

The Structure of Graphite

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complications due to downward diffusion of the solvent, or to upward or downward displacement of its constituents if the diffusion medium is a solution of another substance.

The writer wishes to take this opportunity of expressing her thanks to Prof. Sir James Walker, F.R.S., who suggested the investigation, and who has given much helpful criticism and advice during the course of the work.

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*The Structure of Graphite.*

By J. D. BERNAL, B.A.

(Communicated by Sir William Bragg, F.R.S.—Received July 28, 1924.)

The crystallographic information on the subject of graphite is scanty. It has generally been accepted as hexagonal with a well-marked basal cleavage; but besides the cleavage face few other faces have ever been observed on it. Kenngott,\* the earliest observer, seems to have obtained the best crystal, and measured planes, to which he gave the indices  $10\bar{1}1$  and  $11\bar{2}1$ , making angles of  $58^\circ$  and  $70^\circ 18'$  respectively with the basal plane 0001. (These results are strikingly confirmed by X-ray measurements, which make the corresponding angles  $58^\circ 8'$  and  $70^\circ 13'$ .) Nordenskiöld† considered graphite monoclinic, on account of the variability of its angles; but his conclusions were questioned by Sjögren,‡ who, in a very full paper, adduced a number of reasons (twinning, percussion and etch figures, thermal conductivity) to show that it was hexagonal. Quite recently the researches of Gaubert§ have added a knowledge of the optical properties of graphite. In very thin flakes it is transparent, uniaxial and negatively birefringent, with a refractive index of about 2. This settles definitely that it has trigonal hexagonal symmetry.

The X-ray analysis of graphite has lagged considerably behind that of the

\* Hintze, 'Mineralogie,' vol. 1.

† 'Pogg. Ann.,' vol. 96, p. 110 (1855).

‡ 'Min. Mag.' (Aug., 1885).

§ 'Comptes Rendus,' vol. 177, pp. 1123–1125 (1923).

diamond. Bragg\* in 1914 made a measurement of the spacing of the cleavage planes, finding it to be 3.42 A.U., while Ewald,† in the same year, took a Laue photograph of a crystal, perpendicular to the axis, confirming its hexagonal symmetry. The fuller interpretation of its structure was attempted by Hull‡ and by Debye and Scherrer§ in 1917 by the powder method. Both were able to assign a structure to the element, but these structures have different lattices and belong to different crystal systems. An examination of the original papers shows that the observations of neither investigator are in very good agreement with the structure they propose, and the observations only show the roughest agreement with each other. This is especially marked in the matter of intensities. On the whole, Hull's results are more plausible, because he separated the  $K_\alpha$  and  $K_\beta$  lines of Mo by screening, whereas Debye and Scherrer often mistook  $\alpha$  for  $\beta$  lines, as will be shown subsequently. Since then Backhurst|| has made some measurements on graphite, from the point of view of its expansion and the effect of temperature on the reflection intensities.

It seemed to me that the essence of the problem lay in determining the orientation of the planes giving rise to the spacings observed in the powder photographs. For this a single crystal was necessary. I had the good fortune to secure from Prof. Gordon, of King's College, a specimen of Ceylon graphite, from which, by careful dissection and picking out, I obtained a few crystalline fragments which, though very far from perfect, were sufficiently so for my purpose.

The method of analysis employed was that of the rotating crystal with a concentric cylindrical film. The actual apparatus is shown in the diagram, fig. 1. The rays from the X-ray tube (of the Shearer¶ type, with copper anticathode) passed through the brass tube A, through the two diaphragms B B', which were either holes or slits, and fell upon the rotating crystal C. The crystal was mounted on a goniometrical holder, such as that described by Bragg.\*\* The diffracted rays fall upon the film, which is placed on the inside of the small cylindrical brass camera, D. A small camera, radius 2.25 cm., was used, because the imperfections of the crystals prevented any very sharp

\* 'X-Rays and Crystal Structure,' 4th Ed., p. 131.

† 'Sitzungsberichte, Münch.' (1914).

‡ 'Physical Review,' vol. 10, p. 661 (1917).

§ 'Physikalische Zeitschrift,' vol. 18, p. 291 (1917).

|| 'Roy. Soc. Proc.,' A, vol. 102 (1922).

¶ 'X-Rays and Crystal Structure,' 4th Ed., p. 33.

\*\* 'X-Rays and Crystal Structure,' 4th Ed., p. 20.

reflections, and a larger camera would have decreased the intensity without adding to the accuracy.

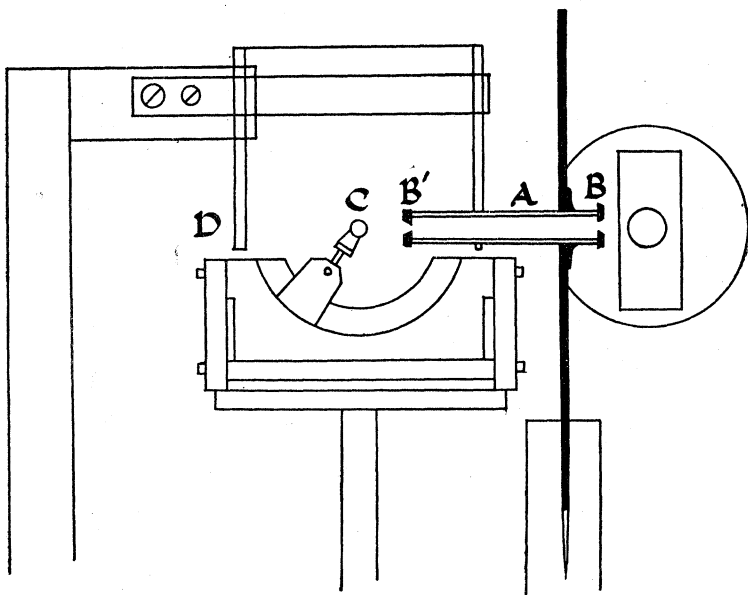


FIG. 1.

*Theory.*

The theory of the method is much simplified by the use of polar coordinates  $r, \chi, \phi$  (see fig. 2) ( $\chi$  is measured from the equator and takes the place of  $\theta$ , as the latter is reserved for the glancing angle). Take the axis of rotation of the crystal as the axis  $\chi = \pi/2$ . The incident beam, supposed perpendicular to it, as  $\chi = 0, \phi = 0$ . Let the incident ray of wave-length  $\lambda$  impinge upon a crystal plane of spacing  $d$ , the normal to which makes an angle  $\alpha$  with the axis of rotation. In general, at some point of its revolution, this plane will come into position where it reflects the incident beam. Its normal then makes with the incident beam an angle  $\pi/2 + \theta$ , where  $\theta$  is given by the familiar formula  $\sin \theta = \lambda/2d$ .

The reflected beam makes an angle  $2\theta$  with the incident beam and its  $\chi \phi$  co-ordinates are given by the two formulæ

$$\cos \chi \cos \phi = \cos 2\theta, \quad \sin \chi = 2 \sin \theta \cos \alpha.$$

From these equations it can be seen that if  $\chi$  and  $\phi$  are one solution corresponding to fixed values of  $\theta$  and  $\alpha$ , so are  $\chi$  and  $-\phi$ ; and as the plane  $\alpha$  is indistinguishable from that  $\pi - \alpha$ . The values  $-\chi, \phi$  and  $-\chi, -\phi$ , also

satisfy the equation. The reflecting position is, in general, reached in four positions of the plane giving four reflected directions, symmetrically distributed about the equator and the plane containing the incident ray and the axis.

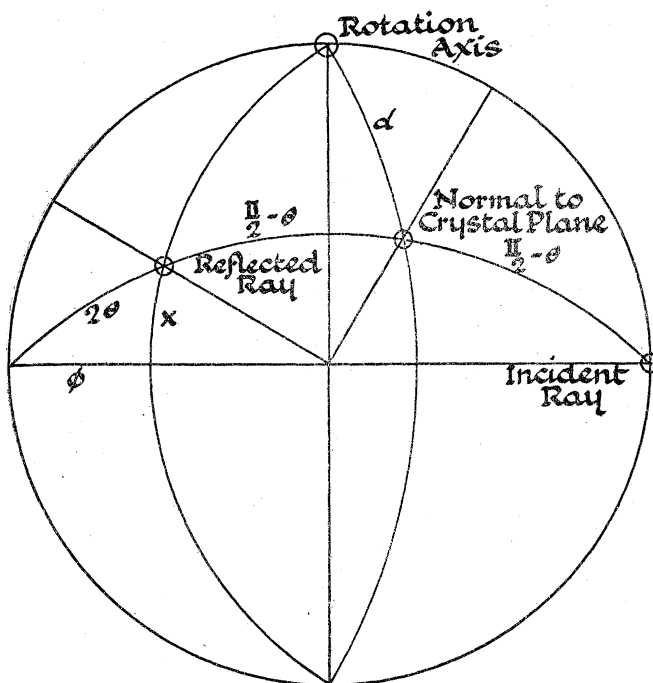


FIG. 2.

butted about the equator and the plane containing the incident ray and the axis. If  $\sin \theta \cos \alpha > \frac{1}{2}$  there is no real value  $\chi, \phi$  that can satisfy the equations. No reflection is therefore possible. This occurs for small spacings and planes nearly perpendicular to the axis of rotation. If  $\alpha = 0$ , *i.e.*, the plane is parallel to the axis,  $\chi = 0$ . There are only two reflections, both in the equatorial plane.

Now consider a cylindrical film of radius  $a$ . The reflected ray meets it at the point  $a/\sin \chi, \chi, \phi$ . If the cylinder is flattened out the  $xy$  co-ordinates of this point referred to axes in, and perpendicular to, the equator are  $x = a \phi, y = a \tan \chi$ . That is, by measuring the co-ordinates of the spots on the film we can obtain  $\chi$  and  $\phi$  and thence  $\theta$  and  $\alpha$ .

These calculations are, however, rather laborious, and the procedure can be simplified by a graphical method. Actually  $x$  and  $y$  were calculated for a cylinder of 10 cms. radius, and for every five degrees in the values of  $\theta$  and  $\alpha$ . These were plotted and the curves  $\theta = \text{const}$  and  $\alpha = \text{const}$  drawn for every

five degrees. The first set are, of course, the familiar Debye curves; the second resemble lemniscates in form. (See fig. 3.) The films were projected on to this chart with suitable magnification, and  $\theta$  and  $\alpha$  read off directly to an accuracy of about one degree.

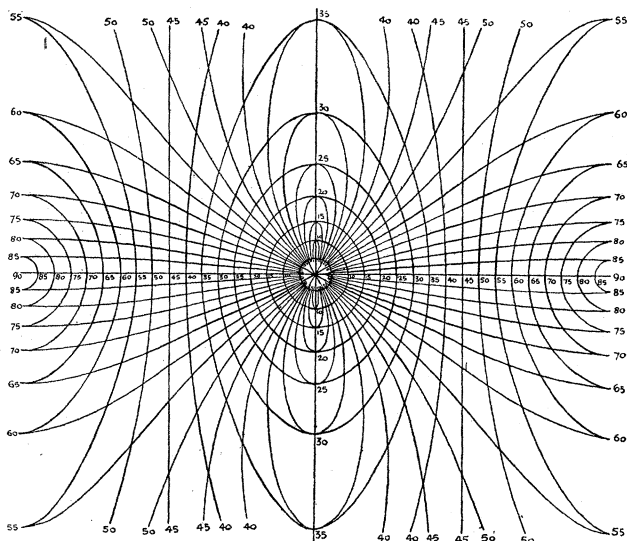


FIG. 3.

Two photographs of a crystal in different settings are theoretically sufficient to account completely for its structure, but to avoid complications these settings are so chosen that the axis of rotation coincides with some important axis of the crystal, and preferably in turn with two axes at right angles. The same planes can always be identified in the two photographs from the fact that they have the same spacing. Allowance has, however, to be made for planes belonging to the same form, and this is usually effected by the setting of the crystal, in which the spots due to such planes are made to superpose their effects. From the two values  $\alpha_1$ ,  $\alpha_2$  of the inclination of the normal of the plane to the axis, the position of the plane relative to the axes can be calculated, and from two pairs of such values the angle between the two corresponding planes in the crystal can be found. It is easier, however, and for the purpose quite accurate enough, to prepare from the measurements a stereographic projection of the crystal in the manner described below.

Let the primitive be chosen to include the two axes of rotation 1 and 2 (see fig. 4), the poles of which are at  $A_1$  and  $A_2$ . About  $A_1$  and  $A_2$  describe small circles of angular diameter  $\alpha_1$  and  $\alpha_2$ .

Where they meet is the projection of the plane. In this way the whole stereographic projection may be mapped out and from it the symmetry and

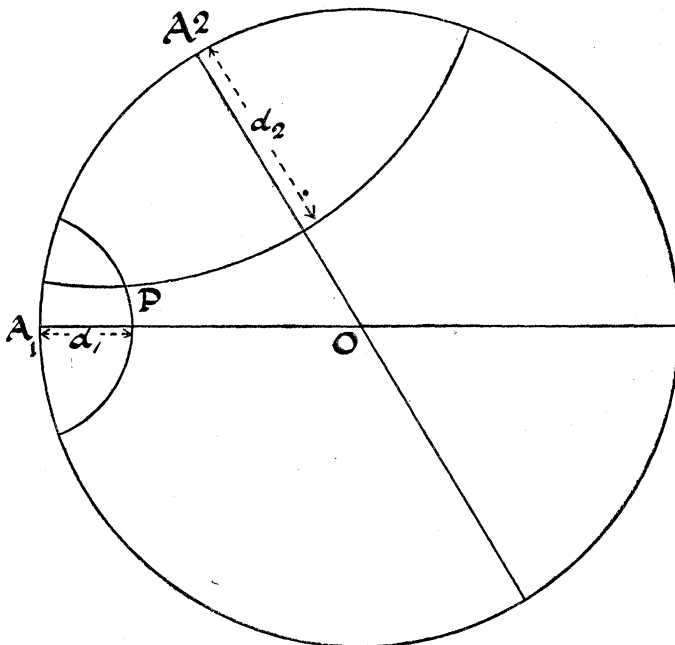


FIG. 4.

axial ratios of the crystal determined. The case is much simplified when the axes are at right angles. Here one axis may be taken as the axis of the primitive and the other to lie in it.

#### *Experimental Procedure.*

The first requirement is a single crystal, or one approximately so; that is, a crystal one of whose constituent pieces is so much greater than the others that the spots on the plate due to it can easily be separated. To secure this several crystals were mounted in turn in an arbitrary manner and photographed with relatively short exposures. Most were found to give a great number of spots due to the cleavage plane, such as photographs, and were consequently rejected. At last one was found which gave an intense single spot reflection with a much fainter halo and subsidiary spots. This crystal was used in most of the subsequent work. It will be referred to as crystal I. The crystal was a small fragment of a cleavage plane, of irregular outline and fairly thick as graphite crystals go. (See fig. 5.) It was first set with its cleavage plane

perpendicular to the axis, giving photograph No. 1. The photograph shows eleven principal planes (not counting the arc of the cleavage powder and the vertical brush due to reflections of white radiation by the cleavage plane).



Nat. Size

FIG. 5.

The values of  $\theta$  and  $\alpha_1$  for each of these are shown in Table I, together with the calculated values on the basis of the Hull lattice.

This photograph is in itself sufficient to determine the graphite lattice, on the sole assumption that it has a trigonal or hexagonal symmetry, for it shows reflections of planes at the spacings and angles demanded by the Hull lattice (see Table I), whereas, according to the Debye and Scherrer lattice, for instance, the spacing of the  $(01\bar{1}0)$  planes should have been one-third of that which appears on the plate.

The crystal was then turned through  $90^\circ$  and another photograph taken. Here the normal to the cleavage plane is in the equator, and it was seen that the planes  $\bar{1}011$ ,  $\bar{1}\bar{1}01$  and other planes in that zone gave reflections near each other, showing that the  $\bar{1}2\bar{1}0$  and  $\bar{1}\bar{1}20$  zones are nearly, but not quite, at  $30^\circ$  to the axis. The angle of mis-setting is  $8^\circ$ , but the method gives no hint of which sense this mis-setting is in; so that the next photograph, where the crystal has been turned through that amount, shows that it has only made things worse. However, in the next (No. 2) the final result is achieved, and the crystal is now set with the zone  $2\bar{1}\bar{1}0$  parallel to the axis.

This photograph shows a large number of planes, the most important being those in the equatorial zone. The definition is sufficiently good to be able to measure 11 planes in this zone, and thus to estimate their spacings to within 1 per cent., *i.e.*, nearly as accurately as Hull's measurements, and at the same time to leave no possibility of doubt in the great majority of cases as to the indices of the plane dealt with. In Table II a comparison is given between Hull's spacing and these, and the agreement is excellent. In the same table there are also given spacings recalculated from Debye and Scherrer's measurements, taking some lines given as  $\beta$  lines as  $\alpha$  lines and using a more correct value for  $\lambda$  K $_{\alpha}$  Cu. This procedure gets rid of some of the most glaring differences; but there are some lines, notably those at spacing 1.48, 1.21 and 0.92, which cannot be accounted for, either as  $\alpha$  or as  $\beta$  lines. All of these lines are marked weak and may conceivably be due to some impurity.



By turning the crystal through  $30^\circ$  the  $2\bar{1}\bar{1}n$  zone is brought into the equatorial plane. The photograph taken in this position shows these reflections, but, unfortunately, showed at the same time that the crystal was not a simple one, but consisted of two crystals having the cleavage plane in common but turned through about  $28^\circ$  with respect to each other—probably twins. There is, however, no difficulty in separating the spots due to the main crystal, and the values of  $\theta$  and  $\alpha_2$  are given in Table I.

Subsequently other photographs have been taken with crystal II (No. 3). This had the advantage of not being twinned and, as it was larger than crystal I, of showing up faint spots better. The results from these photographs are incorporated in Tables I and II.

It can be seen from the tables that of the 25 planes that can reflect copper rays only four have been unaccounted for, and all of these are planes of high indices.

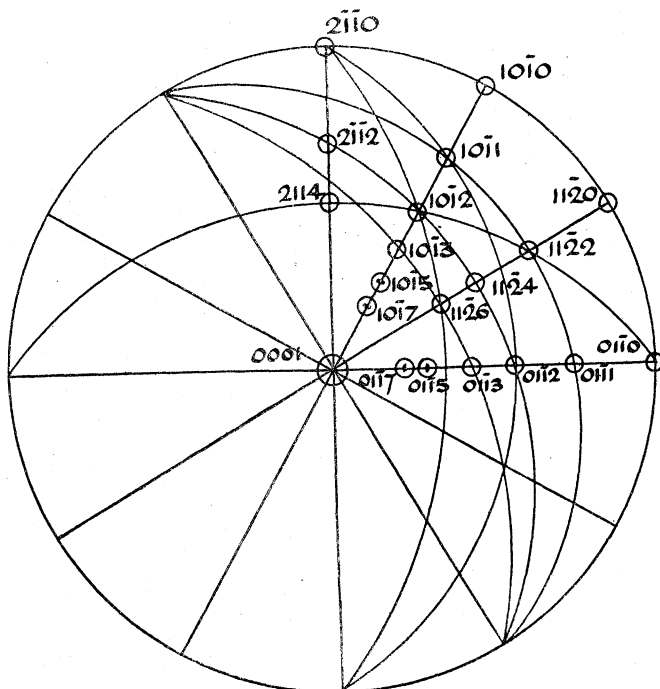


FIG. 6.

All these measurements are relative to the cleavage spacing, the four orders of whose reflections calibrate the photograph. It is difficult to obtain a direct value of the radius of the film, as it is a duplitised one, and its thickness and

that of its paper envelopes are commensurate with that of the camera itself.

The values of  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  observable on the photographs are combined to give a stereographic projection of the crystal in the manner described above. This is shown in fig. 6. It will be seen that the points lie as closely as might be expected to their calculated position.

#### *Measurements by the Ionisation Spectrometer.*

Once the crystal can be set up so that an important zone lies in the equatorial plane, the crystal holder can be removed as one piece on to the table of the ionisation spectrometer.

Mr. Astbury was kind enough to make some measurements of the crystal set up as for photographing, *i.e.* with the zone  $11\bar{1}n$  in the equatorial plane. He was able to detect three orders of the cleavage plane and also the plane  $01\bar{1}1$ , the angle between it and the cleavage plane being measured and found to be  $72^\circ 30'$  as against  $72^\circ 44'$  calculated. Mr. Wood also, using a larger and more imperfect crystal, observed three orders of the cleavage plane, giving a spacing of 3.41 A.U. These measurements will be referred to again in the discussion of the intensity questions. Subsequently Miss Yardley, using crystal II, was able to measure five orders of the cleavage plane reflections, giving a mean value of 3.41 A.U.

#### *Laue Photograph Measurements.*

Mr. Astbury has very kindly taken four Laue photographs of graphite: (i) with crystal II, No. 4; (ii) with crystal IV, which was unfortunately destroyed; (iii) with crystal V; and (iv) with the thick crystal VI. In all cases the cleavage plane is perpendicular to the beam, and the distance between plate and crystal was 2 cms. All the photographs are similar in that they show prominent spots due to the  $01\bar{1}1$  planes, and fainter ones, due to the  $2\bar{1}12$ . These spots are reduplicated on all the plates except one, on account of the twinning to be discussed in a later paper. Besides these spots there are others which from their position and appearance must be referred to distorted portions of the crystal. All the photographs show the hexagonal symmetry.

The large size of the spots, due to imperfections of the crystal, did not permit of accurate measurements. The values of the axial ratio as calculated from photographs (i), (ii), (iii) and (iv) are 2.65, 2.64, 2.63, 2.60. The value from other measurements is 2.77.

Ewald's Laue photograph of graphite taken in 1914 shows a very similar appearance, but it was obviously taken from a better crystal than any at my

disposal. He referred the crystal to different axes, but re-calculating his results gives an axial ratio of 2.79, much closer to the other values.

*Fundamental Lattice.*

All the measurements from the photographs agree with the lattice suggested by Hull, namely, a hexagonal lattice, with length of side of elementary triangle 2.4 A.U. and of height 6.8 A.U. This lattice is shown drawn to scale in fig. 7.

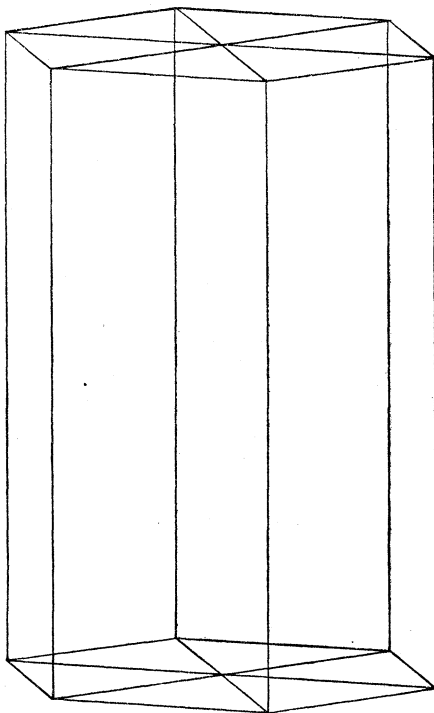


FIG. 7.

To determine the dimensions of this lattice better than could be done by the small circular camera employed, the crystal (in this case crystal II) was mounted on a Müller spectrometer, so that the  $01\bar{1}n$  zone was in the equatorial plane. Three spacings were measured,  $0002$ ,  $01\bar{1}0$ , and  $01\bar{1}1$ . The last two gave rather wide bands even with fine slits, but their spacings could be measured to an accuracy of 1 per cent., while the cleavage plane, which gave sharper reflections, could be measured to an accuracy of  $\frac{1}{2}$  per cent.

The spacings are :—	$0002$	$3.40 \pm .01$	A.U.
	$01\bar{1}0$	$2.13 \pm .02$	A.U.
	$01\bar{1}1$	$2.02 \pm .02$	A.U.

Taking account of the other values of the cleavage-plane spacing, which are all over 3.40, we may take it as 3.41. From this and the values of the other two spacings we arrive at two values for the base length of the elementary triangle, 2.46 and 2.44. We may, therefore, take as the dimensions of the cell of graphite at ordinary temperatures and pressures:—

Height .. .. .	6.82 ± .04 A.U.
Length of sides.. .. .	2.45 ± .03 A.U.
Axial ratio, c : a .. .. .	2.77

*Measurements on Artificial Graphite.*

Through the kindness of Mr. Robert Lennox, of the Lennox Foundry Company, London, I have been able to obtain crystals of artificial graphite which occur loose in pockets in the heads of certain silicon-steel castings. These crystals, while much smaller than the natural crystals employed, were large enough to give photographs by the rotation method, showing four of the most prominent graphite planes in identical positions to those of the natural graphite. A comparison photograph, in which a flake of natural graphite was mounted side by side with one of artificial graphite in a Müller spectrometer, showed that the cleavage spacings of the two forms do not differ by as much as 0.3 per cent. We may, therefore, assume that artificial and natural graphite are identical in structure.

*Position of the Atoms.*

The volume of the unit cell of graphite is

$$6.82 \times 2.45^2 \times 3/2 = 35.5 \text{ A.U.}$$

The specific gravity of graphite is 2.2. If there are N atoms of weight  $12 \times 1.66 = 20.0$  A.U. per cell; then

$$20.N = 35.5 \times 2.2 = 78. \quad N = 4.$$

There are four atoms in the unit cell. The distribution of the four atoms in the cell can only be determined on the basis of the intensities of the reflections from the various planes.

The most important plane, and the only one from which quantitative intensities have been measured, is the cleavage plane. The spacing for this plane is 3.41 A.U. half the height of the unit cell. This shows that in each cell the four atoms must have heights, 0,  $t/2$ ,  $\frac{1}{2}$ ,  $1 + t/2$ , above the basal plane of the cell (these heights refer to fractions of the actual height of the cell). If we consider only half the cell it is clear that the atoms must lie in two planes, the

basal plane and one at a so-far indeterminate height  $t$  above it. To estimate this height we have the intensities of the successive orders of reflection from the cleavage plane. The results of the various measurements are given in Table III. Those of Miss Yardley are the most complete, giving as far as the fifth order. The ionisation spectrometer measurements agree fairly closely with each other, and the photographic measurements bear them out as far as they go. In order to obtain higher orders photographically, I used both a molybdenum and a silver anti-cathode, but in neither case could any order higher than the fifth be detected.

In comparison with the observed values are shown the intensities calculated for various values of  $t$ ;  $0$ ,  $\frac{1}{9}$ ,  $\frac{1}{7}$ . The intensities are given between rather wide limits, the upper being based on the behaviour of the diamond, the lower on the theoretical decrease with  $\text{cosec}^2 \theta$ . It can be seen that none of these calculated values fit the whole of the observed values; for instance,  $t = \frac{1}{7}$  fits the observations fairly well until the fourth order, after which it gives too high values, whereas  $t = 0$  is consistently higher than the observed values. The fact that only on the latter hypothesis each order is weaker than the one before it is very strongly in its favour, and the more rapid falling-off of the intensities of the successive orders may well be accounted for by the following considerations. In fig. 8 curves plotted from Miss Yardley's results are given.

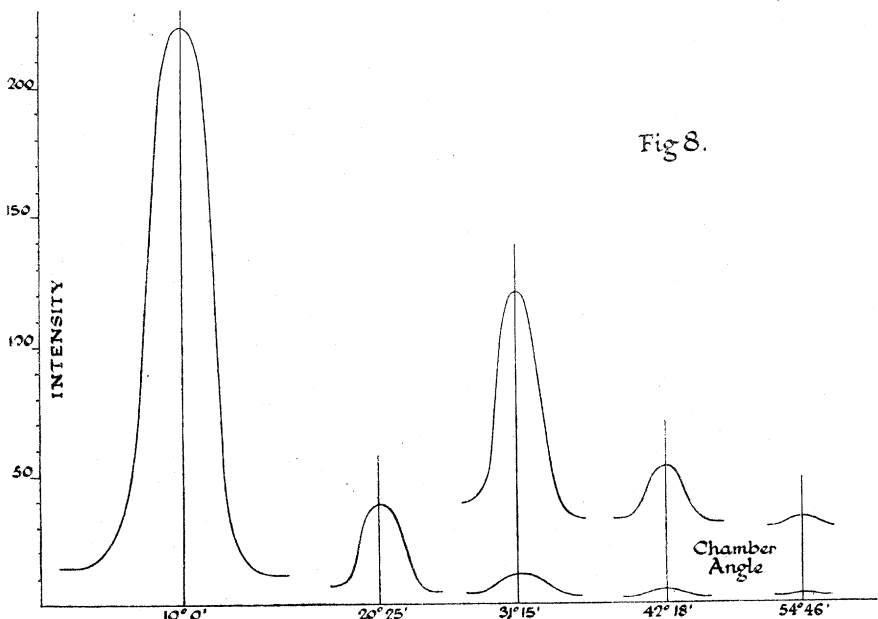


FIG. 8.

The vertical scale of the third, fourth and fifth orders is shown multiplied ten-fold, but the horizontal angular scale is the same for all, and it can be seen that the breadths of the peaks, instead of increasing with the higher orders as they would in a more perfect crystal, actually decrease. The explanation of this is that the reflections from the small crystals nearly coincident with the main crystal contribute to the large peaks of the first orders, but in the higher orders, where the peaks themselves are small, their effect is lost in the general white radiation. At the same time the imperfections of the crystal probably abolish that extinction effect which in the diamond reduces the intensities of the first orders. (Another but more speculative cause for this apparent rapid falling-off of intensity will be dealt with when we consider the positions of the electrons.) If we assume that the first of the above causes is alone operative, it can be allowed for by multiplying the heights of the peaks of the ionisation curves by the corresponding order, and taking the result as the true measure of intensity. The results taken from Miss Yardley's measurements are given in the table, and will be seen to agree much more closely than any of the others with the theoretical values.

Returning now to the interpretation of the intensities, we see that there is a fairly strong probability that all the carbon atoms lie in the basal planes of the cells, and that it is almost certain that half of them do not lie at a distance more than one-ninth of the cleavage spacing from the plane containing the other half.

Whatever the actual symmetry of graphite is, it certainly has a trigonal axis perpendicular to the cleavage plane. This ensures that all the atoms

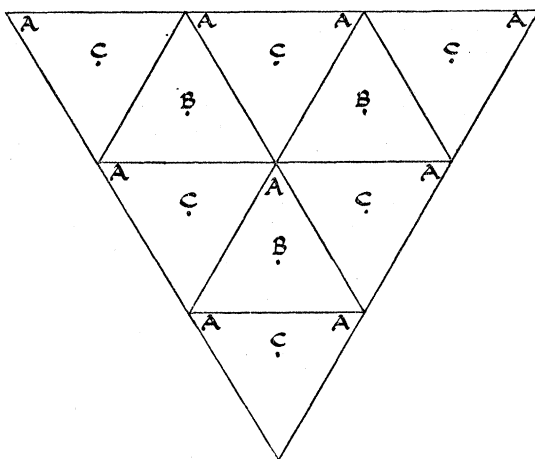


FIG. 9.

must lie either on the axes through the points of the lattice or on axes passing through the centres of the triangles of the hexagonal net (the points A, B, C in fig. 9). Any other arrangement would either not give trigonal symmetry or would lead to more than four atoms in the cell.

We may now consider the evidence of the intensities of reflection from planes of the type  $2\bar{1}\bar{1}n$ . The graphite crystal must, in conformity with what has been said above, present the appearance of fig. 10 when viewed along the

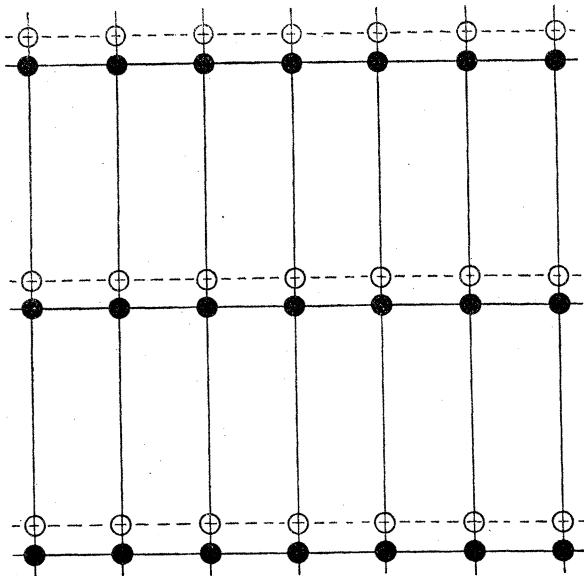


FIG. 10.

common axis of these planes. (In this figure, and in figures 11 and 12, the white circles represent the positions of atoms governed by the undetermined parameter  $t$ , drawn for values of  $t = \frac{1}{3}$  and  $t = 0$ .) It will be seen at once that the planes for which  $n$  is odd are halved. Of the planes of even indices four appear on the photographs:  $2\bar{1}\bar{1}0$ ,  $2\bar{1}\bar{1}2$ ,  $2\bar{1}\bar{1}4$ , and  $2\bar{1}\bar{1}6$ ; the others are beyond the range of copper rays. All these planes give strong reflections. Debye and Scherrer also mark them all as strong; Hull, however, gives the intensities as 35, 50, 15, 2. A plausible explanation for this disagreement is given by the following considerations, to which sufficient notice has not always been given. In the classical expression for intensity

$$\frac{N^2 \lambda^3}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} e^{-B \sin 2\theta} F^2 \frac{e^4}{m^2 c^4} \delta V$$

the term  $\frac{1}{\sin 2\theta}$  is not generally taken into account, and quite rightly, since

it only makes a small difference in the result if the glancing angles are small, that is, if hard rays are used. But Debye and Scherrer used copper rays and a camera of a circular kind, in which the values of  $\theta$  approached 180, which vastly increased the intensity of the reflected beam in these cases. This effect is very noticeable on Debye photographs of nearly all substances; the circle surrounding the opposite point of entry of the X-ray beam being nearly as intense as those surrounding the central spot. The effect is also noticeable in my photographs, notwithstanding the fact that the spots are very much spread out, owing to the large geometrical dispersion and distortion in this part of the field.

To avoid the difficulties these considerations entail it is best to compare only the intensities of points in the same part of the field. Judged in this way the  $2\bar{1}\bar{1}n$  planes still give strong reflections, or at any rate there is no marked falling off. Theoretically the intensities of these planes should be affected in the ratio of  $1 : 1 + \cos 2\pi t : 1 + \cos 4\pi t : 1 + \cos 6\pi t$ .

If  $t = \frac{1}{3}$  this would be  $1.0 : 1.76 : 1.17 : 0.5$ , and  $2\bar{1}\bar{1}6$  would only be one-third as strong as  $2\bar{1}\bar{1}2$ , which would be quite sufficient to show photographically. *A fortiori*, if  $t = \frac{1}{7}$ , as Hull's model makes it, the effect would be unmistakably present. It is only on the assumption that  $t = 0$  that  $2\bar{1}\bar{1}2$ ,  $2\bar{1}\bar{1}4$ ,  $2\bar{1}\bar{1}6$  would all give the same intensity. Thus the evidence from the  $2\bar{1}\bar{1}n$  planes corroborates that obtained from the cleavage plane.

We have shown that the four carbon atoms can only lie on three axes in the cell (the axes marked A, B, C in fig. 9), and that their heights above the base of the cell are  $0, t/2, \frac{1}{2}, \frac{1}{2}(1+t)$ . If we place the first atom on the axis A and at height 0, we have to find how to place the remaining three atoms. Consider the atom at height  $t/2$ , it might be placed on axis A or on axis B or C. There is a good reason why it should not lie on A. The distance between the first two atoms would then be less than  $1/9$  of  $3.41, 0.38$  A.U.;  $\frac{1}{4}$  of the diameter of the carbon atom and much smaller than the diameter of any atom. We must therefore place the second atom on the axis through B or C, which of the two is immaterial.

The third atom, height  $\frac{1}{2}$ , may now be placed on A, B or C—there is nothing so far to say which—and the fourth, height  $\frac{1}{2}(1+t)$ , on any axis on which the third is not placed. If the third atom is placed on A the fourth can only be placed on C; to place it on B would be to repeat the arrangement of the first two atoms and thus halve the height of the lattice. If the third atom is placed on B the fourth can only be placed on A, because the fourth atom must be related to the first of the cell above, as the second atom is to the third,



otherwise the perfect halving of the basal plane could not be maintained; to place the third atom on B and the fourth on C would upset this relation. Similarly, if the third atom is placed on C the fourth must be on B; but this arrangement is essentially the same as the one first mentioned, with B in the place of A, so we are left with only two possible structures, shown in figs. 11, 12.

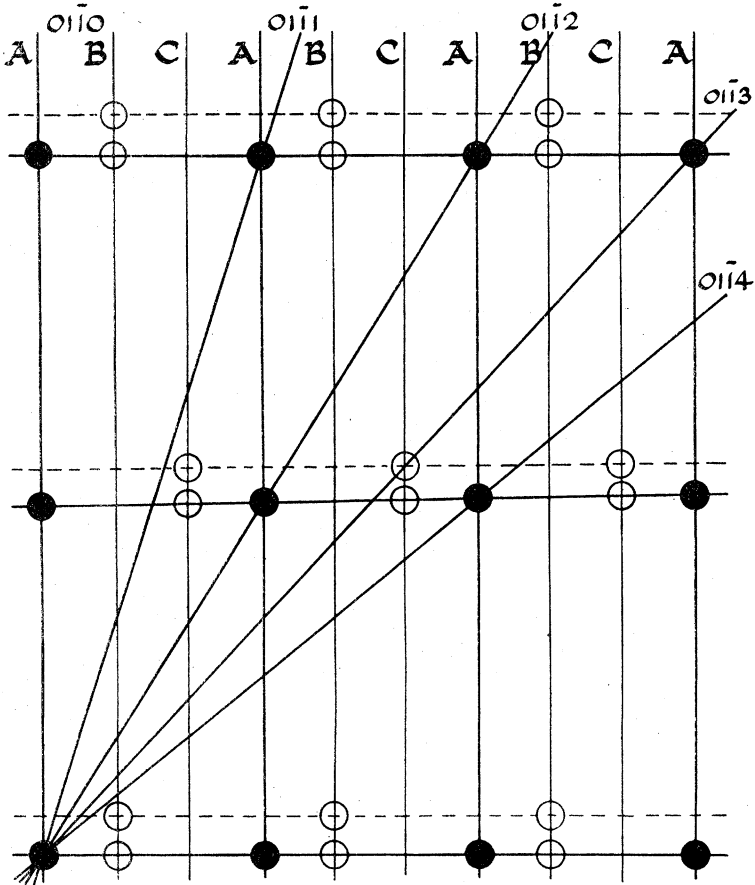


FIG. 11.

To distinguish between them we have the intensities of the planes of the type  $011n$ . The appearance of the two structures (which we will call structures I and II), viewed along their common axis, is shown in figs. 11 and 12. As can be seen, the structure II would degenerate into one with half the lattice height if  $t = 0$ , but this we are not yet justified in assuming. If we calculate

the ratios in which the reflection intensities of various planes of the type  $01\bar{1}n$  would be affected by interleaving in each of the structures we get :—

		For Structure I.	For Structure II.
When $n$ is odd	.. ..	$\frac{3}{16}$	$\frac{3}{4} \sin^2 \frac{1}{2} (n\pi)$
When $n$ is even	.. ..	$\frac{1}{16} + \frac{1}{2} \sin^2 \frac{1}{2} (n\pi)$	$\frac{1}{4} \cos^2 \frac{1}{2} (n\pi)$

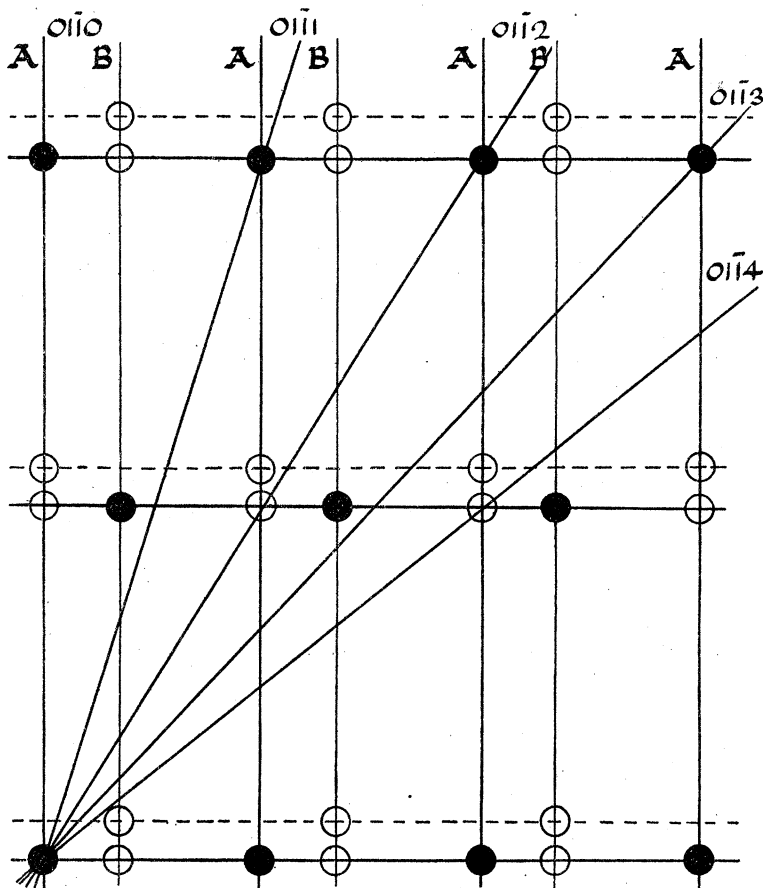


FIG. 12.

Now  $t \gtrsim 1/9$ , so that the reflections from such planes as  $01\bar{1}1$ ,  $01\bar{1}3$ , should according to model LI be very small, much less than those of  $01\bar{1}0$  and  $01\bar{1}2$ . The observed intensities show unequivocally that the reverse is the case.  $01\bar{1}1$  gives a very strong reflection indeed, the next after the cleavage plane in fact;  $01\bar{1}3$  is also strong; while both  $01\bar{1}0$  and  $01\bar{1}2$  are distinctly weak. Structure II must, consequently, be rejected without further consideration.

According to model I, on the other hand, all planes such as  $01\bar{1}1$ ,  $01\bar{1}3$ ,  $01\bar{1}5$ ,

0117, should be equally affected by interleaving; this is borne out by the photographs, which show no marked difference in intensities. On the other hand, the reflections from the 0112 $n$  planes should, except when  $t = 0$ , increase in intensity with  $n$  in a rapid manner. The photographs do not show such an increase and the intensities are less than those from the 011(2 $n + 1$ ) set. This enables us to fix an upper limit for  $t$ . The reflection from the 0117 plane is certainly stronger than that from 0116 (it is probably more than twice as strong). From this we have the inequality:—

$$\begin{aligned} \frac{3}{16} &> \frac{1}{16} + \frac{1}{2} \sin^2 3\pi t : \\ \sin^2 3\pi t &< \frac{1}{4} \\ |\sin 3\pi t| &< \frac{1}{2} \\ 3\pi t &< \pi/6 \\ t &< \frac{1}{18}. \end{aligned}$$

This limitation of  $t$  is much more rigid than the two previously employed. The comparison between the reflections of the odd and the even planes avoids all the allowances for the angle of reflection, the absorption, or any of the general factors which affect intensity.

It may be seen that none of the results, except that from the ionisation spectrometer, suggest that  $t \neq 0$ ; and this method, without the allowances suggested, would equally disagree with any other value of  $t < \frac{1}{18}$ . 0 is a much more probable value than any fraction  $< \frac{1}{18}$ , particularly for reasons of symmetry, and we may therefore adopt it without much fear of error.

In this way the structure of graphite has been completely determined. The model arrived at is shown in fig. 13. It may be described as follows:—

The atoms of carbon in graphite lie in planes in which they form nets of hexagons. These nets are in successive planes, superposed so that half the atoms in one net lie normally above half the atoms of the net beneath, while the other half lie normally above the centres of the hexagons of this net. Alternate nets lie atom for atom normally above each other. The symmetry of graphite is hexagonal holohedral, belonging to the space group  $D_{6h}^3$ . It will be seen that this model, while it accepts Hull's lattice, has the carbon atoms arranged in plane nets, as in the model of Debye and Scherrer, so that it agrees and disagrees with both equally.

The model put forward, though fairly well established by X-ray data, is open to objections on physico-chemical grounds. The first and most obvious of these is that the atoms are actually closer together in the hexagonal nets of graphite than they are in diamond, their centres being 1.42 instead of 1.53 A.U.

apart. This should not be surprising, as in the absence of other carbon atoms in the immediate vicinity the atoms in the rings might be considered to draw

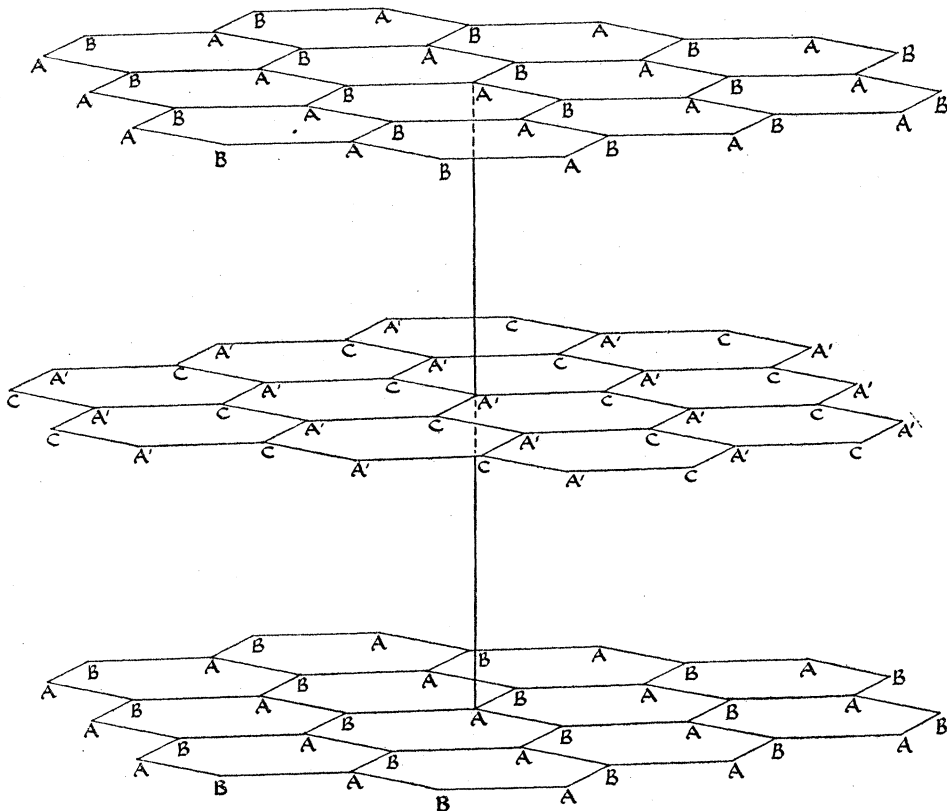


FIG. 13.

closer together than they do in diamond. The great difference between the mechanical properties of graphite and diamond (hardness, flexibility, etc.) is due to the fact that the atoms are linked closely in a two-dimensional net in the former and in a three-dimensional lattice in the latter, and, in fact, graphite exhibits in the plane of the cleavage sheets considerable hardness and tenacity.

Another objection is that the carbon atom in the structure proposed would lose that tetrahedral symmetry so well exhibited in diamond and in organic substances. This is inevitable in any explanation of graphite structure. The relatively large gap between the carbon atoms in successive cleavage planes can only be explained by some virtual extension of the carbon atom along one axis, thus destroying its tetrahedral symmetry.

The third objection is one which was urged against Hull's structure and which

applies in a lesser degree to the one proposed. It is that it makes the carbon atoms fall into two classes. It can be seen from fig. 13 that the carbon atoms at A and A' are geometrically differently placed than those at B and C. This is undeniably displeasing to our sense of the homogeneity of elementary substances. However, this difference is not very great. In fig. 14 we see

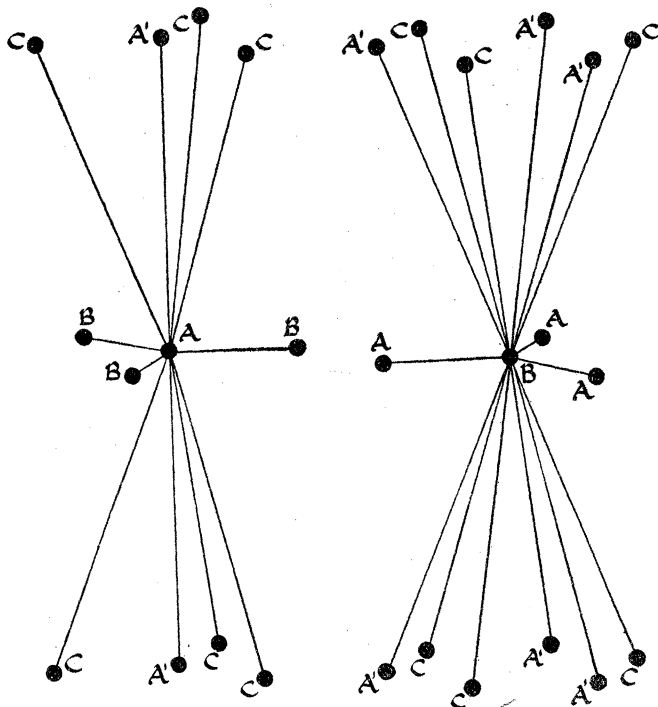


FIG. 14.

the arrangement of the neighbours of a carbon atom in an A and B position ; in both cases the immediate neighbours are three atoms in the equatorial plane at a distance of 1.42 A.U. The next nearest are, in the case of an A atom, two atoms on the vertical axis at a distance of 3.41, and six symmetrically distributed about it at a distance of 3.70 A.U. In the case of a B atom there are 12 at a distance of 3.70 A.U. It is probable that an atom loses most of its directive attraction at distances as large as 3.4 A.U., and the resultant non-directive forces must be very much the same in both cases, so that it must be nearly an indifferent matter whether a carbon atom takes an A or B position. This is borne out by the twinning and glide planes of graphite, in which interchanges of A and B positions take place.

The proposed structure fits in well with the later ideas of Bohr on the

structure of the carbon atom. Instead of the four L electrons being distributed in  $2_1$  orbits whose planes intersect at the tetrahedral angle, he now postulates as the more stable form an atom with only three  $2_1$  orbits and one  $2_2$  orbit. This form would possess trigonal symmetry only. Such atoms would fit very naturally together in the graphite nets, giving the appearance of fig. 15,

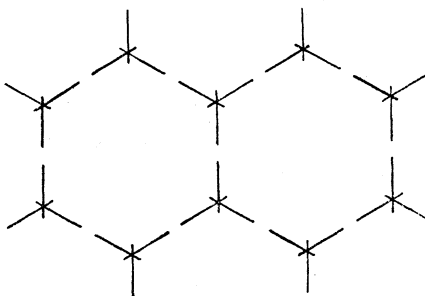


FIG. 15.

the orbits being seen edgeways. The fourth L orbit is not shown, it being doubtful in what form it would persist in the solid, but the existence of such a loosely bound electron would explain at once the relatively large distance between successive planes of atoms and would help to account for the rapid falling-off of the intensities of the orders of reflection from this plane. It would also explain the metallic properties of graphite, such as its thermal and electrical conductivities and its very high absorption of light. A test for this hypothesis would be a determination of the resistances of graphite crystals in different directions: it would be expected that the resistance would be much greater across the cleavage layers than along them. It is hoped that experiments at the Cryogenic Laboratory at Leyden may clear up this point.

Diamond may be considered to consist of atoms with four  $2_1$  orbits, and this would explain both its higher symmetry and its non-metallic qualities. The orbits in diamond would thus suffer more mutual screening action than those of graphite, and might consequently be expected to be larger; this would explain the closer packing of the graphite nets. The existence of two forms of carbon atom in diamond and graphite, analogous to the two forms of helium, may tend to explain the extreme difficulty of converting graphite (obviously the more stable form) into diamond, in a way that no mere difference of arrangement of similar atoms could do.

The chemical bearings of the structure of graphite are still obscure; strictly speaking, its elucidation throws no new light on the vexed question of the plane or puckered benzene ring. Before turning carbon in any form into

any organic substance in any ordinary way, such high temperatures are used that the structure is completely broken up, and we have no more reason for assuming that the flat ring of graphite should persist rather than the puckered one of diamond.

There remains, however, one avenue along which the transition is more gradual. Gaubert,\* in his investigations of the optical properties of graphite, observed its change into graphitic acid under the microscope, and remarked that the crystals of the latter retained the orientation of the original graphite crystals. It is hoped in the future, by X-ray investigation of the transformation graphite—graphitic acid—mellitic acid, to relate the structure of graphite to that of the benzene ring.

*Acknowledgments.*

The author wishes to express his indebtedness to Sir William Bragg for his suggestions and the use of some of his unpublished papers; to the workers of the Davy Faraday Laboratory who materially assisted the course of the research; and to the Master and Fellows of Emmanuel College, Cambridge, whose financial help made the work possible.

*Summary.*

The structure of graphite has been examined by the method of the rotating single crystal. Sufficient evidence has been found to establish the lattice proposed by Hull rather than that proposed by Debye and Scherrer. This is confirmed by measurements by the ionisation spectrometer and from Laue photographs. The structure has also been completely determined. It is essentially that of Hull, but with all the carbon atoms lying in the cleavage plane, as in the Debye and Scherrer model.

Table I.

Indices of Plane.	1			2			3			$\theta$ (cal.)
	Rotation Axis 0001.			Rotation Axis 2110.			Rotation Axis 0110.			
	$\theta$ (obs.)	$\alpha_1$ (obs.)	$\alpha_1$ (cal.)	$\theta$ (obs.)	$\alpha_2$ (obs.)	$\alpha_2$ (cal.)	$\theta$ (obs.)	$\alpha_3$ (obs.)	$\alpha_3$ (cal.)	
0002	° ' "	° ' "	° 0 ' "	13 0	90 0	90 0	13 0	90 0	90 0	13 3
0004			0	27 0	90 0	90 0	27 10	90 0	90 0	26 55
0006			0	43 0	90 0	90 0	43 15	90 0	90 0	42 40
0008			0	63 0	90 0	90 0	65 30	90 0	90 0	64 40
0110				21 0	90 0	90 0			0	
1010	21 0	90 0	90 0	21 30	29 30	30 0	21 30	59 0	60 0	21 20
1100										

\* *Loc. cit.*, p. 1.

Table I—continued.

Indices of Plane.	1			2			3			$\theta$ (cal.)
	Rotation Axis 0001.			Rotation Axis 2110.			Rotation Axis 0110.			
	$\theta$ (obs.)	$\alpha_1$ (obs.)	$\alpha_1$ (cal.)	$\theta$ (obs.)	$\alpha_2$ (obs.)	$\alpha_2$ (cal.)	$\theta$ (obs.)	$\alpha_3$ (obs.)	$\alpha_3$ (cal.)	
0111 0111 1011 1011 1101 1101	22 25	73 30	72 44	22° 40' 22 15	90° 0' 34 0	90° 0' 34 12	22 0	62 30	17 16 61 28	22 20
0112 0112 1012 1012 1102 1102	25 15	59 0	58 8	— 25 5	— 40 10	90 0 42 36	25 0	34 0 66 0	31 52 64 50	25 30
0113 0113 1013 1013 1103 1103	30 0	48 30	47 0	29 40 29 45	90 0 48 0	90 0 50 36	30 0 29 0	45 0 70 20	43 0 68 30	29 36
0114 0114 1014 1014 1104 1104				— —	— —	90 0 57 3	— —	— —	51 12 71 42	36 0
0115 0115 1015 1015 1105 1105				41 0 42 0	90 0 61 0	90 0 62 0	42 0 41 30	59 0 76 0	58 15 74 16	42 6
0116 0116 1016 1016 1106 1106				50 0 50 30	90 0 66 0	90 0 66 22	— —	— —	61 48 76 18	50 6
0117 0117 1017 1017 1107 1107				60 15 60 0	90 0 68 30	90 0 68 45	61 0 58 0	67 0 79 0	65 19 77 54	60 36
0118 0118 1018 1018 1108 1108				76 0 —	90 0 —	90 0 71 6	— —	— —	68 6 79 12	77 0
0220	—	—	90 0	—	—	90 0	—	—	—	46 50
0221 0221	46	82 30	81 12	—	—	90 0	—	—	—	47 50
0222 0222	—	—	72 44	50 0	90 0	90 0	—	—	—	49 50
0223 0223	52 30	64 30	65 0	52 35	90 0	90 0	—	—	—	53 30
0224 0224			58 8	—	—	90 0	—	—	—	59 0
0225 0225			52 15	64 30	90 0	90 0	—	—	—	67 0
2110 1210 1120	38 45	90 0	90 0	39 0	59 0	60 0	39 0	90 0	90 0	39 0
2112 2112 1212 1212 1122 1122	42 0	71 0	70 13	42 0	61 0	61 54	20 47 42 15	90 0	90 0	42 0
2114 2114 1214 1214 1124 1124	51 15	58 0	54 15	50 30	66 0	66 0	35 45 50 18	90 0	90 0	51 0
2116 2116 1216 1216 1126 1126				65 30	70 30	70 4	47 11 67 0	90 0	90 0	67 30
1230	72 30	90 0	90 0	—	—	—	—	—	—	74 15
1231	72 45	84 0	84 0	—	—	—	—	—	—	75 40



Table II.

Indices of Reflecting Plane.	Spacings.				Intensities.		
	Observed.	Observed by Hull.	Observed by Debye and Scherrer (recalculated).	Calculated.	Estimated.	Estimated by Hull.	Estimated by Debye and Scherrer.
Cleavage plane.	Assumed.				Ionisation spectrometer measurements.		
0002	3.41	3.37	3.36	3.41	I 100	100	St
0004	1.71	1.69	1.70	1.71	St 13	3	m
0006	1.14	....	1.13	1.14	S-m 2.5		W
0008	0.85	....	0.851	0.85	S-m 0		
Zone 011 <sub>n</sub>	Observed.				Order of intensity.		
0110	2.13	2.11	2.23	2.12	m (5)	30	VW
0111	2.00	2.03	2.06	2.03	St (1)	60	St
0112	1.79	1.81	1.76	1.80	m (6)	1	m
0113	1.55	1.56	1.66	1.55	St (2)	2	m
			1.48 $\beta$				S-m
0114	1.35	....	1.31?	1.33	VW (7)		VW
0115	1.15	....	1.21	1.14	S-m (3)		VW?
0116	1.01?	0.990	1.01?	1.00	VW (7)		
		(2114)					
0117	0.888	....	0.865	0.88	S-m (3)		VW
0118	0.794?	....	0.79?	0.79	VW? (9)		
Zone 022 <sub>n</sub>							
0220	—			1.06	....		
0221	1.06	1.05	1.06	1.04	W	3	
0222	1.00?	0.990?		1.00	VW?		
0223	0.95	....	0.96	0.96	W		
			0.92?				
0224	—	....		0.89	....		
0225	0.84?	....		0.84	W?		
Zone 2112 <sub>n</sub>							
2110	1.23	1.227	1.25	1.23	S-m (4)	35	St
2112	1.16	1.155	1.18	1.15	St (1)	50	St
2114	1.00	0.990	1.01	0.99	St (2)	15 pt	St
		(0116)					
2116	0.837	0.827	0.838	0.83	St (2)	2	St
Zone 123 <sub>n</sub>							
1230	0.80	0.800		0.80	S-m	} 5	
1231	0.79	0.800	0.79?	0.80	S-m		

Table III.—Cleavage Plane Reflections.

1st Order.	2nd Order.	3rd Order.	4th Order.	5th Order.	6th Order.	Observed by
100	3	0	—	—	—	Hull (photo-metric).
100	16	6	0	—	—	Debye and Scherrer.
100	13·5	2·4	0	—	—	Astbury.
100	12·5	2·1	0	—	—	Wood.
100	12·4	2·0	0·4	0·08	0	Yardley.
100	33	12	4·4	1·5	—	Yardley (corrected).
Calculated.						
100	40 → 25	25 → 11	15 → 6	→ 4	→ 3	No interleaving $t = 0$ .
100	26 → 16	7 → 3	0·5 → 0·2	→ 0·13	→ 0·8	Interleaving $t = \frac{1}{5}$ .
100	19 → 12	1·6 → 0·7	1·0 → 0·4	→ 2·0	→ 2·8	Interleaving $t = \frac{1}{7}$ .

The Constants of the Rydberg-Ritz Equation.

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If the terms of the hydrogen spectrum to which certain quantum numbers have been assigned are compared with corresponding terms in the spectra of other elements, the latter will be found to be greater. While all writers agree that this is due to the presence of other orbital electrons, the structural reasons for this discrepancy are still a matter about which there is considerable difference of opinion. The present paper is an effort to consider this subject from a slightly new point of view.

We may call such spectra hydrogen-like as arise from the radiation of the valence electron when it is alone in the outer shell. The alkali metals have such spectra normally and other elements give it in higher states of ionization. In all the cases to be considered, the valence electron moves about an atomic