteristic of type I diamonds. The spectra of the non-irradiated diamonds show the general characteristics of the spectra of type I diamonds (Robertson *et al.*, 1934; Sutherland, *et al.*, 1954; Kaiser and Bond, 1959). Table IV shows the per cent of transmission of a typical diamond (C-1) as a function of neutron irradiation for selected spectral regions.

The transparent region at  $2\ \mu$  is compared with the absorption band at  $4.60\ \mu$ , an absorption band common to type I and type II diamonds, and absorption bands at  $7.27\ \mu$  and  $9\ \mu$ . The  $7.29\ \mu$  band is a type B band of Sutherland, *et al.* (1954), and the band at  $9\ \mu$  is a type A band. It is clear that the transmission in the transparent region decreases linearly, within experimental error, with the logarithm of the irradiation from  $10^{15}$  to  $10^{18}$  as shown in Fig. 17. The transmission of the absorption bands also seems

TABLE IV. PER CENT TRANSMISSION OF SELECTED PORTIONS OF DIAMOND SPECTRUM (Diamond C-1)

Irradiation nvt (fast)	$2\ \mu$ $5000\ \text{cm}^{-1}$	$4.60\ \mu$ $2175\ \text{cm}^{-1}$	$7.29\ \mu$ $1372\ \text{cm}^{-1}$	$9.1\ \mu$ $1100\ \text{cm}^{-1}$
0	85%	3%	22%	10%
$10^{15}$	72%	3%	15%	7%
$10^{16}$	55%	2%	11%	5%
$10^{17}$	20%	2%	10%	4%
$10^{18}$	0	0	2%	0

to decrease, but the relative error is larger, so that the correlation is not so good as in the first instance.

The band at  $4.60\ \mu$  has been assigned as fundamental to the diamond structure (Sutherland *et al.*, 1954), whereas the  $9\ \mu$  absorption band has been correlated with nitrogen content and the absorption at  $306\ \text{m}\mu$  by Kaiser and Bond (1959). This  $9\ \mu$  band has been correlated by these authors with C-N stretching vibrations.

In general the effect of neutron irradiation has been to decrease the infrared transmission about equally over the entire range from 2 to 10 microns. Some apparent structure was noted in the highly transparent region around  $6\ \mu$ , but in all but the nearly opaque specimens irradiated to  $10^{18}$ , this apparent structure is complicated by an adverse effect of atmospheric  $\text{H}_2\text{O}$  bands.

The effect of annealing on one diamond irradiated to  $10^{15}$  was negligible. The annealing temperatures were 200, 400, and  $600^\circ\ \text{C}$ ., one hour at each temperature. Likewise, the effect of a similar annealing process on a diamond irradiated to  $10^{16}$  was negligible. In a third diamond irradiated to  $10^{17}$  the effect was again small over most of the spectrum, but it was significant near  $2\ \mu$  and in the region around  $6.5\ \mu$ . This stone showed a transmission of zero at  $1\ \mu$  after irradiation. The  $1\ \mu$  transmission was 50% prior to irradiation. The  $200^\circ$  annealing increased the  $1\ \mu$  transmission to 10%. Annealing at  $400^\circ$  and  $600^\circ$  caused no further change. The initial transmission of this diamond was 50% at  $6.5\ \mu$ . The irradiation to

$10^{17}$  reduced the transmission at  $6.5 \mu$  to about 23%. The first two annealing treatments did not produce a significant change, but the third, one hour at  $600^\circ \text{C}$ ., raised the  $6.5 \mu$  transmission to 35%.

The annealing of two diamonds which had been irradiated to  $10^{18}$  restored the transparency of the specimens only slightly. At  $10^{18}$  only a small transmission band remained, as shown in Fig. 18, from 5 to  $7.5 \mu$ . Since the spectra from both diamonds were virtually identical, only one is

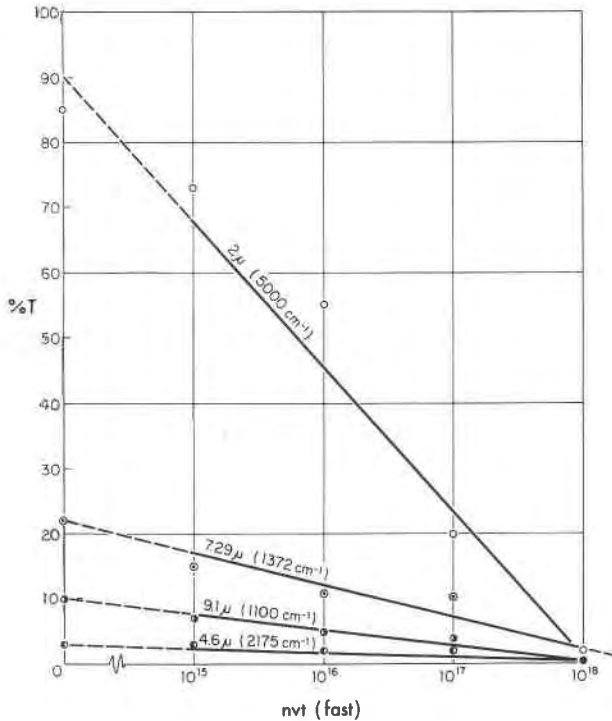


FIG. 17. Transmission of selected infrared regions in diamond as a function of neutron irradiation.

shown. The details which developed in the structure of the spectrum are shown in the diagrams. The band at  $6.5 \mu$  is sharpened by annealing for one hour at  $200^\circ$ . At  $400^\circ$  the band is split into two bands at  $6.3 \mu$  and  $6.8 \mu$ . These bands are further enhanced by an additional hour of annealing at  $600^\circ$ . During the whole annealing process, the  $7.3 \mu$  band is enhanced in a similar manner but it is not split or shifted. The superposed curves indicate the reproducibility with the slow scan rate used.

The general effect of neutron irradiation is the reduction of the optical

transmission. The last transparent region to remain is from  $5 \mu$  to  $7.5 \mu$ . The effect may be accounted for by the growth of zones of amorphous carbon as has been discussed in other sections. Since the absorption which has been attributed to substitutional nitrogens is not removed, it seems clear that during irradiation, there is no preferential breaking of C-N bonds in the diamond.

During annealing, at least as far as has been carried out in these experi-

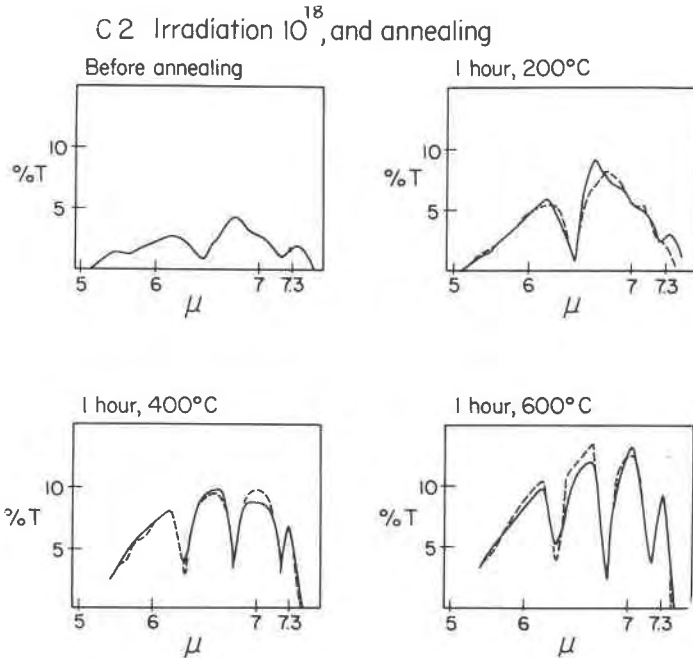


FIG. 18. Effect of annealing on infrared transmission in neutron irradiated diamond.

ments, the radiation damage is only slightly removed. It is believed that the interstitial C-atoms within the mosaic blocks find their way back to normal carbon sites, but few of those in the amorphous zones do so. No doubt, a much higher activation energy would be needed to get a larger proportion of atoms back to their original sites. The development of two absorption bands at the expense of one at  $6.5 \mu$  on annealed diamonds that had received  $10^{18}$  nvt (fast), indicates the development of a structural configuration not initially present in the original diamonds.

#### SUMMARY

Fast neutron irradiation of single crystals of type I diamonds has been observed to have the following effects:

1. Relative grinding hardness is reduced, particularly in the harder directions, so that the usual high anisotropy of grinding hardness is reduced by a large factor.
2. The density remains unchanged through  $10^{17}$  nvt (fast). At  $10^{18}$  nvt (fast) it is reduced by 0.2%.
3. The cell edge as determined by  $x$ -rays is not increased by an amount commensurate with the density decrease up to  $10^{18}$  nvt (fast).
4. The  $x$ -ray diffraction pattern becomes slightly diffuse, the (222) reflection is enhanced, but the (200) reflection is not developed.
5. The cohesion between mosaic units is reduced so that when highly irradiated stones are cleaved, the individual blocks near the cleaved surface rotate so that the elements of the cleaved surface are no longer the ideal (111) planes of the original single crystal. They constitute a series of (111) elements of the blocks which have rotated as a result of the cleaving process. The angular distribution of the newly created surface elements is controlled by the symmetry of the diamond.
6. The refractive index and piezobirefringence are unchanged up to  $2 \times 10^{15}$  nvt (fast).
7. The optical transmission is reduced. At the highest level of irradiation, diamonds from 2 to 3 mm thick are opaque in all but the 5–7.5  $\mu$  range. The reduction in the infrared from 2 to 10  $\mu$  is essentially proportionate throughout. In the initial stages of irradiation, the ultraviolet transmission is differentially reduced, most strongly from 320 to 350  $m\mu$ .

The general effects of annealing in 200° steps to 600° C. (one hour each) on stones irradiated to  $10^{18}$  nvt (fast) follow:

1. The hardness and hardness anisotropy are restored by about 30%.
2. The density is restored by about 40%.
3. The cell edge is not measurably effected.
4. The cleavage behavior is not effected.
5. After diamonds irradiated to  $10^{18}$  nvt (fast) have been annealed, an absorption band at 6.5  $\mu$  is enhanced and finally split into two components. A similar appearing band at 7.3  $\mu$  is enhanced and sharpened, but it is neither shifted nor split.

#### CONCLUSIONS

During neutron irradiation, Frenkel defects are initially produced. As radiation progresses, the displaced carbon atoms collect to form a three dimensional network so that ultimately the diamond consists of a mosaic structure of diamond crystals which contain vacant carbon sites. The mosaic blocks are of the order of 0.1  $\mu$  in diameter. Interstitial carbon (and

perhaps nitrogen) atoms are no doubt present in these crystal units, but a large proportion of the carbon atoms are distributed in the amorphous boundary layers which separate the mosaic units. Channels parallel to [110] in the structure provide paths for migration. The mosaic units become slightly disoriented (less than  $1^\circ$ ) as radiation progresses.

The effect of annealing is to partly restore the mosaic blocks of the diamond to their original state. The amorphous carbon layers persist so that after the maximum annealing treatment used at least two-thirds of the atoms in the mosaic boundary layers remain in these layers. From the optical observations, it seems clear that prolonged annealing cannot restore the irradiated diamond to its original condition.

Cleavage of the stones following irradiation permits a rotation of the mosaic units up to  $5^\circ$  and thus strain energy is released near the cleaved surface.

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