In conclusion I should like to express my indebtedness to Prof. Pope for his sympathetic interest and generous assistance. Dr. Hutchinson, with the greatest kindness, has overcome the only experimental difficulties connected with this subject by supplying the necessary crystal sections; but for his help it would have been impossible to obtain the very large number of photographs used in the investigation. These photographs were obtained at the Cavendish Laboratory, and I wish to thank Prof. Sir J. J. Thomson for his kind interest in the experiments. The measurements with the X-ray spectroscope were, as already stated, made by my father in the laboratory of the University of Leeds.

The Structure of the Diamond.

By W. H. BRAGG, M.A., F.R.S., Cavendish Professor of Physics in the University of Leeds, and W. L. BRAGG, B.A., Trinity College, Cambridge.

There are two distinct methods by which the X-rays may be made to help to a determination of crystal structure. The first is based on the Laue photograph and implies the reference of each spot on the photograph to its proper reflecting plane within the crystal. It then yields information as to the positions of these planes and the relative numbers of atoms which they contain. The X-rays used are the heterogeneous rays which issue from certain bulbs, for example, from the commonly used bulb which contains a platinum anticathode.

The second method is based on the fact that homogeneous X-rays of wave-length λ are reflected from a set of parallel and similar crystal planes at an angle θ (and no other angle) when the relation $n\lambda = 2d \sin \theta$ is fulfilled. Here d is the distance between the successive planes, θ is the glancing angle which the incident and reflected rays make with the planes, and n is a whole number which in practice so far ranges from one to five. In this method the X-rays used are those homogeneous beams which issue in considerable intensity from some X-ray bulbs, and are characteristic radiations of the metal of the anticathode. Platinum, for example, emits several such beams in addition to the heterogeneous radiation already mentioned. A bulb having a rhodium anticathode, which was constructed in order to obtain a radiation having about half the wave-length of the platinum characteristic

rays, has been found to give a very strong homogeneous radiation consisting of one main beam of wave-length 0.607×10^{-8} cm.,*, and a much less intense beam of wave-length 0.533×10^{-8} cm. It gives relatively little hetero-geneous radiation. Its spectrum, as given by the (100) planes of rock-salt, is shown in fig. 1. It is very convenient for the application of the second method. Bulbs having nickel, tungsten, or iridium anticathodes have not so far been found convenient; the former two because their homogeneous radiations are relatively weak, the last because it is of much the same
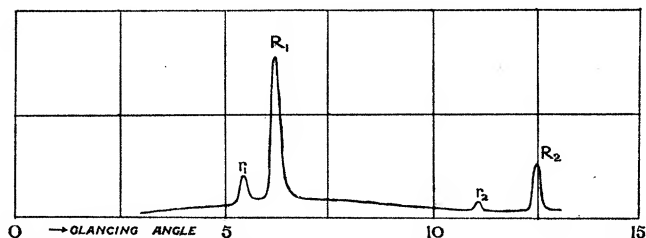

Fig. 1.—Spectra of rhodium rays : 100 planes of rock-salt.

wave-length as the heterogeneous rays which the bulb emits, while it is well to have the two sets of rays quite distinct. The platinum homogeneous rays are of lengths somewhat greater than the average wave-length of the general heterogeneous radiation; the series of homogeneous iridium rays are very like the series of platinum rays raised one octave higher. For convenience, the two methods may be called the method of the Laue photograph, or, briefly, the photographic method, and the reflection method. The former requires heterogeneous rays, the latter homogeneous. The two methods throw light upon the subject from very different points and are mutually helpful.

The present paper is confined almost entirely to an account of the application of the two methods to an analysis of the structure of the diamond.

The diamond is a crystal which attracts investigation by the two new methods, because in the first place it contains only one kind of atom, and in the second its crystallographic properties indicate a fairly simple structure. We will consider, in the first place, the evidence given by the reflection method.

The diagram of fig. 2 shows the spectrum of the rhodium rays thrown by the (111) face, the natural cleavage face of the diamond. The method of obtaining such diagrams, and their interpretation, are given in a preceding

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* This value is deduced from the positions of the spectra of the rhodium rays in the (100) planes of rock-salt on the assumption that the structure of rock-salt is as recently described (see preceding paper).

paper.* The two peaks marked R_1, r_1 constitute the first order spectrum of the rhodium rays, and the angles at which they occur are of importance in what follows. It is also a material point that there is no second order spectrum. The third is shown at R_3, r_3; the strong line of the fourth order is at R_4, and of the fifth at R_5.

The first deduction to be made is to be derived from the quantitative measurements of the angle of reflection. The sines of the glancing angles
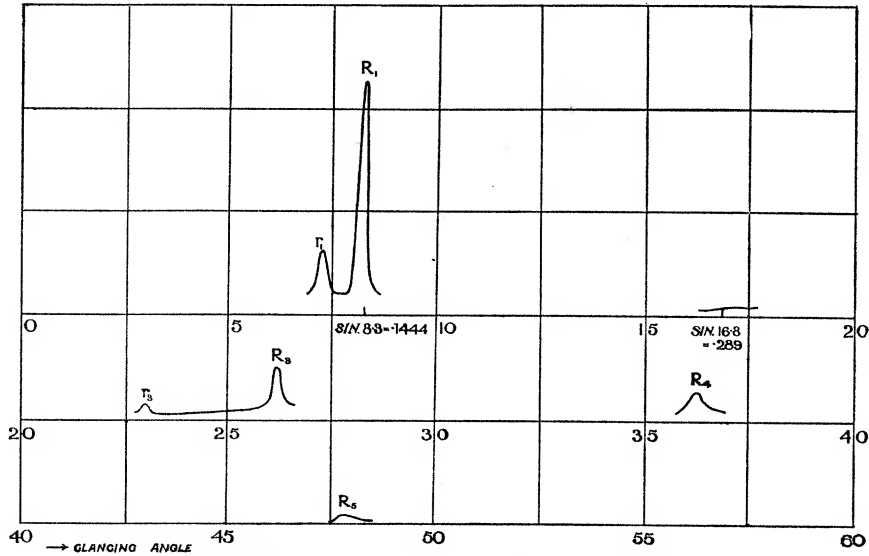

Fig. 2.—Spectra of rhodium rays: 111 planes of diamond.

for R_1, R_3, R_4, R_5 are (after very slight correction for errors of setting) 0·1456, 0·4425, 0·5941, 0·7449. Dividing these by 1, 3, 4, 5 respectively, we obtain 0·1456, 0·1475, 0·1485, 0·1490. These are not exactly equal, as they might be expected to be, but increase for the larger angles and tend to a maximum. The effect is due to reasons of geometry arising from the relatively high transparency of the diamond for X-rays, and the consequent indefiniteness of the point at which reflection takes place. The true value is the maximum to which the series tends, and may with sufficient accuracy be taken as 0·1495. In order to keep the main argument clear, the consideration of this point is omitted.

We can now find the distance between successive (111) planes.

We have

$$\lambda = 2d \sin \theta, \qquad 0\cdot607 \times 10^{-8} = 2d \times 0\cdot1495, \qquad d = 2\cdot03 \times 10^{-8}.$$

The structure of the cubic crystals which have so far been investigated by

* 'Roy. Soc. Proc.,' vol. 88, p. 428.

these methods may be considered as derived from the face-centred lattice (fig. 3): that is to say, the centres which are effective in causing the reflection of the X-rays are placed one at each corner and one in the middle of each face of the cubical element of volume. This amounts to assigning
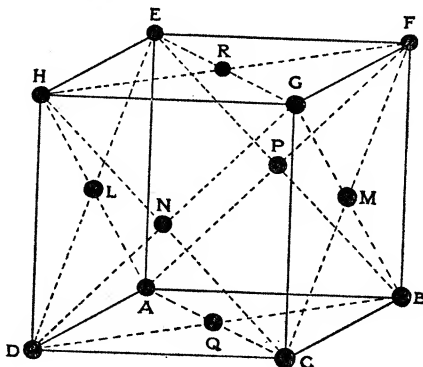

·Fig. 3.

four molecules to each such cube, for in general one atom in each molecule is so much more effective than the rest that its placing determines the structure from our point of view. There are four, because the eight atoms at the corners of the cube only count as one, each of them belonging equally to eight cubes, and the six atoms in the centres of the faces only count as three, each of them belonging equally to two cubes. The characteristics of the reflection are then as follows:—

Let ABCDEFGH be the cubical element. There are effective centres at all the corners and at L, M, N, P, Q, R, the middle points of the faces. The edge of the cube being denoted by $2a$, the reflecting planes which are parallel to a cube face, called generally the (100) planes, are spaced regularly, the distance from plane to plane being a. All the planes contain equal numbers of centres.

The (110) planes, of which the plane through ACGE is a type, are regularly spaced at a distance $a/\sqrt{2}$, and also are all equally strewn with effective centres.

The (111) planes, of which the planes through EDB, HCF are types, are regularly spaced at a distance $2a/\sqrt{3}$, and again are all similar to each other.

In what may for the present be called the normal case, any one of these sets of planes gives a series of spectra which diminish rapidly in intensity as we proceed from lower to higher orders, as, for example, the spectra of the rhodium rays given by the (100) planes of rock-salt. (Fig. 1 shows the spectra of the first two orders.)

The relative spacings of the spectra given by these three sets of planes are shown in fig. 4. Spectra of the (100) planes being supposed to occur at values of $\sin \theta$ proportional to $1, 2, 3, \ldots$, it follows from the above argument that the (110) planes will give spectra at 1·414, 2·828, 4·242, ..., and the (111) planes at 0·866, 1·732, 2·598 ....

The position of the first spectrum of the (111) planes (fig. 4) is a peculiarity of the face-centred lattice. If the effective centres were at the corners only
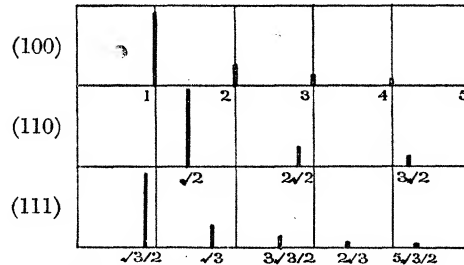

Fig. 4.—Spectra of face-centred lattice.

of a cube whose length of side was a, the spacings of the three sets of planes would be a, $a/\sqrt{2}$, and $a/\sqrt{3}$, and the three sets of spectra would occur at $1, 2, 3$; $\sqrt{2}, 2\sqrt{2}, 3\sqrt{2}$; $\sqrt{3}, 2\sqrt{3}, 3\sqrt{3}$.

The cubical crystals which we have so far examined give results which resemble the diagram of fig. 4 more or less closely. Individual cases depart so little from the type of the diagram that the face-centred lattice may be taken as the basis of their structure and the departures considered to reveal their separate divergencies from the standard. For convenience of description we will speak of the first, second, third spectra of the (100) or (111) planes and so on, with reference to fig. 4. We may then, for example, describe the peculiarity of the rock-salt (111) spectrum* by saying that the first order spectrum is weak and the second strong. The interpretation (*loc. cit.*) is that the sodium atoms are to be put at the centres of the edges of the cubic element of volume, and the chlorine atoms at the corners and in the middle of each face or *vice versâ*: for then the face-centred lattice (cube edge $2a$) is brought half way to being the simple cubic lattice (edge a) having an effective centre at every corner. The first (111) spectrum tends to disappear, the second to increase in importance. In the case of potassium chloride, the atoms are all of equal weight and the change is complete : the first order spectrum of the (111) planes disappears entirely. In zincblende or iron pyrites one atom is so much more effective than the other that the diagram of spectra is much more nearly characteristic of the face-centred

* See preceding paper.

lattice : at least so far as regards the spectra of the lower orders. We hope to deal with these cases later.

Let us now consider the case of the diamond. The spectrum given by the (111) planes is shown in some detail in fig. 2. It should be stated that the ordinates represent the gross currents observed; nothing has been subtracted for natural leak, scattered radiation, and so forth.

We first use the angular measurements to enable us to determine the number of carbon atoms in the elementary cube of side $2a$. Let us assume provisionally that there are four carbon atoms to each cube, making the face-centred lattice. The density of the diamond is 3·51, and the weight of each atom is 12 times the weight of each hydrogen atom or $12 \times 1·64 \times 10^{-24}$.

The volume of the cube is therefore

$$\frac{4 \times 12 \times 1·64 \times 10^{-24}}{3·51} = 22·4 \times 10^{-24}.$$

The length of each edge (*i.e.* $2a$) will then be

$$\sqrt[3]{(22·4 \times 10^{-24})} = 2·82 \times 10^{-8}.$$

The distance between consecutive (111) planes

$$= 2a/\sqrt{3} = 1·63 \times 10^{-8}.$$

Now we have found experimentally that the right value is $2·03 \times 10^{-8}$. These two numbers are very nearly in the ratio of $1 : \sqrt[3]{2}$. It is clear that we must put eight, not four, carbon atoms in the elementary cube ; we then obtain $2a/\sqrt{3} = 2·05 \times 10^{-8}$, and this close agreement with the experimental value suggests that we are proceeding in the right way. The value of $2a$ is $3·55 \times 10^{-8}$.

We have therefore four carbon atoms which we are to assign to the elementary cube in such a way that we do not interfere with the characteristics of the face-centred lattice.

It is here that the absence of the second order spectrum gives us help. The interpretation of this phenomenon is that in addition to the planes spaced at a distanc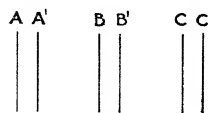e apart $2·03 \times 10^{-8}$ there are other like planes dividing the distances between the first set in the ratio $1 : 3$. In fact there must be parallel and similar planes as in fig. 5, so spaced that $AA' = A'B/3$, and so on. For if waves fall at a glancing angle θ on the system ABC, and are reflected in a second order spectrum we have $2\lambda = 2 AB \sin \theta$. The planes $A'B'C'$ reflect an exactly similar radiation which is just out of step with the first, for the difference of phase of waves reflected from A and B is 2λ, and therefore the difference of phase of waves reflected from A and A' is $\lambda/2$. Consequently the four atoms which we have

A A'   B B'   C C'

Fig. 5.

at our disposal are to make new (111) planes parallel to the old and related to them as A′B′C′ are to ABC. When we consider where they are to go we are helped by the fact that being four in number they should go to places which are to be found in the cubes in multiples of four. The simplest plan is to put them in the centres of four of the eight smaller cubes into which the main cube can be divided. We then find that this gives the right spacing because the perpendicular from each such centre on the two (111) planes which lie on either side of it are respectively $a/2\sqrt{3}$ and $\frac{1}{2}(a\sqrt{3})$, where a is the length of the side of one of the eight smaller cubes. For symmetry it is necessary to place them at four centres of smaller cubes which touch each other along edges only: *e.g.* of cubes which lie in the A, C, H and F corners of the large cube. If this is done in the same way for all cubes like the one taken as unit it may be seen on examination that we arrive at a disposition of atoms which has the following characteristics :—

(1) They are arranged similarly in parallel planes spaced alternately at distances $a/2\sqrt{3}$ and $a\sqrt{3}/2$, or in the case of the diamond $0·508 \times 10^{-8}$ and $1·522 \times 10^{-8}$ cm.: the sum of these being the distance $2·03 \times 10^{-8}$ which we have already arrived at.

(2) The density has the right value.

(3) There is no second order spectrum in the reflection from (111) planes.

It is not very easy to picture these dispositions in space. But we have come to a point where we may readjust our methods of defining the positions of the atoms as we have now placed them, and arrive at a very simple result indeed. Every carbon atom, as may be seen from fig. 5, has four neighbours at distances from it equal to $a\sqrt{3}/2 = 1·522 \times 10^{-8}$ cm., oriented with respect to it in directions which are parallel to the four diagonals of the cube. For instance, the atom at the centre of the small cube A*bcdefgh*, fig. 6, is related in this way to the four atoms which lie at corners of that cube (A, *c*, *f*, *h*), the atom at the centre of the face ABFE is related in the same way to the atoms at the centres (P, Q, R, S) of four small cubes, and so on for every other atom. We may take away all the structure of cubes and rectangular axes, and leave only a design into which no elements enter but one length and four directions equally inclined to each other. The characteristics of the design may be realised from a consideration of the accompanying photographs (figs. 7 and 8) of a model, taken from different points of view. The very simplicity of the result suggests that we have come to a right conclusion.

The appearance of the model when viewed at right angles to a cube diagonal is shown in fig. 7. The (111) planes are seen on edge, and the
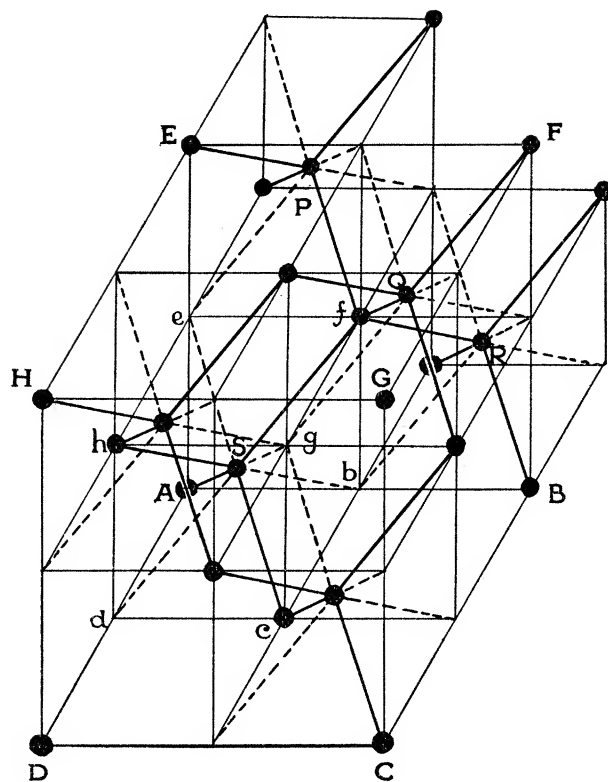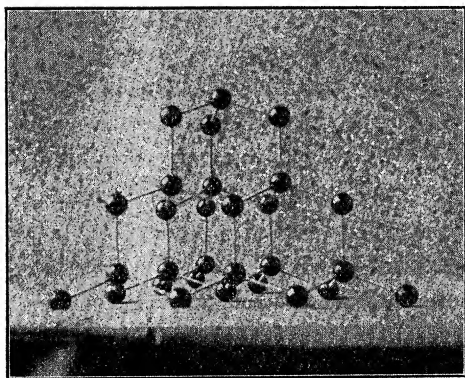
Fig. 6.

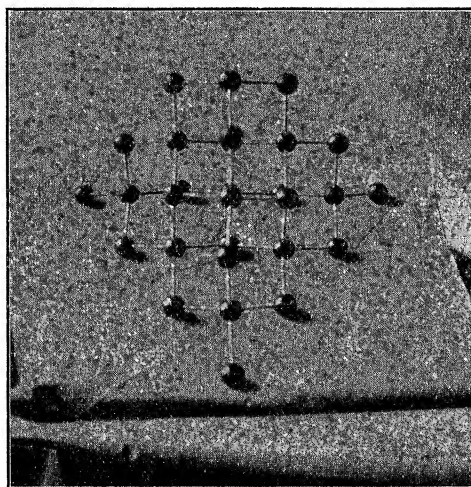Fig. 7.—View perpendicular to a (111) axis.

Fig. 8.—The (110) planes are vertical and horizontal.

1 : 3 spacing is obvious. The union of every carbon atom to four neighbours in a perfectly symmetrical way might be expected in view of the persistent tetravalency of carbon. The linking of six carbon atoms into a ring is also an obvious feature of the structure. But it would not be right to lay much stress on these facts at present, since other crystals which do not contain carbon atoms possess, apparently, a similar structure.

We may now proceed to test the result which we have reached by examining the spectra reflected by the other sets of planes. One of the diamonds which we used consisted of a slip which had cleavage planes as surfaces; its surface was about 5 mm. each way and its thickness 0·8 mm. By means of a Laue photograph, to be described later, it was possible to determine the orientation of its axes and so to mount it in the X-ray spectrometer as to give reflection from the (110) or the (100) planes as desired.

As regards the former there should be no special features, for the four carbon atoms which we placed at the centres of four of the eight smaller cubes all now lie in (110) planes. The latter are equally spaced and all alike, the space distance being $a/\sqrt{2}$ or $1·25 \times 10^{-8}$. The first glancing angle at which reflection occurs is, therefore, $\sin^{-1} \dfrac{0·607 \times 10^{-8}}{2·5 \times 10^{-8}} = 14·15°$. The experimental value was 14·35°. The spectra of higher orders occurred at 29·3° and 47·2°. The sines of these three angles are 0·2478, 0·4894, and 0·7325, or nearly as 1 : 2 : 3. Great precision was not attempted; to attain it would have been needlessly troublesome. The intensity of the different orders fell off in the usual way.

On the other hand, the (100) spectrum might be expected to show certain peculiarities. By placing four atoms at the centres of the four small cubes we have, in fact, interleaved the 100 planes, as it were: and these now consist of similar planes regularly spaced at a distance $a/2$ or $0·885 \times 10^{-8}$. The first spectrum should therefore occur at an angle $\sin^{-1} \dfrac{0·607 \times 10^{-8}}{1·77 \times 10^{-8}}$ $= \sin^{-1} 0·343 = 20·0$. Using the language already explained, we may say that the first (100) spectrum has disappeared, and, indeed, all the spectra of odd order. Spectra were actually found at 20·3° and 43·8°: the sines of these angles being 0·3469 and 0·6921, the latter being naturally much less intense than the former. A careful search in the neighbourhood of 10° showed that there was no reflection at all at that angle.

The results for all three spectra are shown diagrammatically in fig. 9, which should be compared with fig. 4.

It is instructive to compare the reflection effects of the diamond with those

of zincblende. Our results seem to show that it is built up in exactly the
same way, except that the (111) planes contain alternately zinc atoms only
and sulphur atoms only. If the zinc atoms are placed at each corner of the
cube and at the centre of each face, the sulphur atoms lie at four of the eight
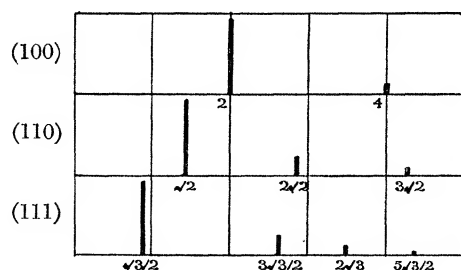centres of the smaller cubes. The (100) planes, like the (111) planes, contain

Fig. 9.—Spectra of diamond.

alternately zinc and sulphur atoms. These alternations of constitution
modify the forms of the various spectra, so that they lie between the forms
of the space-centred lattice (fig. 4) and the forms of the diamond (fig. 9).
The first (100) spectrum is not entirely absent but is much smaller than the
second, and in the same way the second (111) spectrum, though it is to be
seen, is smaller even than the third. The scheme of the zincblende spectra
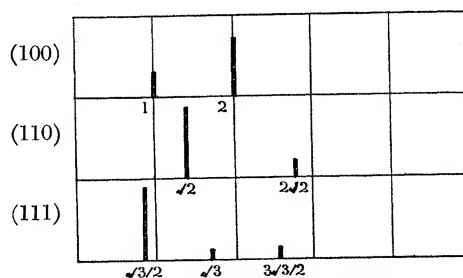is shown in fig. 10. Their actual positions agree perfectly with those which

Fig. 10.—Spectra of zincblende.

can be calculated from a knowledge of the density of the crystal, the weight
of the ZnS molecule, and the wave-lengths employed. In consequence of the
alternation of zinc and sulphur planes at unequal spacings along the (111)
axis, the crystal ceases to be symmetrical about a plane perpendicular to that
axis. It becomes hemihedral, and acquires polarity.

We now go on to consider the Laue photograph of the diamond. A
photograph taken with a section of diamond cut parallel to the cleavage
plane (111) is shown in fig. 11. The experimental arrangement was similar

to the original arrangement of Laue, the distance from diamond to photographic plate being 1·80 cm., and the time of exposure four hours. A test photograph was taken first, which made it possible to calculate the exact orientation to be given to the diamond in order that the incident X-rays might be truly parallel to a trigonal axis. The symmetry of fig. 11 shows
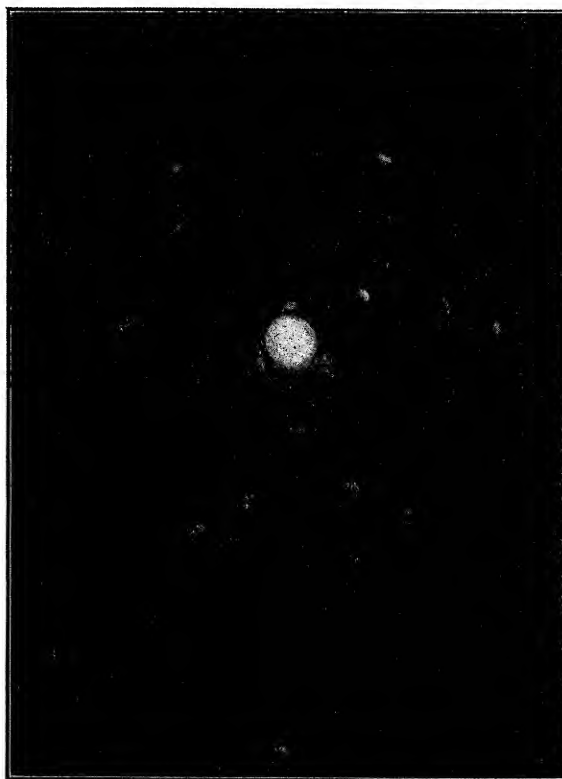

FIG. 11.

that a close approximation to this orientation has been obtained. The X-ray bulb had a platinum anticathode.

In fig. 12 is given the stereographic projection of this pattern.* The spots of the photograph are represented in the diagram by dots of corresponding magnitude, and several circles, each passing through the spots reflected by the planes of one zone, are drawn. The indices placed next the spots are the Millerian indices of the planes which reflect these spots, the planes being referred to three equal axes making 60° with each other as in the case of the examples zincblende and fluorspar given in the above paper. Imagining a

* See preceding paper.

cube with one corner at the diamond and the long diagonal of the cube parallel to the incident X-rays, the three cube edges would meet the photographic plate at the points marked X, Y, Z. The spot (110) is thus reflected in the cube face, meeting the plate along XY, (110) being the indices of a cube face referred to the axes employed.

It will now be shown that on analysis the photograph appears to be in accordance with the structure which we have assigned to the diamond on the
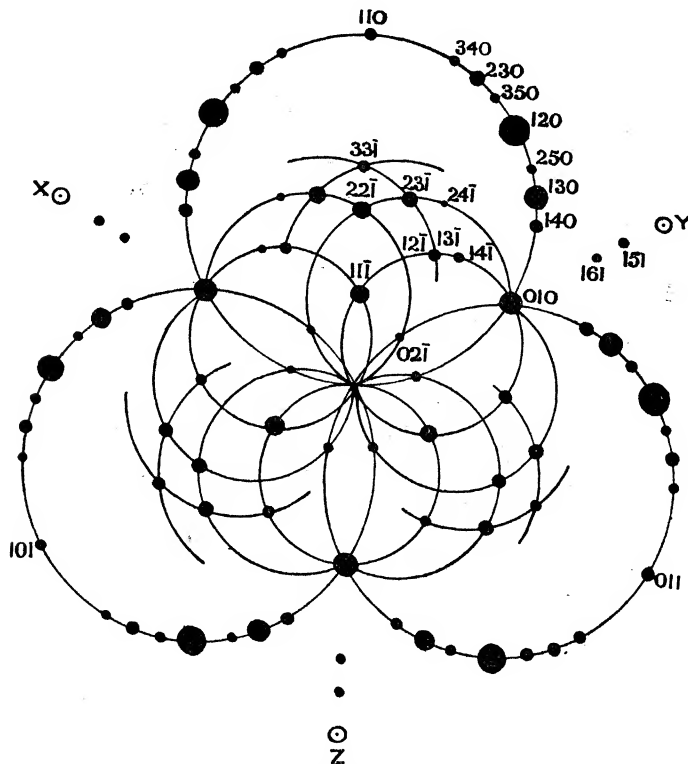

Fɪɢ. 12.

result of the reflection experiments. In the first place, of the three cubic space lattices it is evidently that which has points at cube corners and at the centres of the cube faces which is most characteristic of the diffracting system. For our purpose this space lattice is most conveniently referred to three axes which are diagonals of the cube faces meeting in a corner. The co-ordinates of any point of the system may then be written

$$pc, \qquad qc, \qquad rc,$$

where p, q, r are any integers, positive or negative, and c is half the diagonal of the square of edge $2a$.

The indices of the reflecting plane are given for each spot of the photograph, and it will be seen that they could not possibly have a more simple form. If referred to the cubic axes they become much more complex. Along the axes chosen, the interval between successive points of the lattice is the smallest possible, and these axes are very important point-rows of the system. The remarkable series of spots lying on the three circles in the diagram which culminate at the points (110), (101), (011), are due to planes which pass through these point-rows, and this alone is good evidence of the paramount importance of the cube face diagonals as axes.

It is thus clear that a simple analysis of the pattern can be made if the planes are referred to axes of the face-centred cubic lattice. It is also evident, however, that the pattern is more complex than it should be if due to a set of identical points arranged in this lattice, of which examples have been given in a former paper. For instance, there are spots reflected by the planes $(11\bar{1})$, (131), (141), and $(22\bar{1})$, $(02\bar{1})$, and yet none by the plane $(12\bar{1})$ (see diagram, fig. 12). In the case of zincblende and fluorspar no complications of this kind occur, although in these cases the presence of the lighter atoms of sulphur and fluorine must affect somewhat the diffraction pattern given by the lattice arrangement of heavy atoms of zinc and calcium. Yet here, where carbon atoms alone are present, the pattern is not as straightforward as those given by zincblende and fluorspar. We thus come to the conclusion that the carbon atoms are not arranged on a single space lattice.

If the structure assigned to diamond in the former part of this paper is correct, a simple explanation of the diffraction pattern can be arrived at. According to this structure the carbon atoms are not arranged on a space lattice, but they may be regarded as situated at the points of two inter-penetrating face-centred space lattices. These lattices are so situated in relation to each other that, calling them A and B, each point of lattice B is surrounded symmetrically by four points of lattice A, arranged tetrahedron-wise and *vice versâ.* This can be seen by reference to the diagram of fig. 6.

It is now clear why the pattern must be referred to the axes of the face-centred lattice, for if the structure is to be regarded as built up of points arranged on the simple cubic lattice, with three equal axes at right angles, no fewer than eight interpenetrating lattices must be used to give all the points.

Consider lattice A referred to the cube face diagonals as axes. Then all the points of that lattice have indices

$$pc, \qquad qc, \qquad rc,$$

p, q, r being any integers. The relative position of lattice B is arrived at if we imagine lattice A to suffer a translation along the trigonal axis which is

the long diagonal both of the elementary parallelepiped and of the cube, the amount of this translation being one-fourth of the long diagonal.   Reference to one of the diagrams will make this more clear than any explanation which could be given here.   The points of lattice B then have co-ordinates

$$(p+\tfrac{1}{4})c, \qquad (q+\tfrac{1}{4})c, \qquad (r+\tfrac{1}{4})c.$$

The planes of lattice A which have Millerian indices (lmn) are given by

$$lx+my+nz = \mathrm{P}c,$$

where P is any integer.   The corresponding planes of lattice B are given by

$$l(x-\tfrac{1}{4}c)+m(y-\tfrac{1}{4}c)+z(n-\tfrac{1}{4}c) = \mathrm{Q}c,$$

or

$$lx+my+nz = \left(\mathrm{Q}+\frac{l+m+n}{4}\right)c.$$

When the (lmn) planes of both lattices are considered together, three cases present themselves :—

(1) When $l+m+n$ is a multiple of four, the planes of lattice B are coincident with those of lattice A, both being given by

$$lx+my+nz = (\text{integer} \times c).$$

An example of this is found in the plane $(1\bar{1}0)$ or (130).

(2) When $l+m+n$ is a multiple of two but not of four, the planes of lattice A are given by

$$lx+my+nz = \mathrm{P}c.$$

Those of lattice B are given by

$$lx+my+nz = (\mathrm{P}+\tfrac{1}{2})c,$$

and are thus half-way between the planes of lattice A.

Examples.—Planes such as (110) and $(12\bar{1})$.

(3) When $l+m+n$ is odd, the equations of the two sets of planes are

$$lx+my+nz = \mathrm{P}c,$$

and

$$lx+my+nz = (\mathrm{P}+\tfrac{1}{4}c),$$

or

$$lx+my+nz = (\mathrm{P}-\tfrac{1}{4})c,$$

and the planes occur in pairs, in such a way that the two planes of a pair are separated by one-fourth of the distance between the successive pairs.

Examples.—Octahedron faces (100), (010), (001), and (111).

It is now clear wherein lies the difference between planes $(11\bar{1})$ and (131), on the one hand, and $(12\bar{1})$ on the other.   The $(12\bar{1})$ planes of the one lattice alone would probably give a strong reflection of a part of the X-ray spectrum in

which there was a large amount of energy, but the presence half-way between them of the planes of the other lattice $(1+2-1=2)$ annuls their effect. On the other hand, though the $(13\bar{1})$ and $(11\bar{1})$ planes now occur in pairs, the wave-length reflected from them is the same as that for a single lattice. On looking over the indices of the reflecting planes, it will be seen how large a proportion of them have $l+m+n$ either odd or a multiple of four; in fact, the departure of the pattern from simplicity is just that which would be expected from the nature of the point system, which differentiates the planes into these three sets.

A more complete analysis of the pattern would be of little interest here because the positions of the reflection peaks afford a much simpler method of analysing the structure. In comparison with the examples given in the former paper, this is a case where the diffraction is caused by a point system as against a space lattice, both a translation and a rotation being necessary to bring the system into self-coincidence. This gives special interest to the photograph.
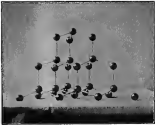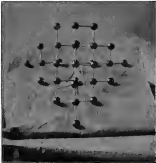
Fig. 7.—View perpendicular to a (111) axis.

Fig. 8.—The (110) planes are vertical and horizontal.

Fig. 11.