

X-RAY TOPOGRAPHS OF DIAMOND—PART II

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1. INTRODUCTION

IN an earlier paper by the author (1944 *a*) bearing the same title, a method was described by which it is possible to obtain a photographic reproduction (X-ray topograph) of the variations in the X-ray reflecting power over the area of a cleavage plate of any crystal. The method consists in using white X-rays diverging from a pinhole and obtaining Laue reflections from the full area of the cleavage plate. The reflections may be obtained either from the internal or surface crystallographic planes. In the former case, the crystal and the photographic plate have to be kept inclined at definite angles to the X-ray beam to obtain a non-distorted picture of the crystal, the values of which for any experimental arrangement could be obtained from formulæ given in the earlier paper. When X-ray reflections are obtained from the surface cleavage plane, it is only necessary to keep the photographic plate parallel to the crystal to obtain a perfect reproduction. A number of X-ray topographs obtained by the former method were reproduced in the paper quoted above and were discussed. These topographs were, however, defective for two reasons. Firstly, since duplitized X-ray films were used, two images were produced which were not in register on account of the oblique incidence of the X-ray beam on the film. This seriously affected the clarity of the topographs. It was found that the use of photographic plates eliminated this defect, although this necessitated the giving of fairly long exposures. Using this technique, some of the cleavage plates of diamond studied earlier have been reinvestigated and new specimens have also been studied. The other defect in the earlier photographs arose out of the use of fairly thick specimens. Since internal reflections were invariably involved, the reflections given by different layers of the diamond parallel to the surface were superimposed, thus obliterating many of the fine details (*e.g.*, lines and streaks) lying parallel to the plane of incidence and emphasizing those lying perpendicular to it. This defect was appreciably reduced by the use of thin plates. Five such thin specimens, N.C. 151, N.C. 155, N.C. 156, N.C. 160 and N.C. 162 have been studied. The clarity of the photographs obtained

with the new technique makes more precise observations possible. The present paper embodies the results of such further studies made on the X-ray topographs of diamond. In particular, the crystallographic orientation of the various bands and streaks found in the X-ray topograph is discussed and the significance of the topographs in relation to the various other patterns exhibited by diamond is brought out.

Since the publication of the previous paper by the author on the subject, a note has appeared in *Nature* by N. and W. A. Wooster (1945) describing their experiments for obtaining topographs using the principle of Bragg reflection from the surface. The author wishes to point out that the possibility of obtaining topographs using the surface reflection from a stationary crystal was envisaged in the earlier paper (1944 a) where it was stated that, in this case, "the condition for no distortion is extremely simple, namely that the film must be parallel to the crystal." The surface reflection method was not used by the author since the reflected X-rays were even more obliquely incident on the film than in the other method and would completely mask all details if duplitzed films were used. The method has later been tried with photographic plates, and the surface topographs thus obtained were essentially the same as those produced by internal reflection. An advantage of the ingenious modification of the method by N. and W.A. Wooster, in which the crystal and film are simultaneously oscillated and the characteristic X-radiation is employed, is that the exposure times are reduced very much.

2. CRYSTALLOGRAPHIC ORIENTATION OF THE PLATES STUDIED

Most of the specimens studied were of octahedral cleavage. However, it is interesting to note that a few diamonds were found in the collection of Sir C. V. Raman which were cleavage plates with their faces parallel to the (211) plane. N.C. 82, for instance, whose topograph is reproduced in this paper, is one such diamond. It is a fairly large plate (8 mm. \times 10 mm.) having a thickness of about 2 mm. N.C. 60 is a rectangular block 10 mm. \times 6 mm. \times 1.5 mm. whose broad faces are parallel to the (211) plane, while the two edges are respectively parallel to (111) and (01 $\bar{1}$) planes. N.C. 178 is another specimen whose broad faces are parallel to the (211) plane. The large size of these diamonds and the fact that the orientations of the surfaces were found to differ by less than 1° from those of the crystallographic planes suggest that these plates should have been obtained by cleavage. The slight deviations are to be explained as due to errors in polishing. These facts suggest that *diamond has a cleavage parallel to the {211} planes*, although this is not as often observed as the octahedral cleavage.

3. INTERPRETATION OF THE TOPOGRAPHS

In the previous paper by the author (1944 *a*), it was mentioned that any increased reflection that is observed must be attributed to mosaic structure, arising from the angular deviation of fine crystallites in a sub-microscopic scale from their mean orientation. It is a point of interest to find out whether this is really the case, or whether there is a misorientation of fairly large layers or blocks in the crystals. In another investigation, the author (1944 *b*) has studied the angular divergence of the X-ray reflections given by blue-luminescent diamonds and has found that the reflection from the (111) planes had an angular half-width of nearly 60 seconds in an intensely luminescent diamond while it was only 3" with a feebly luminescent diamond. The measurements were made on the Bragg reflections obtained from the surface of a stationary crystal using X-rays diverging from a very fine slit. The line obtained on the photographic plate was very regular and of uniform width, showing that the mosaic structure is on a very fine scale. When the same technique was tried with a non-luminescent diamond of the ultraviolet transparent variety, it was found that the line was very much distorted. The width of the reflected X-ray beam was of the order of a few minutes of arc, and the distribution of intensity over the width was highly irregular, the $K\alpha_1$ and $K\alpha_2$ lines being not at all resolved. These phenomena suggest that, in this variety of diamonds, misorientations on a fairly large scale also occur.

The question can also be settled in another way, namely by taking distortionless topographs at different distances from the crystal. This is best accomplished by obtaining topographs using surface reflections and keeping the photographic plate parallel to the surface of the crystal, when one obtains a slightly enlarged non-distorted image. In practice, this was done by having a long arm capable of rotating about the axis of the crystal, and setting this at double the angle of reflection to the direct beam of X-rays. The film-holder was kept at the requisite angle to the arm and by moving it towards or away from the crystal along it, topographs at various distances were obtained. It may be remarked that errors in the angular setting of the arm and the film holder would produce the same amount of distortion in all the pictures, so that the comparison can be done exactly. If the relative distances of the various streaks remain the same in all the topographs, then there is no gross misorientation, while the measurement of differences in these relative distances, if any, would give the angular tilting.

Actually, no such tilting could be found in the ultraviolet opaque diamonds showing blue luminescence, while a small angular tilting of a few minutes of arc was found in some ultraviolet transparent diamonds. This

probably explains why the latter class of diamonds give rise to much more intense X-ray reflections and why, in some cases, the diamonds themselves come out into curious shapes. The topographs reproduced in this paper are a true representation of the relative intensities of reflections from the different diamonds, for the exposure times were adjusted to give approximately the same density in all the cases. An idea of the relative intensity of scattering of reflection given by the ultraviolet transparent diamonds may be obtained from the fact that NC 125 in Fig. 1, which has a surface area of 1.5 sq. mm. required only an exposure of 15 minutes, while the topograph of NC 126 in the same figure, which is a diamond opaque to the ultraviolet, required an exposure of 10 hours' exposure.

4. DISCUSSION OF THE TOPOGRAPHS

For the purpose of this discussion, we shall consider only the topographs reproduced in this paper, but also those reproduced in the earlier paper by the author (1944*a*). Where reference is made to figures reproduced earlier, the new catalogue (NC) numbers are also given. For a proper appreciation of the discussion below, it will be useful to compare the topographs with the luminescence, ultraviolet transparent and X-ray patterns of the same diamond reproduced in a paper by Brindley (1946) appearing in this symposium.

It is convenient to divide the diamonds that were examined into three classes:

- (a) those exhibiting pure blue luminescence
- (b) those that are non-luminescent

and (c) those exhibiting both blue and yellow luminescence.

(a) As was remarked in the earlier paper, the topographs of purely blue-luminescent diamonds, which are opaque to the ultraviolet below 3000 Å.U., did not exhibit any streaks but only areas of varying intensity, these corresponding closely with those occurring in luminescence patterns, whose topograph is shown in Fig. 1. Plate X is a good example. The central bright portion here corresponds exactly with the bright portion of the luminescence pattern. The central bright area has a marked extension to the left in the luminescence pattern, which is correspondingly reproduced in the X-ray topograph. In the case of other diamonds of this class like D 36 (NC 71), D 45 (NC 72) and D 46 (NC 73) mentioned earlier, both the luminescence pattern and the X-ray topograph are similar. There is thus no doubt that, in diamonds of the blue-luminescent class, the X-ray reflecting power increases with increasing intensity of luminescence.

(b) In contrast to the above class of blue-luminescent diamonds, there is a class which transmits down to 2250 Å.U., and which does not exhibit any luminescence, examples of which are N.C. 124, N.C. 125 and N.C. 126. A characteristic feature of the X-ray topographs of these diamonds is the existence of sets of parallel streaks.

As has been shown by the author in another paper (Ramachandran, 1946) appearing in this symposium, diamonds of this class possess a laminated structure, the laminations being generally parallel to octahedral planes and less often to dodecahedral planes. It is of interest to know if the streaks found in the X-ray topographs also represent these laminæ. A study of the directions of the streaks showed that they were invariably parallel to the intersection of either an octahedral or a dodecahedral plane with the surface. However, if the laminæ observed optically are very fine and closely spaced, then the corresponding streaks are not found in the X-ray topograph. This is the case, for example, with N.C. 124 (D 207), which reveals fine laminæ under the polarising microscope. These lines, however, are absent in the topograph. The reason why this happens is that the reflection takes place not only from the surface of the crystal plate but also from the interior. Consequently, the streaks get superposed on one another and they disappear, if they are very fine. For the same reason, details consisting of lines running perpendicular to the plane of reflection are lost, while those parallel to it come out clearly. This is why only one set of streaks running at about 30° to the horizontal is found in the topograph of N.C. 125 in Fig. 1. These correspond to dodecahedral laminations seen under crossed nicols. Optically, octahedral laminations running perpendicular to these have been observed; but they are not found in the topograph since they are at right angles to the plane of reflection. With N.C. 126 (D 209), only a coarse pattern is observed in the topograph, presumably due to misorientations. The laminations are very fine and are not found in the topograph.

(c) The most interesting class of diamonds, in so far as the relationship between X-ray topographs and other patterns is concerned, is that which exhibits both blue and yellow luminescence. A number of such diamonds have been studied in detail and most of the topographs reproduced in this paper belong to this class. These diamonds can again be subdivided into two varieties, *viz.*, (i) those in which the blue and yellow luminescence patterns are identical and (ii) those in which they are different. To the former class belong N.C. 113 shown in Fig. 1, N.C. 156 and N.C. 160 in Fig. 2 and N.C. 80 (D 38 of author's earlier paper). In all cases, it is found that the topograph and the birefringence pattern follow the luminescence pattern, parallel bands occurring in the topograph in the same places as in

luminescence. In N.C. 113, there are also large variations in ultraviolet transparency, the two margins being more transparent than the rest of the diamond. These correspond with the bright bands seen in the topograph in the same regions.

The latter class is even more interesting, typical examples of which are N.C. 115, N.C. 82, N.C. 108 and all the diamonds in Fig. 2 except N.C. 156 and N.C. 160. As a result of a comparison of these topographs with the other patterns of the same diamonds, the following general results may be stated:

(1) The bands of yellow luminescence have their counterpart in the topograph.

(2) Also, these bands correspond to the lines found in the birefringence pattern, the similarity between the topograph and the birefringence pattern being generally very striking.

(3) Variations in blue luminescence are not generally reproduced in the topographs.

(4) Although the blue luminescence pattern shows a great similarity to the ultraviolet transparency pattern, bright areas in the one corresponding to dark areas in the other, no particular similarity is observed between the topograph and the transparency pattern.

These may be illustrated with special reference to the diamonds whose topographs are reproduced in Figs. 1 and 2. The blue luminescence pattern of N.C. 115 consists of a central triangular bright patch with dark areas surrounding it near the margins. The ultraviolet transparency pattern has an inverse relation to this, as described above. The X-ray topograph does not show these differences, but the three bands found in the yellow luminescence pattern are beautifully recorded in it. There is also some similarity to the birefringence pattern.

N.C. 82 exhibits exactly similar features, the blue luminescence and transparency patterns corresponding inversely, while the yellow luminescence pattern is different, namely consisting of bands running diagonally. The latter are found both in the X-ray topograph and the birefringence pattern.

The blue luminescence pattern of N.C. 155 is practically uniform, while parallel bands are seen in both the yellow luminescence and birefringence patterns. These correspond exactly with the fine bands found in the X-ray topograph. (It may be noted that the diamond is inverted in the topograph with respect to the other patterns, right side here corresponding to left in the others and *vice versa*.)

N.C. 151 is another typical case in which the blue and yellow patterns are quite different. The birefringence pattern consists of bands running parallel to the yellow luminescence pattern and the topograph also shows these same bands. As will be seen from the topograph, there is some sort of discontinuity in the middle of the diamond. This could be seen visually in the birefringence pattern also when the nicols are oriented properly.

The patterns of N.C. 108 are rather confused, but still a general similarity is observable between the various patterns.

5. INTERPRETATION OF THE RESULTS

A theoretical background on the basis of which one may attempt to interpret the above results is furnished by Sir C. V. Raman's theory (1944) of the ultimate structure of diamond. According to Sir C. V. Raman, diamond can have four different structures. Two of these, called TdI and TdII, have tetrahedral symmetry, and by virtue of the selection rules exhibit an absorption for infra-red radiation in the region of 8μ . They are physically identical with each other, differing only in their geometrical orientation. The other two structures, OhI and OhII, possess octahedral symmetry and are consequently transparent to the infra-red. They are however, distinct from each other and also from the tetrahedral varieties. The various structures may exist side by side in the same specimen of diamond and it is the differences in the nature and the extent of interpenetration of the various structures that produces the amazing variations in the properties of diamond.

The blue luminescent diamonds on account of their infra-red absorption, should consist solely of the TdI and TdII varieties. According to Raman's theory, blue luminescence arises from the intermixture of these two varieties, the intensity being determined by the extent of their interpenetration. Although the two structures are physically identical, nevertheless there would be discontinuities at the places where they join with each other, so that a sort of mosaic structure should result, the magnitude of the mosaicity being larger, the more intimately the two structures are mixed. These considerations give a satisfactory explanation of the direct correlation observed between the intensity of X-ray reflection and that of blue luminescence.

The non-luminescent diamonds are transparent both to the ultra-violet below 3000 \AA.U. and to the infra-red in the region of 8μ . These should therefore consist only of the OhI and OhII varieties. The two structures are physically different and consequently one would expect the diamond to be subject to severe strains. In fact, in another paper appearing in this symposium, the author (1946) has shown that the lattice spacings of the two

structures are different, that the diamond consists of laminae alternately made of OhI and OhII structures and that these laminae are alternately under compression and tension. It is therefore not at all surprising that these diamonds possess a large mosaic structure and that they often show gross misorientations.

The other type of intermixture that is possible is that between a Td and an Oh structure. Raman supposes that, in this case, yellow luminescence results. This is supported by the author's observations on the laminations in such diamonds. If, in the midst of a blue-luminescent diamond, a yellow streak is observed, then it is found that birefringence is produced at this region and that the diamond composing the thin lamina has either a larger or a smaller spacing than the bulk of the specimen. (For further details, see the paper by the author quoted above.) Thus, at places where a band of yellow luminescence is observed, there should be a comparatively large mosaic structure, since the structure there has a spacing different from the rest of the crystal, in contrast with the areas of blue luminescence where the two intermingling structures are of identical lattice spacing. This explains why yellow bands are invariably represented in the topograph as bright streaks while variations in blue luminescence are not represented.

The facts described in the previous section thus find a reasonable explanation on the basis of Raman's theory.

I wish to express my indebtedness to Sir C. V. Raman for the constant encouragement that he gave me during the course of this investigation.

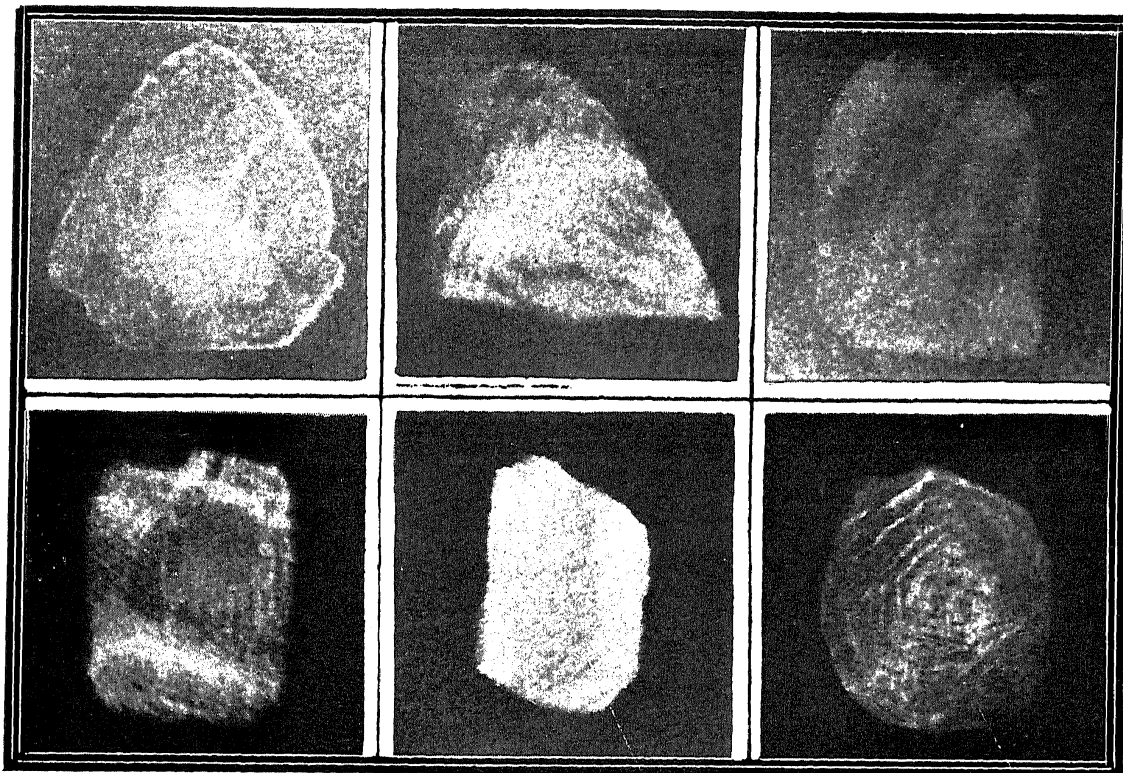
SUMMARY

X-ray topographs (*viz.*, photographic representations of the variations in the X-ray reflecting power over the area of a crystal plate) of a number of diamonds have been obtained and studied. Comparing these with the other patterns of the same diamonds, the following results emerge: (1) In purely blue-luminescent diamonds, there is a direct correlation between the intensity of luminescence and the X-ray reflecting power. (2) Topographs of non-luminescent diamonds show parallel bands, which often correspond with the bands in the birefringence patterns. They also suggest that gross misorientations of fairly large crystalline blocks sometimes occur in these diamonds. (3) In diamonds showing both blue and yellow luminescence patterns, the topograph exhibits a correspondence only to the yellow luminescence pattern if the two are different, and to both if they are similar. An explanation of these results is given on the basis of Raman's theory of the structure of diamonds.

N.C. 100

N.C. 115

N.C. 82



N.C. 125

N.C. 113

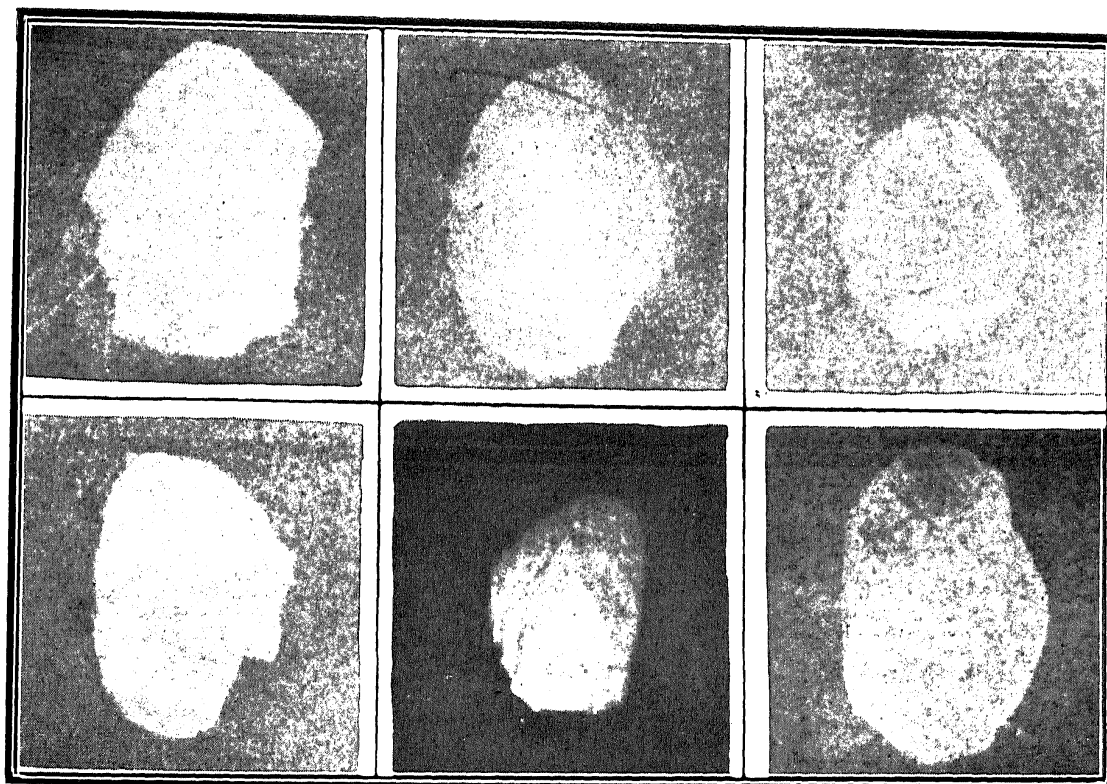
N.C. 108

FIG. 1. X-Ray Topographs of Diamond

N.C. 155

N.C. 156

N.C. 162



N.C. 114

N.C. 160

N.C. 151

FIG. 2. X-Ray Topographs of Diamond

A study of the orientation of a number of cleavage plates made in connection with this investigation showed that although most of them were of octahedral cleavage, at least 3 of the diamonds had their *large* faces parallel to the (211) plane, showing that diamond has also a direction of easy cleavage parallel to the {211} planes.

Note added on 17th June 1946.—Since the above was written, it has been discovered by Ramaseshan (1946) that diamond possesses many other cleavages besides the new one (211) reported in section 2 of this paper. Consequently, a systematic study of the orientation of a number of diamonds in the collection of Sir C. V. Raman was undertaken to see if any of the cleavage plates belonged to any of these new classes. Out of a total of 48 diamonds studied, it was found that 42 were of octahedral cleavage. Of the remaining, 3 diamonds (N.C. 60, 82 and 178) had their surfaces parallel to a {211} plane, N.C. 88 was parallel to a {322}, N.C. 123 to a {320} and N.C. 174 to a {431} plane. The orientation of the last one was not very definite, since it was less than 5° away from a {331} or a {321} plane. The fact that such large cleavage plates having a surface area of 20 sq. mm. and above could be obtained parallel to these planes is very striking. It shows that the cleavages are fairly well-defined, and thus supports the findings of Ramaseshan.

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