THE CLEAVAGE PROPERTIES OF DIAMOND

By S. Ramaseshan

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received June 5, 1946

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The easy and perfect cleavage of diamond along the (111) plane has long been known to the Indian lapidaries. Cleavage plates of large area polished and slightly facetted at the edges were extensively used in jewellery, but this form of adornment has in recent years gone out of fashion. In consequence, such plates can be purchased from the jewellers in the larger cities of India. Sir C. V. Raman has in his collection several of these plates and they have proved extremely useful in the study of the different properties of diamond. During his investigation of the X-ray topographs of diamond, Mr. G. N. Ramachandran examined this material and found that three out of the fifty plates studied had a (211) cleavage. Sutton (1928) in his book on the South African diamonds remarks that while the (111) cleavage is most common, the (110) is also occasionally found.

In view of the facts stated above, it appeared desirable to undertake a systematic investigation of the cleavage properties of diamond. A calculation of the cleavage energy of various planes in diamond indicated the possibility of numerous other cleavages besides those mentioned above. A careful goniometric study of 15 crystal fragments in Sir C. V. Raman's collection was accordingly made which resulted in a striking confirmation of this idea. The paper records the results of these studies.

2. The Nature of Cleavage

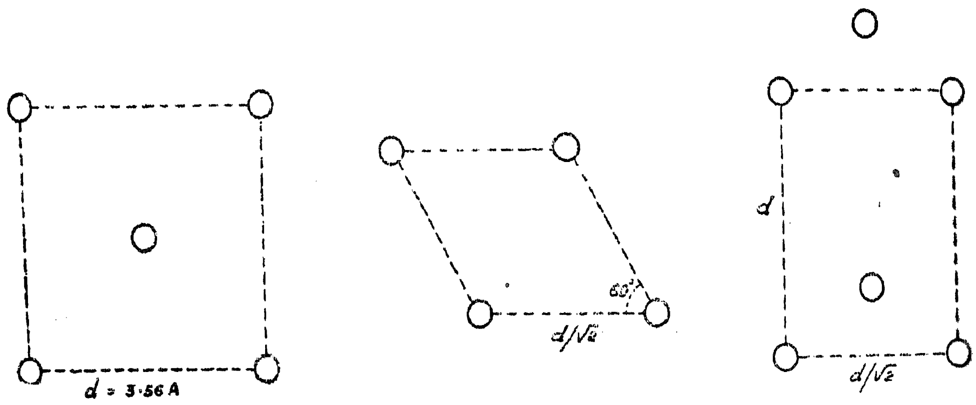
"Cleavage is not merely a tendency to fracture with the production of two more or less plane fracture surfaces along an approximately definite direction. It is the facility for splitting along an absolutely *true* plane having an orientation within the crystal definitely fixed within one or two minutes of arc" (Tutton). The (111) cleavage of diamond is a striking example of the above definition. Many writers (1932) have tried to give an explanation for the presence of the (111) cleavage. One set of authors attribute the perfection of the cleavage to the fact that the spacing is a maximum for the (111) planes, while others suggest that it is because the surface energy is minimum for the (111) plane. A calculation of the surface energies of different planes shows that this is indeed the case, but this energy is not greatly different from that for the other nearby planes. Bearing in mind the fact that in the crude method used for cleaving diamonds the energies employed may be much in excess of what is required to effect cleavage in any direction, one would expect to have a fracture rather than a perfect cleavage. From these facts it would seem that considerations of surface energy alone are not sufficient to explain the "atomic accuracy" of the (111) cleavage.

An inspection of the diamond model shows that the (111) planes are not equally spaced, the ratio of the distances between alternate planes being 1 : 3. It is also found that the number of bonds cut per unit area depends on the place at which the two parts of the crystal are separated. If cleavage is effected between the two octahedral layers which are farther apart, then one bond per atom will have to be cut. On the other hand, if diamond is cleaved between the octahedral layers that are closer together, three bonds per atom will have to be ruptured. It is, therefore, obvious that a cleavage in the former position requires only a third as much energy as for one in the latter position. If, therefore, a cleavage starts parallel to the (111) plane between two layers which are farther apart, it will continue in the same plane since any slight deviation in the direction would involve a threefold increase in energy. This sudden increase in energy which accompanies any deviations appears to be responsible for maintaining the (111) cleavage along a true geometric plane.

3. The Calculation of the Energy of Cleavage

It is reasonable to assume that the energy required to cleave a diamond along a particular plane is equal to that required to rupture the bonds connecting atoms situated on either side of the plane. The number of bonds cut per unit area thus gives a measure of the energy of cleavage for a particular plane. Harkins (1942) has used this idea to calculate the surface energy of the (111) and (100) planes. Since two surfaces are formed by cleavage, the surface energy should be equal to half the cleavage energy. In this section we shall calculate the cleavage energy of a few planes in diamond.

In the case of simpler planes such as (100), (111) and (110), the calculations can be made in a very simple manner. In Fig. 1 *a*, the area bounded by dotted lines represents the repetitive unit cell in the (100) plane which is a square whose side is $d = 3 \cdot 56$ Å, the length of the unit cubic cell in the diamond lattice. There are two atoms per unit cell (one at the corner and one at the centre) so that the number of atoms per unit area is $2/d^2$. As two bonds connect each atom with the atoms in the neighbouring plane the number of bonds ruptured per unit area is $n_{100} = 4/d^2$.



(a) (b) (c)

FIG. 1

For the (111) plane the unit cell is a rhombus of side $d/\sqrt{2}$ and angle 60° which is shown in Fig. 1 b. There is only one atom per unit cell whose area is $d^2\sqrt{3}/4$. One bond connects each atom with an atom in the upper layer, while three connect it with atoms in the lower layer. The number of bonds cut per unit area n_{111} is therefore, $4/d^2\sqrt{3}$ or $4\sqrt{3}/d^2$ according as the cleavage is above or below the plane under consideration.

The unit cell in the case of (110) is shown in Fig. 1 c. It is a rectangle of sides d and $d/\sqrt{2}$ containing two atoms. Since each atom in this plane

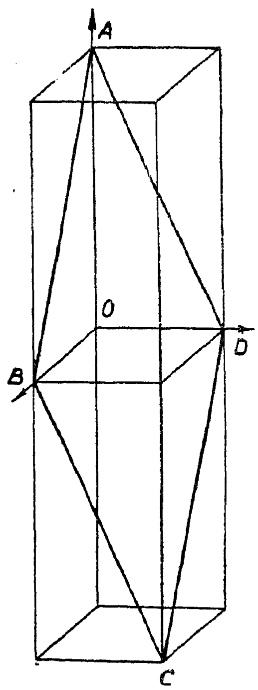


FIG. 2

is connected by one bond to an atom in the neighbouring plane, the number of bonds cut per unit area n_{110} is $2\sqrt{2}/d^2$.

For more complicated planes the following general analytical method is adopted. Considering the (hkl) plane, let H, K and L be the corresponding indices in the Weiss notation (*i.e.*, H, K and L are the smallest integral intercepts made by the plane on the co-ordinate axes). In Fig. 2 the unit cell in the (hkl) plane is represented by the parallelogram ABCD the area of which can be calculated from the condition OB $= \mathrm{H}d$, OD $= \mathrm{K}d$, and OA $= \mathrm{L}d$. The equation to this plane is

$$hx + ky + lz - p = 0$$

where $p = h\mathrm{H} = k\mathrm{K} = l\mathrm{L}$. If the co-ordinates of an atom are substituted in the expression on the left hand side, the sign of the quantity obtained indicates the position of the atom with respect to the plane. The atom lies on the same or the opposite side of the plane as the origin according as the sign is negative or positive. Having thus found out the position of all the atoms in the diamond structure with respect to the plane (hkl), the number of bonds which connect atoms on opposite sides of the plane can be counted. A difficulty arises when an atom lies on a plane. In this case the plane of separation is slightly shifted away from or towards the origin and the number of bonds cut is counted in either case. The two may either be equal or different. If different the lower value is taken to calculate the cleavage energy. As an example we shall take the (221) plane. Here OB $= d$, OD $= d$ and OA $= 2d$ and the area of the cell is $3d^2$. It is found that the number of bonds cut per unit cell is 8 or 12 according as the cleavage takes place in the positive or the negative side of the plane ABCD. Consequently $n_{221} = 8/3d^2$. Similar calculations have been made for other planes.

The energy required to rupture a C—C bond has been calculated from thermo-chemical consideration to be $6 \cdot 22 \times 10^{-12}$ ergs. (Harkins, *loc.cit.*). Accepting this value the cleavage energy of various planes have been determined. The results are tabulated in Table I with the planes arranged in order of increasing energy. It is found that the number of bonds cut per unit area can be given by the expression

$$n_{hkl} = \frac{4}{d^2} \frac{h}{\sqrt{h^2 + k^2 + l^2}}$$

where h is the largest of the three indices.

A study of Table I shows that the energy of the (111) plane is the least and is an absolute minimum. The (111) plane must, therefore, be a plane of easy cleavage. The energy of the [illegible] about 80% higher than that for the (111) planes and [illegible] energies intermediate between these. As has been [illegible] and the (112) cleavages have been observed [illegible] that there are planes having energies less than these [illegible] that

Table I

Plane	Angle between plane and the (111) plane	[illegible]	[illegible]	[illegible]
111	0°	[illegible]	[illegible]	[illegible]
332	10° 0'	[illegible]	[illegible]	[illegible]
221	15° 48'	[illegible]	[illegible]	[illegible]
331	22° 0'	[illegible]	[illegible]	[illegible]
110	35° 16'	[illegible]	[illegible]	[illegible]
322	11° 24'	[illegible]	[illegible]	[illegible]
321	22° 12'	[illegible]	[illegible]	[illegible]
211	19° 28'	[illegible]	[illegible]	[illegible]
320	36° 48'	[illegible]	[illegible]	[illegible]
210	39° 14'	[illegible]	[illegible]	[illegible]
311	29° 30'	[illegible]	[illegible]	[illegible]
100	54° 44'	[illegible]	[illegible]	[illegible]

cleavages parallel to these might also occur under [illegible] One should expect the relative abundance of the cleavage planes [illegible] order listed in Table I, (111) being most frequent and (100) [illegible] absent. From the general expression for the cleavage energy [illegible] it can be shown that the cleavage energy diminishes as the plane [illegible] progressively towards a (111) plane. Consequently curved cleavages [illegible] would also be expected to occur in diamond. If these curved [illegible] directions near about an octahedral plane they might actually [illegible] with it and become plane cleavages.

4. Methods of Study

To verify the deductions from theory, a systematic study [illegible] fragments of diamond in Sir C. V. Raman's collection was made. A [illegible] examination with a pocket lens of these fragments revealed that [illegible] contained the usual (111) cleavages, but 9 of them appeared to have cleavages other than the (111). Each of these nine was used for careful goniometric study, and it was found that while four crystals had planes other than the octahedral, the rest had very interesting fractures which were irregular and more or less curved. A Mier's student goniometer with a collimator and telescope attachment capable of reading upto 1 minute of arc was used. The crystal was attached to the instrument with soft wax and all adjustments of the crystal were made by hand. The angles between the cleavage faces were measured with an accuracy not greater than 15 minutes of arc, but these were quite sufficient to identify the different planes. The octahedral cleavages were very easy to recognise from the perfection and splendent lusture they exhibited. While these planes gave extremely sharp signals in the telescope, the other planes did not give such sharp ones. Only the angles between those surfaces which gave good signals were measured. Care was always taken to see that curved surfaces were not used for observation. When a low-power microscope was focussed on the diamond and the milled head of the goniometer rotated, reflections from the plane faces flashed into the microscope and they did not remain in the field of view for a rotation of more than 15 minutes of arc. In the case of curved planes or faces, the reflection remained in the field of view even when the head was rotated through 2°. It must also be mentioned that reflections from curved faces were extremely feeble and diffuse when observed with a telescope and could easily be distinguished from the reflection from plane faces.

5. Observational Data

N.C. 42 had three large cleavage faces which were octahedral. Two of these were absolutely plane. The third showed the existence of two or three other cleavage faces. They lay in the [110] zone and measurement showed that two of them were (221) faces. The third which gave a feeble but sharp signal was near about the (332). There were also some curved fracture faces on the surfaces of the crystal.

N.C. 59 was a crystal fragment with a large number of cleavage faces on its surface. The specimen is one of the collection of diamonds presented to Sir C. V. Raman by the De Beers Corporation of Kimberley. In one of the [110] zones the following planes were identified: 4 beautiful (111) planes, one (331), one (110), one (322) and one (211). In another perpendicular zone, two (111), one (221), one (331), one (110) and one (322) were found. Although all the planes were quite small, the signals obtained from (111), (221), (110) and (322) were extremely sharp. One octahedral face which appeared to be very drusy was found on examination, to consist of hundreds of tiny (111) planes. In a third zone, one (111) and a tiny (322) plane were found. There were also some curved faces on the diamond, and some of the curved faces ended as tiny flat (111) cleavage faces.

N.C. 45 was a natural crystal which had been broken on one side. Three large prominent cleavage planes are visible on its surface. Two of them were (111) and the third a (110) plane. There was also another tiny (110) plane on the crystal. The large (110) surface had large striations, which mainly consisted of fine (221) planes arranged in a step-like order.

N.C. 174 was a thick flat polished plate with a few cleavage faces on the girdle. Four of these were octahedral cleavages. One (331), one (110), one (221) and a tiny (332) were also found. The angles between the two large faces of the plate and the planes of known indices in the girdle were measured and it was found that the flat face was approximately a (431) plane. In view of the fact that the surface is polished and the plate is quite thick, it is impossible to say whether the two flat faces are cleavage planes or not. The other crystals examined had the (111) cleavage and also irregular and curved fractures. N.C. 194 was a rectangular cleavage plate, all its six faces being perfect octahedral cleavages. N.C. 49 had a large octahedral cleavage followed by a curved face with fine striations. N.C. 39 was a yellowish crystal with two (111) faces and a fracture containing a large number of tiny octahedral faces. N.C. 32 was a black diamond with two large (111) faces and with several tiny curved faces. N.C. 50 had a good many cleavage faces and many of them were curved.

Table II gives the collection of the results obtained. The numbers in the vertical columns indicate the number of independent planes of a specific

TABLE II

Diamond Planes	N.C. 42	N.C. 59	N.C. 45	N.C. 174	N.C. 49	N.C. 39	N.C. 32	N.C. 50	N.C. 194
111	3*l*	6*l*	1*l* 1*t*	4*l*	2*l*	3*l*	2*l*	3*l*	6*l*
332	1*t*			1*t*					
221	1*s*	2*m*	1*s*	1*s*					
331		2*s*		1*s*					
110		2*m*	1*l* 1*t*						
322		3*s*							
211		2*s*							

index on a particular diamond. All the planes which gave a common signal at a particular setting have been taken together and counted as one. The letters accompanying each number indicate the size of the planes. *l* (large) signifies planes having an area greater than two sq. mm., *m* (medium) those with areas between one and two sq. mm., *s* (small) those with areas between a half and one sq. mm., while *t* (tiny) those with areas less than half a sq. mm.

Table II can in no way be said to represent the relative abundance of different cleavages, as the number of cases examined has been too few. Even so, an idea of the relative frequencies of different planes can be obtained from the table. The planes have been arranged in order of increasing energy and one could see that the lesser the energy of a plane the more frequent is its occurrence. It may be mentioned here that amongst the planes of cleavage listed above, (111), (221), (331) and (322) belong to the category in which the distance between alternate layers of atoms are not equal.

In conclusion, the author wishes to express his thanks to Sir C. V. Raman for his encouragement and interest in this investigation.

Summary

Calculations of the cleavage energies of various planes in diamond indicated the presence of cleavages other than those already known. A careful goniometric study of several crystal fragments in Sir C. V. Raman's collection revealed numerous other cleavages. The presence of the following cleavage has been definitely established: (111), (221), (110), (322), (331), (211) and (332). The (111) cleavage was found to be by far the most perfect and most abundant, while (221) and (110) cleavages were not uncommon. It is suggested that the perfection of the (111) cleavage is not merely because that plane has the minimum cleavage energy but also due to the fact that on either side of the plane of easy cleavage lie layers of atoms having three times the cleavage energy. It was also found that diamond definitely has curved fractures and the theory developed in the earlier part of the paper accounts for the existence of these.

References

Harkins, W. D. .. *Jour. Chem. Phys.*, 1942, **10**, 268.

Sulton, J. R. .. *Diamond*, Van Nostrand, 1928, 16.

Tutton, A. E. H. .. *Crystallography and Practical Crystal Measurement*, MacMillan, 1922, **1**, 527.

Wooster, N. .. *Science Progress*, 1932, **103**, 462.