

## The Intensity of X-Ray Reflection by Diamond

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XXVII. *The Intensity of X-Ray Reflection by Diamond.*  
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ABSTRACT.

The Paper describes an investigation of the relative intensities of the reflections of monochromatic X-rays by the various crystallographic planes of diamond. The special difficulties due to the small size of available crystals and the modification of the usual method required to obviate them are discussed. An interesting feature of the results is that they lie very closely on smooth curves, which indicates that if the outer electrons of the carbon atom lie at any considerable distance from the centre they must be in motion over a wide range, or for some other reason must contribute little to the reflection.

It is shown that the properties of the carbon atom in diamond are based on a tetrahedral and not a spherical form. The tetrahedra point away from any (111) plane in the case of half the atoms, and towards it in the case of the other half. Consecutive 111 planes are not exactly of the same nature and consequently some slight second order reflection from the tetrahedral plane might be expected. This effect, though slight, has been found.

A KNOWLEDGE of the relative intensities of the reflections of monochromatic X-rays by the various planes of diamond might be expected to give useful information for several reasons.

The most important is the general reason that such relative intensities for any crystal depend on the arrangement of the atoms round each point on the lattice and on the arrangement of the electrons in each atom, and are markedly characteristic of each crystal. Nevertheless, because of insufficient knowledge, it is not easy to interpret the results.

Consequently, a study of these intensities in the case of diamond might be particularly useful, because there is but one kind of atom and because the structure is simple and exactly known. Interpretation might be easier than in the case of more complicated crystals.

There is, however, one difficulty which is not met with in the case of rock-salt or other crystals which can show faces of large area, either natural or prepared. When a fine pencil of X-rays is allowed to fall on a large enough face the dimensions of the crystal need not enter into the calculations; because the face may be so large that the pencil cannot miss it, and the depth of the crystal below the face may be so great that the rays are wholly absorbed.

This cannot be realised in the case of diamond, and a different plan must be followed. Instead of making the pencil of rays small, and using a large crystal, it is necessary to make the pencil so broad that the diamond is entirely bathed in it. All the slits of the spectrometer are opened wide, and the dimensions of the reflected pencil are determined by the size of the crystal.

The diamond is mounted on a stand somewhat similar to that of a goniometer, and its position is so adjusted by means of the X-ray reflections that any convenient zonal axis coincides with the axis of the spectrometer. It is then easy to revolve the crystal from one position to another, and to test the intensity of reflection by any of the planes belonging to the zone.

The zonal axis most used was that which is determined by the intersection of (110) and (001); all the important planes pass through it. In measuring the intensity for any particular plane, the ionisation chamber was first set at the proper angle, and the crystal was then turned at a uniform and definite rate through the small range of angle for which it reflects. The intensity was measured by the calibrated movement of the electroscope leaf during the sweep. Allowance was made for the small amount of general radiation which entered the chamber during the time of observation. The method has been described in the "Philosophical Magazine," May, 1914.

The results shown in Table I. were obtained with a diamond weighing 9.8 milligrams. When the current in the Coolidge bulb was 1 milliampere and the potential about 40,000 volts, and when the electroscope was adjusted to a moderate sensitiveness, such as 20 divisions to the volt, the reflection from the 111 plane caused the leaf to move at a rate of about 5 divisions in a second. The divisions were such as could be readily divided into 10 by eye. The bulb had a rhodium anticathode.

The diamond\* was chosen of a form as nearly as possible spherical; it showed no well-marked faces. This was done because it was expected that the reflected intensities would show the influence of absorption within the crystal, as actually proved to be the case. If the diamond had been very irregular

\* This and other stones were most kindly given to me by Mr. Alphonse Abrahams.

in shape, the intensities corresponding to the different planes would have been affected thereby in different degrees, and it would have been very difficult to make the correct allowances. This difficulty was largely avoided by choosing a diamond nearly spherical in form, and by measuring the intensities of all the planes belonging to three out of the six different zonal axes of the type already mentioned. The intensities agreed among themselves to about 10 per cent. The figures in Table I. are averages, and are probably correct to 5 per cent. They are given exactly as they were found, without allowance for polarisation, temperature or other influence.

TABLE I.

Indices of plane.	Cosec $\theta$ .	Intensity.
111	6.72	200 (standard)
110	4.10	145
311	3.51	84
222	3.36	4
100	2.41	97
331	2.67	62
211	2.38	81
333 } 511 }	2.24	45
220	2.05	62
310	1.83	52*
533	1.76	29
444	1.68	38
711 } 551 }	1.63	21.5
321	1.56	36*
553	1.51	19
200	1.45	28
733	1.42	16.5
411 } 330 }	1.37	26
555	1.34	11.5

The results are plotted in Fig. 1, the ordinates being the intensities and the abscissæ the cosecants of the angles of reflection.

The curves show certain well-marked features. All the planes which have any even numbers in their indices lie on one smooth line; the rest lie on another. This is obviously due to the fact that the spacings of planes of the first kind are all equal to each other. The spacings of the second kind are alternately as 1 to 3. This is most easily realised in the case of the (111) or tetrahedral plane, and is a consequence of the fact that every atom is at the centre of gravity of its four nearest neighbours.

\* Only single instances of these planes were examined.

In the case of the first and third order reflections from any plane whose indices are all odd, the reflections from alternate sheets of atoms are in quadrature with each other. In the case of the fourth order reflection all sheets act together. For these reasons the (444) point lies on the

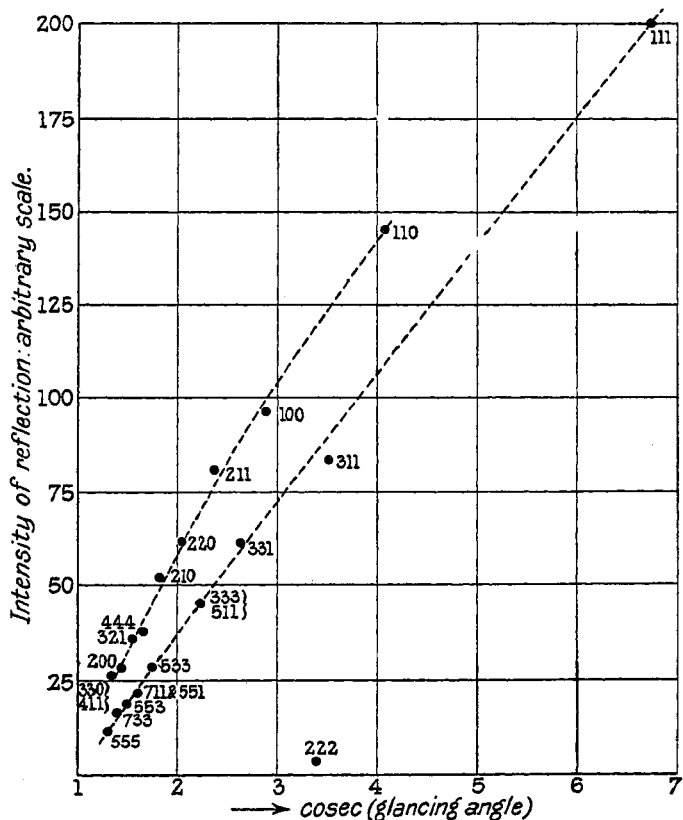


FIG. 1.—RELATIVE INTENSITIES OF REFLECTION FROM VARIOUS PLANES OF DIAMOND.

upper curve in the figure, but the points representing the intensities of (111) and (333) lie on the lower.

The influence of the arrangement which is characteristic of diamond structure and which causes alternate sheets of a set to act at one time in unison with each other and at

another time in quadrature should cause the ordinates of the upper curve to be twice those of the lower. For if we start with a set of equal and equidistant sheets, and then take half the atoms out of each sheet to form a new set of sheets which divide the spacings of the old set in the ratio 1 : 3, the intensity of the reflection of the  $n$ th order is diminished in the ratio

$$1 : \{ (1 + \cos n\pi/2)^2 + \sin^2 n\pi/2 \} / 4.$$

If  $n=1$  or  $=3$ , the ratio is 2 : 1.

This is far from being the case, particularly on the right of the diagram. The fact is that absorption of the rays has to be taken into account, and in particular, the special absorption which occurs when the crystal is so arranged as to be reflecting.

When a crystal is made to revolve through its range of reflection as in these experiments the total intensity of the rays reflected by a small element of the crystal is proportional to the intensity of the rays incident on the element and to the volume of the element. The pencil of rays that has passed through the element has lost energy on account of the reflection that has taken place. A similar loss or absorption of energy of the original pencil takes place all along its path, while reflection is occurring. The ordinary absorption co-efficient  $\rho$  is supplemented by a special absorption co-efficient which may for present purposes be assumed to be proportional to the amount of reflection; and to be capable of addition to the former. This co-efficient  $r$  will be different for different planes, and for any one plane it will vary with the glancing angle, having a sensible value for only a very small range on either side of the true angle of reflection.

The primary pencil has to traverse a certain distance in the crystal before it reaches any element of volume  $dv$ ; and the reflected pencil has to traverse a further distance before it emerges. Along both these paths the absorption co-efficient is equal to  $\rho+r$ . If  $d$  is the sum of the two paths, the contribution of the element to the reflection intensity is proportional, for any given value of the glancing angle, to

$$r dv e^{-(r+\rho)d}.$$

Secondary and further reflections are neglected.

The intensity of the whole reflection is obtained by integrating this expression over the volume of the crystal. The result depends on the shape of the crystal as well as on its

volume, and also on the values of  $r$  and  $\rho$ . For our present purpose, a very approximate estimate is enough. It is sufficient to suppose the crystal to be so small that only first powers of  $(r+\rho)d$  need be retained.

If  $(r+\rho)d$  is neglected altogether the intensity of reflection is proportional to  $rV$  where  $V$  is the volume of the crystal. If first powers are retained the integration of  $rdv(1-r+\rho.d)$  will yield an expression  $rV(1-k.r+\rho)$  where  $k$  is a linear quantity depending on the form of the crystal.

If, then, a point on the upper curve of Fig. 1 is compared with a point on the lower for which the abscissa is the same, the ratio of the ordinates ought to be less than two to one. The ratio would be exactly two to one if the crystal was extremely small, but, taking in first powers of  $(r+\rho)d$  it is now, for the particular glancing angle in question, of the form

$$2. \frac{1-k(2r+\rho)}{1-k(r+\rho)},$$

which is always less than 2 and diminishes as  $r$  increases.

When, as in these experiments, the crystal is made to revolve through an angular range which includes the true angle of reflection, the numerator and denominator of this fraction require separate integration over that range; but the final ratio is still less than 2, and the more so the stronger the reflection.

If the diamonds are so large that it is not enough to limit the calculation to first powers of  $(r+\rho)d$ , the general conclusion is not affected. So also, if diamonds of different weight are compared with each other the larger crystals should show the effect of absorption more than the smaller, since  $k(r+\rho)$  increases with the dimensions of the diamond.

The comparative intensities for a few diamonds of different weight are shown below :—

Weight in mgm.	TABLE II.					
		(111)		(333)		(444)
61.4	...	100	...	33.5	...	26
9.8	...	45	...	10.4	...	8.5
4.55	...	34	...	7.0	...	5.4

The largest stone weighs more than thirteen times the smallest, but the (111) reflection is only three times larger, and even the (444) reflection, for which  $r$  is smaller, is only five times larger than the corresponding reflection of the small stone. In the case of a large diamond of a roughly triangular

form, and of more than 2 mm. thickness, the relative intensities for the three planes of Table II. were 100 to 45 to 39. This stone was kindly lent to me by Sir George Beilby.

Perhaps the most remarkable feature of the results represented in the diagrams is that such smooth curves can be drawn through the various points. If the outer electrons of the carbon atom lie at any considerable distance from the centre they must be in motion over a wide range,\* or for some other reason they must contribute little to the reflection. For if not, their effects on different planes would vary greatly. If they all lie close to the centre such large motions need not be assumed. The question may be settled by an absolute measure of the intensity of diamond reflections, but the experiments are not yet complete.

Another point of interest is the existence of a small 222 reflection. This has been looked for previously but without success. The structure of the diamond cannot be explained on the hypothesis that the field of force round the carbon atom is the same in all directions: or in other words, that the force between two atoms can be expressed simply by a function of the distance between their centres. If this were so the spheres, which would then represent the carbon atoms appropriately, would adopt the close-packed arrangement. Each atom would surround itself with twelve others, all similarly placed. As a matter of fact, each atom is surrounded by four neighbours only, and the structure is so hollow that it is possible to add to the atoms in a given space others in number equal to those already there. The arrangement then becomes that of the centred cube, and each atom has eight neighbours instead of four.

It is necessary, therefore, to suppose that the attachment of one atom to the next is due to some directed property, and that the carbon atom has four such special directions: as indeed the tetra-valency of the atom might suggest. In that case the properties of the atom in diamond are based upon a tetrahedral not a spherical form. The tetrahedra point away from any (111) plane in the case of half the atoms in the diamond and towards it in the case of the other half. Consecutive 111 sheets are not exactly of the same nature; and it might reasonably be expected that they would not entirely destroy

\* See Papers by Coster, *Proc. Roy. Acad. Sci.*, Amsterdam, Oct., 1919; and by Kolkmeijer, *ibid.* Jan. 1920.



each other's effects in the second order reflection from the tetrahedral plane. It is this effect which is now found to be quite distinct, though small.

#### DISCUSSION.

Dr. ANDRADE asked if surface tension effects entered into the problem.

Dr. RAYNER asked if there was any chance of obtaining the arrangement of carbon atoms in the benzene ring.

Prof. BRAGG explained that surface tension effects did not come in. In reply to Dr. Rayner, he exhibited a model of the benzene group.

#### EXHIBIT OF PHOTOGRAPHS BY M. LE DUC DE BROGLIE.

Prof. BRAGG exhibited and explained photographs by M. le Duc de Broglie of the "Magnetic Spectra" obtained when the  $\beta$ -rays produced when X-rays strike copper are deflected on to a photographic plate by a magnetic field.