

A THEORY OF THE CRYSTAL FORMS OF DIAMOND

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1. INTRODUCTION

THE number of different kinds of planes permitted by the law of rational indices to appear as faces on a crystal is practically unlimited. The number of "forms" actually observed, however, is limited and there is a decided preference for a few amongst them. This is one of the most striking facts of geometric crystallography and its explanation is obviously of importance. Pierre Curie (1885) stressed the role played by the surface energy of the faces in determining the "forms" of the crystal. According to him, the different faces of a crystal have different surface energies and the form of the crystal as a whole is determined by the condition that the total surface energy of the crystal should be a minimum. According to W. Gibbs (1877), on the other hand, it is the velocity of growth in different directions which is the determining factor, while the surface energy of the crystal plays a subordinate role and is only effective in the case of crystals of submicroscopic size.

We have little direct knowledge as to how diamond is actually formed in nature. It is necessary, therefore, to rely upon the indications furnished by the observed forms of the crystals. One of the most remarkable facts about diamond is the curvature of the faces which is a very common and strongly marked feature. This is particularly noticeable in the case of the diamonds found in the State of Panna in Central India. Writing after a visit during which he had the opportunity of examining several hundreds of specimens, Sir C. V. Raman (1942) drew attention to the remarkable beauty of the Panna crystals with their exquisitely perfect geometric forms, their smooth lustrous surfaces and the sharpness of the edges which divide the curved faces into distinct sections. Basing himself on the characters exhibited by the Panna diamonds, he outlined a theory of the crystal forms of diamond which may be usefully quoted here *in extenso*.

"I wish to put forward tentatively a suggestion which seems to me to offer a reasonable interpretation of the facts stated above. If carbon liquefied under suitable conditions of temperature and pressure when surrounded by molten silicious material, the form of the drops of the liquid diamond

would be determined by the interfacial tension and would be spherical, provided the valence bonds between the atoms of carbon in the liquid were oriented completely at random. If, however, some measure of regularity in the orientation of the valence bonds could be assumed, the conditions within the liquid would roughly approximate to those in the solid crystal; in other words, *diamond in the molten state would be a liquid crystal*. The interfacial tension would then vary with direction and the surfaces of minimum energy would not be spherical but would tend to show some resemblance to the forms exhibited by a cubic crystal. If the shapes assumed by diamond in the liquid crystalline state persisted on solidification or else suffered only minor changes, we would have an explanation of the forms now observed."

The ideas expressed in the foregoing quotation have been made use of in the introductory paper of this symposium (Raman and Ramaseshan,

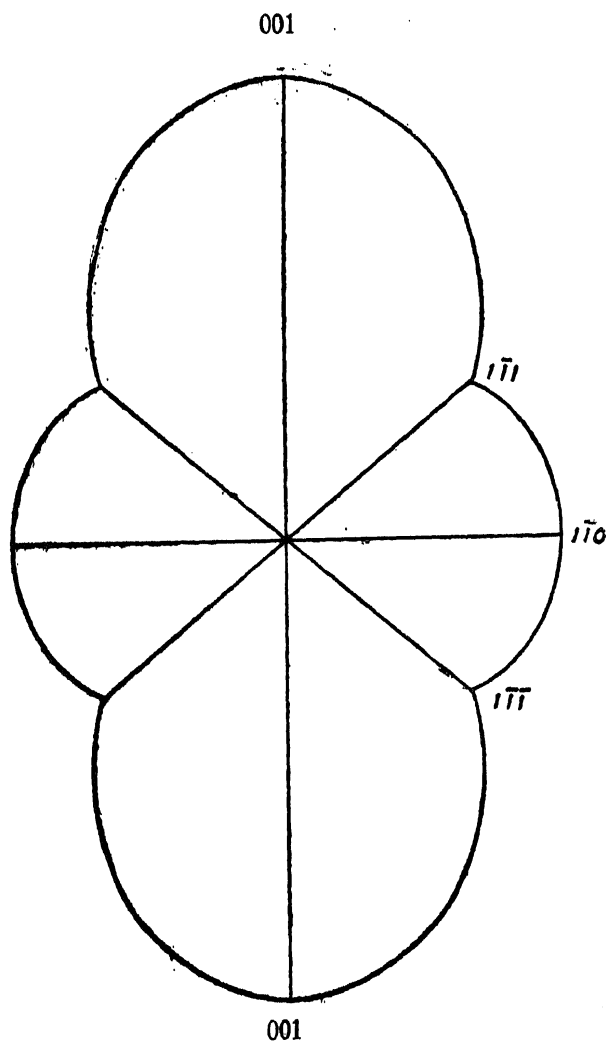


FIG. 1. Surface Energies in the [110] zone

1946) in connection with the scheme of classification of the crystal forms of diamond adopted in that paper. In the present paper, the same ideas are

developed further and given a semi-quantitative form. For this purpose, the calculation of the surface energy of the various crystallographic planes in diamond made by the present writer for a different purpose (Ramaseshan, 1946) are utilised. The theory succeeds in explaining some of the principal facts which emerge from a study of the crystal forms.

2. SURFACE ENERGIES OF THE CRYSTAL PLANES

The surface energy of the different crystallographic planes in diamond is very large, being at least ten times as great as the surface tension of mercury at ordinary temperatures. Hence, the surface tension may be expected to play a notable part in shaping the crystals of diamond under the conditions of their formation. For a proper approach to the subject, it is necessary to evaluate the surface energy for numerous planes lying in different zones. This has been already done by the present author in the paper on the cleavage properties of diamond appearing in the present symposium (Ramaseshan, 1946), and we may use the results here, taking the surface energy per unit area to be half the energy of cleavage. In Figs. 1, 2 and 3 the surface energies of the various crystallographic planes in the $[110]$, $[100]$ and $[111]$ zones have been represented in the form of polar diagrams.

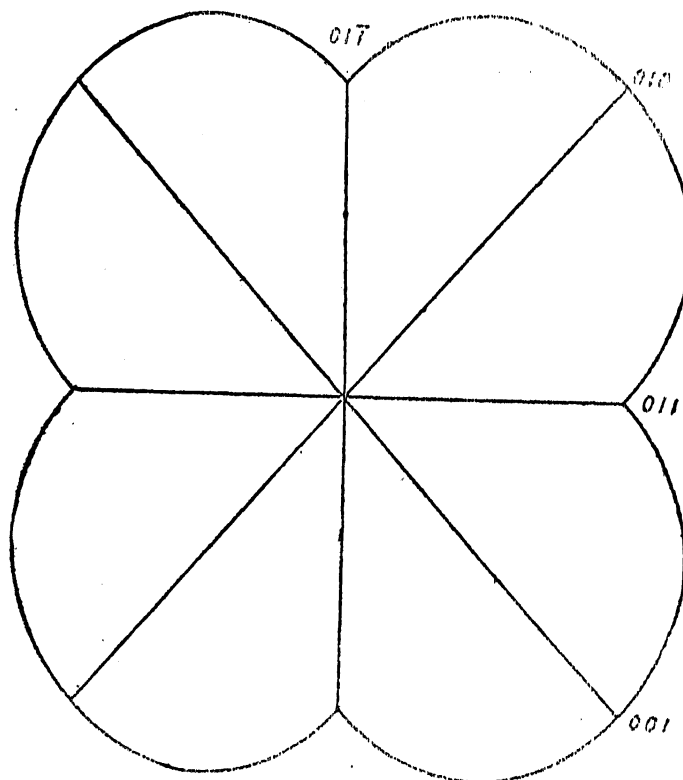


FIG. 2. Surface Energies in the $[100]$ zone

The following points emerge from a scrutiny of the figures. The surface energy is an absolute minimum for the (111) planes, and an absolute maximum

for the (100) planes; in the [110] zone the surface energy is a minimum for the (111) planes and a maximum for the (100) planes, while there is an intermediate maximum for the (110) planes; in the [100] zone, the surface energy is a minimum for the (110) planes and a maximum for the (100) planes; in the [111] zone, the surface energy is a minimum for the (110) planes and a maximum for the (211) planes. The situation thus described enables us at least qualitatively to understand the following empirically known facts:

(1) The plane faces which have been noticed to occur in diamond either by themselves or in combination with curved forms are, in the great majority of cases, if not in all, the (111) planes.

(2) Curved forms *approximately* parallel to either to the (111) or the (110) planes are a common feature in diamond.

(3) Curved forms parallel to the (100) planes are rarely, if ever, observed.

(4) Many diamonds exhibit forms which may be *approximately* described as a combination of the (111) and (110) forms, these however exhibiting a marked curvature.

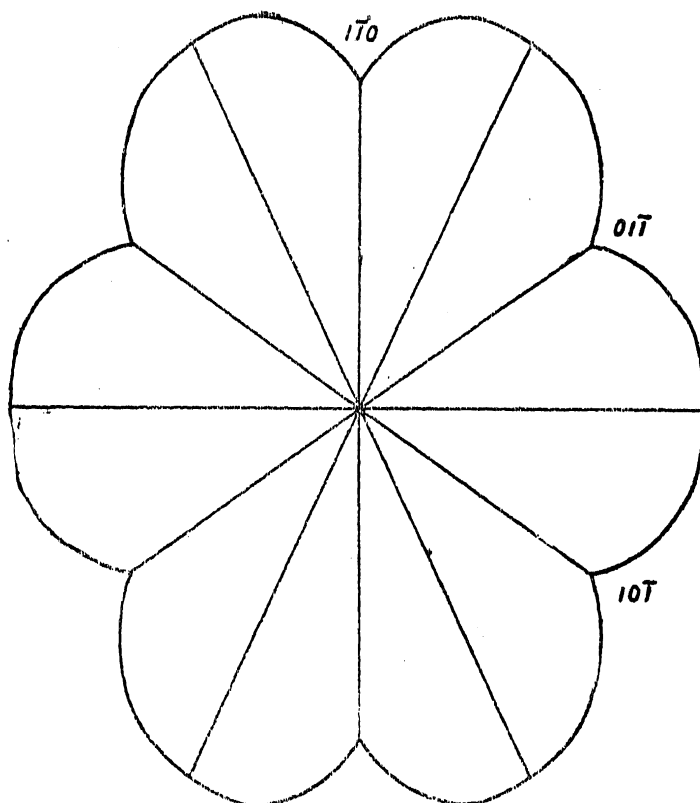


FIG. 3. Surface Energies in the [111] zone

3. THE AGGREGATE SURFACE ENERGY

According to P. Curie (*loc. cit.*), it is the total surface energy of the crystal that plays the determining role in respect of the forms assumed by

it. In the case of diamond, this would have to be found by integration over the curved areas and by addition of the surface energies of the plane areas (if any) appearing in combination with them. It is not without interest, however, to consider the purely hypothetical cases of the various regular forms, bounded by plane faces all of the same kind and to evaluate the surface energy of each of these. It then becomes evident that forms which present faces with a relatively small surface energy may nevertheless have greater aggregate energies by reason of their presenting a larger area for the same volume.

TABLE I

I	II	III	IV	V
Plane	Surface energy per unit area	Description	Area $\frac{\text{Area}}{(\text{Volume})^{2/3}}$	Product of II and IV
111	5665	Octahedron	5.718	32390
		Tetrahedron	7.204	40810
221	6545	Tris-octahedron	5.26	34430
		Tris-tetrahedron	5.793	37910
110	6945	Dodecahedron	5.346	37130
321	7870	Hexakis-octahedron	5.009	39430
		Hexakis-tetrahedron	5.395	42460
210	8780	Tetrakis-hexahedron	5.119	44940
100	9815	Cube	6	58890

The figures set out in Table I furnish us with some useful pointers. If, for instance, we were concerned with forms of diamond exhibiting full octahedral symmetry, the simple octahedron with eight faces would be a more probable form than the others having that symmetry but exhibiting 24 or 48 faces. On the other hand, if we are concerned with diamond having a tetrahedral symmetry of structure, its appearance in the forms specifically exhibiting that symmetry is not favoured. In particular, the appearance of the form of the simple tetrahedron would be much less probable than that of the rhombic dodecahedron which is common to both the tetrahedral and octahedral symmetry classes. It is also noticed that the appearance of the other forms common to the two symmetry classes, viz., the tetrakis-hexahedron and the cube, is much less probable than that of the dodecahedron. Similar considerations may also be applied to find the likelihood of appearance of various interpenetration forms. It is readily shown, for instance, that the Haidinger diamond or one similar thereto would have a surface energy for any given volume only slightly greater than that of a simple octahedron and hence that its appearance would be favoured.

4. RELATION OF CURVATURE TO SURFACE ENERGY

A liquid drop composed of isotropic material would naturally assume the shape of a sphere. Whether a liquid with anisotropic structure would show a similar behaviour depends on whether its surface energy is independent of orientation or not. In the particular case of molten carbon, it would seem that a variation of surface energy with orientation is very probable and hence the liquid would tend to take up a configuration different from that of a sphere. There would be clearly two opposing effects; areas having a smaller tension would tend to enlarge at the expense of areas having a greater, thereby diminishing the total energy, while on the other hand, the pressure within the drop would cause areas with a smaller tension to become more strongly curved, thereby diminishing their extent. What the resulting configuration would be is a problem—and not a simple one—in the calculus of variations.

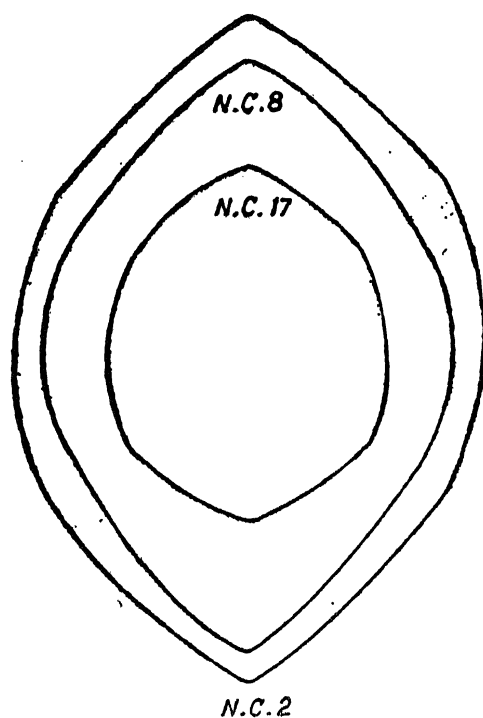


FIG. 4. Form of N.C. 2, N.C. 8 and N.C. 17 in the [110] zone

For our present purpose, it is sufficient to draw attention to the obvious correlations which exist between the surface energy diagrams reproduced as Figs. 1, 2 and 3 above with the observed forms of diamond in the respective zones. For this purpose, the outlines of three diamonds in the collection, N.C. 2, N.C. 8 and N.C. 17 of progressively diminishing size and having a fairly symmetrical shape have been photographically recorded for these zones. The outlines have been reproduced inside each other in Figs. 4, 5 and 6 respectively in the same zones.

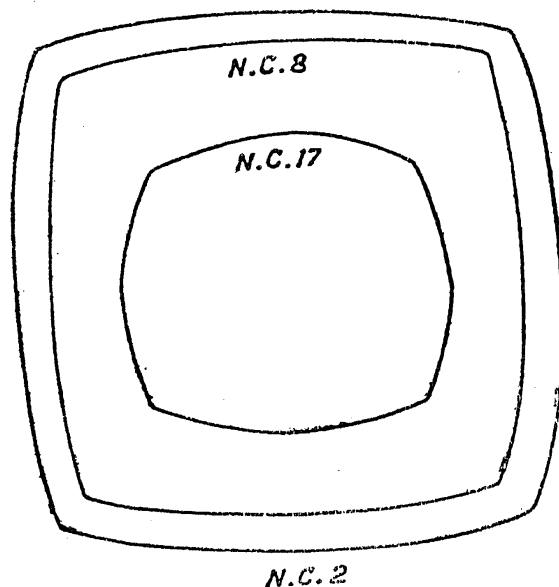


FIG. 5. Form of N.C. 2, N.C. 8 and N.C. 17 in the [100] zone

Comparisons of Fig. 4 with Fig. 1, Fig. 5 with Fig. 2 and Fig. 6 with Fig. 3 are instructive. In each case, the following features are noticed. The smaller the diamond, the more marked is the curvature of its faces. At the same time, the outlines of the form for the diamonds of different sizes tend to run parallel to each other. The areas in the vicinity of the triad axis in the [110] zone are the flattest, while in the vicinity of the dyad axes, the surfaces present sharp edges; in the (110) directions, there is a marked curvature.

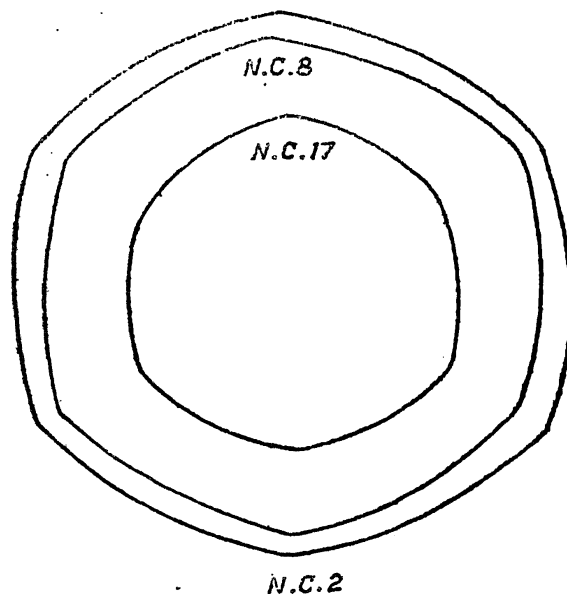


FIG. 6. Form of N.C. 2, N.C. 8 and N.C. 17 in the [111] zone

In the [100] zone, the surface exhibits a relatively small curvature in the (110) directions and others adjacent to it, while in the (100) direction, the surface presents sharp edges. In the [111] zone, the curvature is throughout very marked, but there are distinct kinks in the (112) directions, *viz.*, those normal to which the surface tension is greatest in that zone.

In conclusion, the author wishes to thank Sir C. V. Raman for his kind interest and useful discussions.

5. SUMMARY

The calculations of the energies of different crystallographic planes of diamond made in another paper by the author have been utilised to give a semi-quantitative form to the theory of crystal shapes of diamond. According to this theory (due to Sir C. V. Raman), diamond is formed by carbon liquified under pressure which retains the shape of the liquid drops with only minor modifications during solidification. Accordingly, the shape of the crystal is controlled by the varying surface tension of the molten liquid in different directions due to the non-random orientation of the valence bonds between the carbon atoms contained in it. It is found possible on this basis to explain various characteristic features of the crystallography of diamond, including especially the preference for certain forms, the influence of the size of the diamond on its shape, and the varying curvature in different zones of the crystal.

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