

# X-RAY REFLECTION AND THE STRUCTURE OF DIAMOND

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## 1. Introduction

ACCORDING to the well-known Ewald-Darwin theory of the reflection of X-rays by perfect crystals, the integrated reflection, or the total intensity reflected as the crystal is swung through the Bragg angle, is proportional to the structure factor of the particular set of planes concerned. On the other hand, if the crystal were ideally imperfect, so that one can neglect the effect of both primary and secondary extinction, then the integrated reflection becomes proportional to the square of the structure factor (Darwin, 1914 *a*, 1922). In general, therefore, the intensity of reflection is much greater for an imperfect crystal than for a perfect one. Crystals have generally been classified as either perfect or ideally imperfect, according as the integrated reflection approximates to the theoretical value calculated for the one or the other. To the latter class are assigned most of the crystals like rocksalt, fluorspar and barytes (Bragg, Darwin and James, 1926). Calcite is the only example for which values of the integrated intensity approaching that for a perfect crystal have been obtained (for references see Compton and Allison, 1935, pp. 399 to 405). Although the integrated reflection has not been measured for diamonds, measurements of the width of reflection have been made by Ehrenberg, Ewald and Mark (1928), who found values remarkably close to that for a perfect crystal with some specimens.

As already said, ordinary crystals either belong to the perfect or to the imperfect variety. It is not easy to get samples of the same crystal possessing varying degree of mosaic structure. However, in the case of diamond, such a procedure is possible. For, diamond can exist in four allotropic modifications, and, in an actual crystal, these can appear either alone, or two or more structures can appear intermingled (Raman, 1944 *a* and *b*). The extent of interpenetration of the different structures may also vary from sample to sample. Thus, one can obtain various types and degrees of mosaic structure by having crystals of diamond which exhibit different

colour and intensity of fluorescence. *Vice versa*, by studying the reflection of X-rays by different crystals of diamond, one can obtain some knowledge of the nature of the mosaic structure in diamond.

That such a mosaic structure exists in blue-fluorescent diamonds was first shown by R. S. Krishnan (Sir C. V. Raman, 1942), who obtained the Laue photographs of two such diamonds, one of which D31 was feebly blue-fluorescent and the other D224 was strongly fluorescent, also blue. He found that all the spots in the Laue pattern of the latter were more intense than the corresponding ones of the former. Following this discovery, P. S. Hariharan (1944) studied the intensity of the (111) Bragg reflection given by a number of diamonds, and found that there is a direct correlation between the intensity of X-ray reflection and of blue-fluorescence. It was therefore thought worthwhile to extend the investigation to some of the other important reflections given by diamond. This was done by taking the Laue patterns of two typical blue-fluorescent diamonds, which differ widely in their intensity of fluorescence.

## 2. *Experimental Details and Results*

The specimens used were carefully selected out of the collection of Sir C. V. Raman so as to have as nearly as possible the same thickness, and to be as perfectly isotropic as could be obtained. The diamonds used were D31 and D41, both octahedral cleavage plates of very nearly the same thickness, about 1 mm. The actual thicknesses were 0.96 mm. and 1.0 mm. D31 was feebly blue-fluorescent, while the other one was intensely fluorescent, also blue.

The source of X-rays consisted of a self-rectifying Shearer tube, excited by a transformer, and worked at 50 K.V. and 9.5 milliamperes. This was kept steady by continuous adjustment of the air-leak and the resistance in the primary circuit of the transformer. The X-ray beam was collimated through a pinhole 1 mm. in diameter and 10 cm. long.

The diamond plate could not be mounted on a goniometer since this prevented the photographic film from being brought close to the crystal so as to record the complete pattern. Consequently, the goniometer was dispensed with, and the diamond was placed straight against the exit end of the slit and stuck to it by means of wax. As already said, the surface of the diamond was parallel to the (111) plane, so that it was most convenient to mount the plate with the surface (111) planes normal to the X-ray beam. This was done by hand, the normality being judged by taking a picture of the  $(11\bar{1})$ ,  $(\bar{1}11)$ , and  $(\bar{1}\bar{1}1)$  Laue spots and verifying

that they are at equal distances from the central spot. After this adjustment was made, the complete pattern was photographed by placing the film quite close to the crystal (at a distance of 9.5 mm.) and normal to the X-ray beam. An exposure of 3 hours was required to obtain a clear picture. Throughout the exposure, both the voltage applied and the current through the tube were maintained rigorously constant by continuous manipulation.

With diamond 31, standard pictures with exposures of 5, 90 and 180 minutes were taken. Then, using diamond 41, a series of pictures were taken with exposures varying from 2 to 180 minutes (for reasons to be explained shortly) under the same conditions as for D31. All the films were developed under standard conditions in the same stock developer.

The photographs obtained with an exposure of three hours in the two cases are reproduced in Fig. 3, Plate XXIV in a previous paper by the author appearing in this symposium. The Laue pattern consists of spots lying in the three zones, the  $(1\bar{1}0)$ ,  $(10\bar{1})$  and  $(01\bar{1})$ , and the indices of the spots in any zone belong to the forms  $\{111\}$ ,  $\{211\}$ ,  $\{311\}$ ,  $\{511\}$ ,  $\{711\}$  and  $\{100\}$ . It will be seen from the figure the intensities of the spots are greater in the pattern of D41 than of D31.

A detailed microphotometry of the peak intensities of the various spots was then undertaken. In this connection, it must be noted that the wave-lengths of the X-rays giving rise to the different Laue spots are different. Consequently, the calibration curve for the determination of the intensity had to be plotted for each wave-length required. It was for this purpose that a number of photographs were taken with a wide range of exposures, with the diamond giving stronger reflections. Using these photographs, and assuming the well-known result that the Schwarzschild's constant for X-rays does not differ appreciably from unity, the density-log intensity curve was drawn for each of the wave-lengths. From this curve, the intensity of the corresponding spots in the pattern of D31 were evaluated. It may be remarked in this connection that the Laue photographs obtained are not absolutely symmetrical, but that there is a small asymmetry. In order to avoid the errors arising from this, the intensity of all the six or three (as the case may be) spots having the same indices were measured, and the average was taken as the correct value.

The ratios of the intensities obtained in this way are shown in the second row in Table I.

TABLE I

Indices of the reflection ..	111	422	311	511	711	400
$I_{41}/I_{31}$ .. ..	3.36	2.24	2.31	1.93	1.49	2.72
$I_{224}/I_{31}$ .. ..	..	3.20	3.61	2.55	1.81	4.61
$I_{224}/I_{41}$ .. ..	..	1.54	1.56	1.32	1.21	1.69

It will be seen from the table that the ratio of the intensities given by the two diamonds is not a constant for all the planes, but that it varies from one to another. In order to confirm this fact, the photographs taken by Dr. R. S. Krishnan with diamonds 31 and 224, which were reproduced in *Current Science* (Sir C. V. Raman, 1943) were subjected to microphotometry. The original negatives of these were kindly lent to the author by Dr. Krishnan. Although the thicknesses of these two diamonds were not the same, still the photographs could be used for the purpose of a check. The values obtained for the ratio  $I_{224}/I_{31}$  are shown in the third row in Table I. The ratios deduced for  $I_{224}/I_{41}$  from the above are tabulated in the fourth row. Although no claim is made as to the accuracy of the values of  $I_{224}/I_{31}$  and of  $I_{224}/I_{41}$ , it is clear that the ratio of the intensities of reflection given by two blue-fluorescent diamonds is not the same for all the planes, but that it varies. Further, the plane whose intensity is affected most is the same for all diamonds, and the order in which the intensities are enhanced is also the same.

### 3. Interpretation of the Results

From the experimental results described in the preceding section, it is clear that the enhancement in intensity produced by the mosaic structure which is present in blue-fluorescent diamonds is not the same for the various planes. A clue to the understanding of the cause for this comes out of a study of the intensity of X-ray reflection by perfect and by ideally imperfect crystals. According to Darwin (*loc. cit.*), the expressions for the integrated intensity reflected out of a crystal plate are, for a perfect one,

$$I_p = \frac{8}{3\pi} N\lambda^2 F \frac{e^2}{mc^2} \cdot \frac{1 + |\cos 2\theta_0|}{2 \sin 2\theta_0},$$

and for an ideally imperfect one,

$$I_i = \frac{N^2\lambda^3}{2\mu} \cdot \left(F \frac{e^2}{mc^2}\right)^2 \cdot \frac{1 + \cos^2 2\theta_0}{2 \sin 2\theta_0},$$

where  $N$  is the number of unit cells per c.c.,  $F$  is the crystal structure factor for the unit cell,  $\lambda$  is the wave-length reflected, and  $\theta_0$  is the angle of

incidence for the particular reflection,  $\mu$  is the linear absorption coefficient, and  $e$ ,  $m$  and  $c$  have their usual significance. The perfect crystal formula is true only for a non-absorbing crystal, and for one which is not so  $I_p$  would obviously be less. Consequently, while comparing the two quantities  $I_p$  and  $I_i$ , we need not consider the factor  $1/\mu$  in the expression for  $I_i$ , and the ratio of the two may be written as

$$\frac{I_i}{I_p} \propto N\lambda F \frac{e^2}{mc^2} \cdot \frac{1 + \cos^2 2\theta_0}{1 + |\cos 2\theta_0|}$$

Here,  $e^2/mc^2$  is a universal constant, and  $N$  is a constant for a particular crystal, so that one may write

$$I_i/I_p \propto k\lambda F,$$

where  $k$  stands for the ratio  $(1 + \cos^2 2\theta_0)/(1 + |\cos 2\theta_0|)$ .

The above expression relates to the increase in intensity when a perfect crystal is completely broken up. However, in the case of diamond, with which we are concerned, the crystal approaches perfectness, but possesses a slight mosaic structure, which increases with increase in the intensity of blue-fluorescence. Therefore, we may expect the ratio of the intensities for two blue-fluorescent diamonds to be some function of  $(k\lambda F)$ . In Fig. 1, the quantities  $I_{41}/I_{31}$ ,  $I_{224}/I_{31}$  and  $I_{224}/I_{41}$  (which may be denoted by  $r_1$ ,  $r_2$  and  $r_3$  respectively) are plotted as ordinates against  $(k\lambda F)$  as abscissæ.

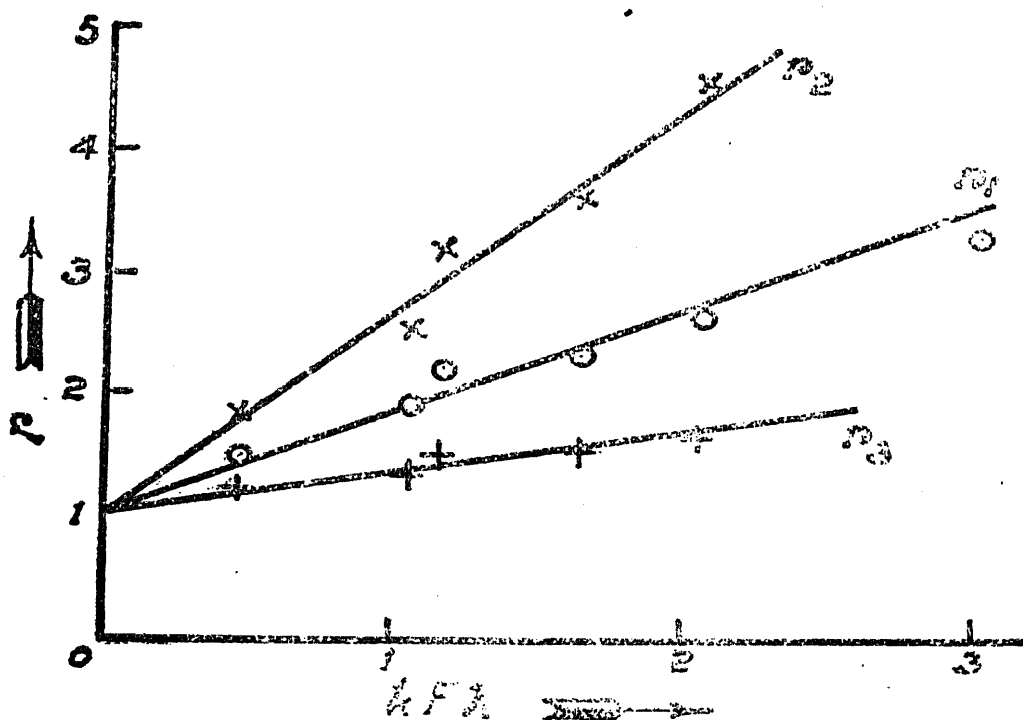


FIG. 1. X-Ray Reflection and the Structure of Diamond

The plotted points are found to lie approximately on straight lines, the equations to which are:

$$(r_1 - 1) = c_1 (k\lambda F); (r_2 - 1) = c_2 (k\lambda F); (r_3 - 1) = c_3 (k\lambda F),$$

where the  $c$ 's are constants. Thus the ratio  $r$  depends linearly on the product  $(k\lambda F)$ , having a value unity when the structure factor  $F$  is zero.

The author is not in a position at present to give a theoretical explanation for this empirical relation connecting  $r$  and  $(k\lambda F)$ . It may be remarked that even if  $r$  is plotted against  $(\lambda F)$ , then also the points lie on straight lines intersecting the  $r$  axis at  $r = 1$ .

In conclusion, I wish to express my deep sense of gratitude to Prof. Sir C. V. Raman for the suggestion of the problem and for the encouraging guidance which he gave me during the investigation. My thanks are also due to Dr. R. S. Krishnan for the loan of the two negatives taken by him.

### Summary

Laue photographs with the X-ray beam normal to the surface (111) planes have been taken for two typical blue-fluorescent diamonds exhibiting widely different intensities of fluorescence, but similar in other respects. Microphotometry of the peak intensity of the various spots shows that although the intensity of all the spots is greater with the more fluorescent diamond, the ratio ( $r$ ) of the intensities of the corresponding spots varies. Empirically, it is found that  $(r - 1)$  is proportional to the product of the structure factor, the wave-length reflected and a function of the angle of incidence.

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