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Bakerian Lecture: X-Rays and Crystal Structure

W. H. Bragg

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IX. Bakerian Lecture.—*X-rays and Crystal Structure.*

By W. H. Bragg, *D.Sc., F.R.S., Cavendish Professor of Physics in the University of Leeds.*

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The method of investigating crystalline structure by the use of X-rays has already been explained in papers read before this Society. It will be convenient nevertheless to re-state its principle very briefly in order to introduce some further considerations which I propose to lay before you.

The statement of the principle may be made in the following way. Let a train of waves of length λ be passing through a medium in which are particles having the power of scattering the radiation. Suppose, further, that the scattering power is not distributed evenly through the medium, but that directions can be found along each of which there is a periodic variation of the scattering power of the material contained in strata perpendicular to the given direction, strata being, of course, taken of equal thickness for comparison. Let the distance of recurrence or spacing be called d. Let θ be the angle between the rays and the strata. Then there will be a "reflection" of the radiation by the medium of $n\lambda = 2d \sin \theta$, where n is any integer.

For instance, the Lippmann process of colour photography produces such a distribution of scattering power in the sensitive film through the agency of stationary waves.* If light is incident on the film it is strongly reflected when $\lambda = 2d \sin \theta$; if the light is white the film selects the appropriate wave for reflection, and this is the origin of the colour manifestation.

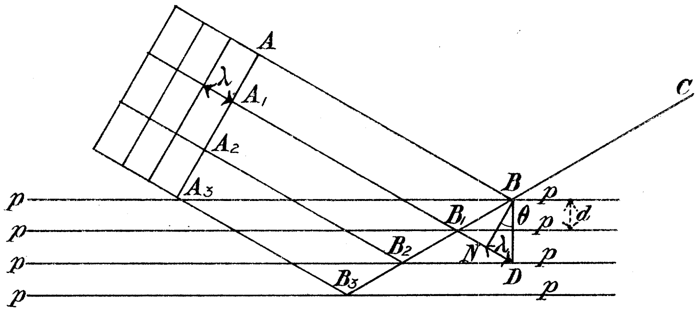

Fig. 1.

The formula is readily explained by aid of the figure, which shows a set of regularly spaced planes $p, p, p, \ldots$, each reflecting a minute fraction of the incident

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* 'Physical Optics,' Wood, p. 149.

radiation, and transmitting the remainder. All the reflected portions which unite to travel along BC will be in the same phase if

$$n\lambda = A_1B_1 + B_1B - AB = A_1D - AB = DN = 2d \sin\theta,$$

where n is any integer. In the figure $n = 1$. Only when this relation is satisfied is there any sensible reflection. The greater the number of planes concerned in the action the more abruptly does the effect disappear if θ is slightly varied.

We speak here of reflecting planes and represent them as surfaces. But the general result is exactly the same if we replace a plane by a thin layer containing scattering particles; and it still holds exactly if we suppose a continuous succession of thin layers of varying density forming the periodic structure to which we have referred.

The atoms of a crystal are distributed in an orderly manner. They can be thought of as arranged on series of parallel planes; and this can be done in many ways. A natural face is always parallel to a series of this kind.

An atom possesses the power of scattering X-rays to an extent which appears to depend mainly upon its mass. It is not quite clear how this power is distributed within the atom; one would expect that both nucleus and electrons share in it, and that it extends more or less over the whole atom. As the diameter of the atom is of the same order of magnitude as the spacings of the crystal planes this last consideration is of importance, and I propose to return to it later. For the present we may observe that if the scattering power were confined to one central point in each atom we should be able to represent the "reflection" by a plane containing atoms as if it occurred in a reflecting surface, as in fig. 2. If, on the other hand, we suppose the scattering power to be distributed through the atom, and if we take a section through the crystal perpendicular to the direction x (see fig. 2), the scattering power of the substance in the layer δx will be a periodic function of x. In either case the formula $n\lambda = 2d \sin\theta$ gives the only values of θ at which reflections can occur.

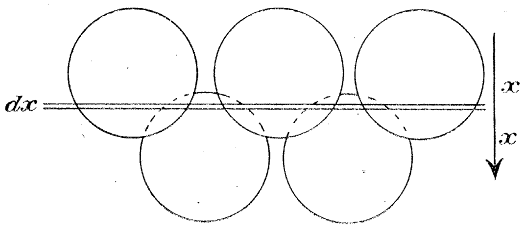

Fig. 2.

Let us take a numerical instance. The atoms of rock salt are now known, as the result of the investigations we are considering, to be arranged as in fig. 3. The plane of the paper is parallel to a cube face. The atoms are represented as circular, and as having a definite boundary; but that is merely because we must give some form in a drawing. In reality we know very little about such things.

The atoms of the crystals may be considered as arranged in a series of planes which are perpendicular to the paper and cut it in lines parallel to AB. These planes all contain equal numbers of Na and Cl atoms and are all alike. The spacing is 2·81 Å.U. (10^{-8} cm.).

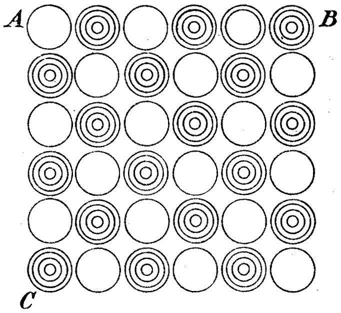

Fig. 3. Arrangement of atoms in any plane in rock salt which is parallel to a cube face. Blank circles represent sodium atoms; the others chlorine, or *vice versâ*.

On the other hand, we may think of the atoms as lying on sets of planes which are perpendicular to the paper and intersect it in lines parallel to BC. These planes are also all alike, containing equal numbers of Na and Cl atoms, although the atoms lying along the lines of intersection with the paper are all of one or of the other kind. The spacing is very nearly 2 Å.U., being $\sqrt{2}$ times less than the former spacing.

Again, if we proceed in a direction parallel to a cube-diagonal of rock salt, we encounter alternately planes containing nothing but Na atoms, and planes containing nothing but Cl atoms. The periodicity now has a spacing 3·24 Å.U.; extending, say, from one Cl plane to the next.

If we pass a pencil of X-rays of wave-length λ through a piece of rock salt, there will be a reflection in the planes parallel to a cube face if the rays make with those planes an angle θ where $\sin\theta = \lambda/5{\cdot}62$, in the planes perpendicular to a face-diagonal if the angle made with these planes is given by $\sin\theta = \lambda/4$, and in the planes perpendicular to the cube-diagonal if the angle made with such planes is given by $\sin\theta = \lambda/6{\cdot}48$. Of course it is extremely unlikely, though quite possible, that more than one of these conditions can be satisfied at one time by the same set of homogeneous rays. But if the pencil of X-rays contains rays of a great range of wave-lengths various constituents may be found to satisfy the condition of reflection not only by these but by many other planes, or by many others and not by these. In this way a number of different constituents of the original pencil may be reflected in different directions, which will have an ordered arrangement dependent on the symmetry of the crystal. This is the explanation of the photographs first obtained by FRIEDRICH and KNIPPING as the result of the brilliant suggestions of LAUE.*

The X-rays usually penetrate such a little distance into a crystal that the reflection seems to occur at the face of the crystal in the ordinary way. It is usual though not always possible to cut the crystal so that the surface is parallel to the set of planes to be considered, unless a natural face is available. If the crystal is cut imperfectly so that the face is not parallel to the planes, the angle between the incident and reflected rays is not affected thereby, because the reflection is truly related to the set of the planes and ignores the face. Moreover it is just as sharp where the face is rough as when it is smooth, so long as the crystal is uniform.

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* The explanation was given in this simple and complete form by W. L. BRAGG, 'Proc. Camb. Phil. Soc.,' vol. xvii., Pt. I., p. 43.

In practice a fine pencil of X-rays is allowed to fall upon a crystal face, natural or prepared, and the crystal is gradually turned so that the angle between rays and face, called the glancing angle, steadily increases from zero onwards. Reflection takes place whenever the formula is satisfied, the reflected pencil being detected by the ionisation which it produces in a chamber containing a heavy gas. The chamber can be made to turn about the same axis as the crystal.

If the incident rays are heterogeneous and contain pencils of various wave-lengths, each is reflected at the proper angle, and the rays are analysed, forming a spectrum. The figure shows the analysis of the rays issuing from an X-ray bulb in which the anti-cathode is made of rhodium; the spectrum is therefore characteristic of rhodium. The abscissæ are the various values of the glancing angle, the ordinates are the measured intensities of the reflected rays. It may be mentioned that glancing angles can be measured with little difficulty to a minute of arc. Intensities can be measured to one or two parts in a hundred if the circumstances are not varied. If the experiment is repeated under fresh circumstances the agreement is not quite so good.

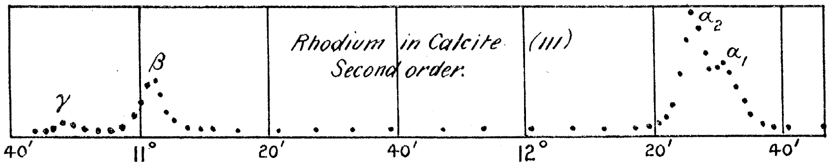

Fig. 4. Spectrum of Rh X-rays. Each dot records a separate measurement.

It will be observed that the rhodium spectrum contains four "lines." In other words, when stimulated by the impact of the cathode stream rhodium emits four pencils of different wave-lengths. These have been calculated* to be 0·534, 0·545, 0·614 and 0·619 Å.U. respectively. The crystal planes here used are the (111) planes of calcite, those which are perpendicular to its axis. The spacing is 2·83 Å.U. The doublet α_1, α_2 is very convenient for crystallographic work.

If we always make use of the same homogeneous X-rays, for example of the line α_2 (or, which is much the same thing in most experiments, the doublet α_1, α_2) we can compare the spacings of different sets of planes, whether of the same or of different crystals. This is one step towards the determination of crystalline structure. In order to make its significance clear it will be well to consider certain elementary principles of crystallography.

However complicated may be the arrangement of the atoms in a crystal with respect to each other they must allow of being grouped into units which are repeated regularly throughout the crystal. Every unit resembles every other exactly as regards both the internal disposition of its members and the external disposition of group to group. The grouping may, however, be effected in more than one way. If

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* 'Phil. Mag.,' March, 1914.

a point in each group is chosen to represent that group—it must be similarly situated in each group—the points will lie at the intersections of such a set of lines as are shown in fig. 5. If they do not do so the unit chosen must be incomplete and is indeed not a unit at all. The figure may be regarded as composed of rhomboidal cells, and in the most general case three unequal edges of each cell meet at every corner and include three unequal angles.

The determination of the form of this fundamental lattice is a necessary preliminary in any investigation of crystal structure. It involves the measurement of the three edges and three angles of the elementary rhomboidal cell.

But the form of the crystal structure is not fully known until we have also determined the disposition of the atoms about the representative point in each unit.

There are thus two stages in such an investigation, and the X-ray method operates in entirely different ways in the two.

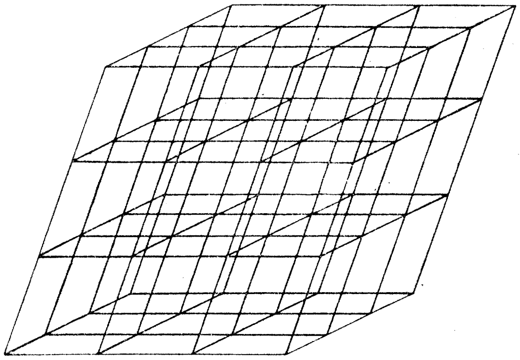

Fig. 5.

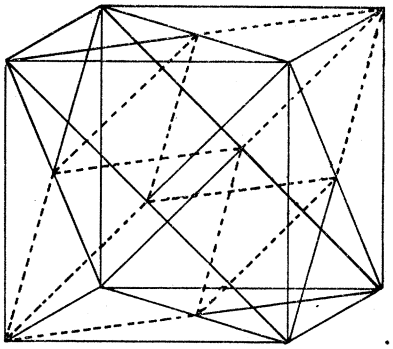

Fig. 6.

Let us first consider the determination of the fundamental lattice.

If we knew what faces of the crystal, if any, were parallel to the faces of the cell, we should merely have to measure the spacings perpendicular to the faces and our work would be done. It might not even be necessary to make more than one such measurement because the relative values of the spacings might be known from considerations of crystalline form. The same knowledge of form which told us the faces to measure, would give us also the angles of the cell, and so all the quantities would be known.

Although, however, a knowledge of crystalline form gives the most valuable suggestions as to the dimensions of the elementary cell, its indications are not always definite. A very interesting and important example occurs in the case of cubic crystals. If the elementary cell were a cube, we should certainly expect the form of the crystal to be cubic; but there are also two other forms of lattice which may lead to the cubic habit and one of these is of the greatest importance to us. If the three edges are all equal, and the three angles are all 60 degrees, we have the cell shown in the dotted lines of fig. 6, and the distribution of points which it gives may also be represented, as crystallographers have shown us, by the "face-centred" cube drawn in full line. The cubic habit may therefore be acquired in this way also. By the X-ray method we can easily tell one from the other. For the spacings of the (100), (110) and (111) planes are, in the case of the simple cube, in the ratio $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$. Consequently the series of the corresponding glancing angles are as $1 : \sqrt{2} : \sqrt{3}$. We have no real example of this lattice, though potassium chloride (sylvine) accidently gives it. The potassium and chlorine atoms are nearly of equal weight, and weight is all that seems to affect the scattering of X-rays, so that the arrangement of the atoms shown in fig. 7 is effectively equivalent to the simple cubic arrangement.

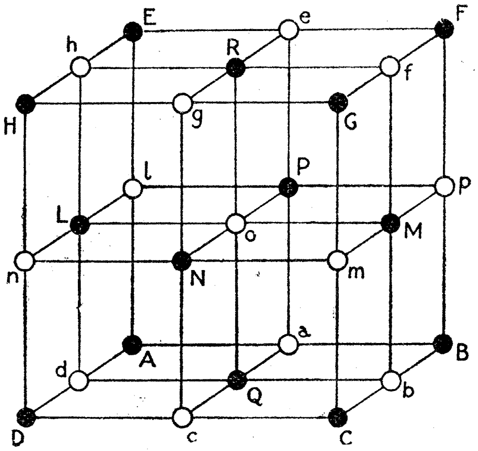

Fig. 7.

On the other hand, it may easily be calculated that the spacings of the face-centred cube are in the proportion $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$; and the series of the corresponding angles of reflection are as $1 : \sqrt{2} : \sqrt{3}/2$. A very good example occurs in the case of copper; the angles are given in fig. 8, and the relations can be readily verified. The copper atoms are therefore arranged on the lattice in which the elementary cell has three equal sides meeting at a point and including three equal angles of 60 degrees.

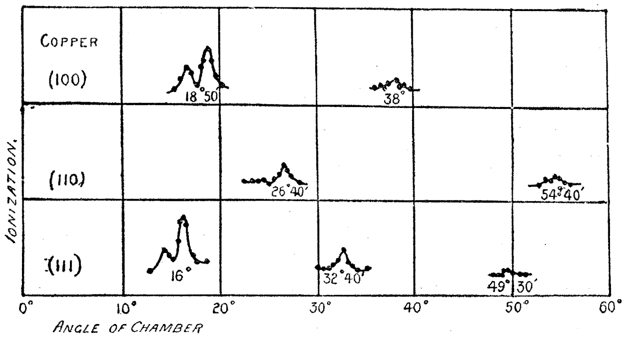

Fig. 8. Spectra of Pd rays given by certain planes of a copper crystal. The angles recorded refer to the α ray.

Rock salt, diamond, zinc blende, fluor-spar and other cubic crystals are all built on the same fundamental lattice. In all cases the sines of the angles of the first order spectra of the (100), (110) and (111) planes are in the ratio $1 : \sqrt{2} : \sqrt{3}/2$; except by accident, the manner of which will be explained presently.

The prevailing occurrence of the face-centred form suggests that even in calcite, which is not cubic, the representative points may be conceived of as being placed at the corners and the face-centres of a rhomb of the same form as the calcite crystal itself. Calculating the spacings of various planes on this basis, we find that the corresponding angles of reflection are correct to the minute when determined by experiment. It may be interesting to give part of the calculation.

Let the side of the rhomb be a. The angles of the rhomb being known, it may easily be calculated that the volume is $a^3 \times 0{\cdot}925$. Since the specific gravity of the crystal is 2·712, the mass in the rhomb is $a^3 \times 0{\cdot}925 \times 2{\cdot}712$.

But there are four molecules to each rhomb,* the weight of each being 100 times the weight of the H atom, which is $1{\cdot}64 \times 10^{-24}$ gr.

Hence

$$a^3 \times 0{\cdot}925 \times 2{\cdot}712 = 4 \times 100 \times 1{\cdot}64 \times 10^{-24}$$

or

$$a = 6{\cdot}40 \times 10^{-8}$$

$$= 6{\cdot}40 \text{ Å.U.}$$

From this other linear dimensions of the rhomb may be found. For instance, the spacing of the planes parallel to the face is 3·025 Å.U., and the reflection of the α_2 rhodium ray should occur at an angle θ given by

$$0{\cdot}614 = 6{\cdot}05 \sin \theta.$$

Hence $\theta = 5^\circ\ 48'$, and this is exactly verified by experiment.

It is easy to find the dimensions of the elementary cell of the lattice. The three equal edges join the blunt corner of the rhomb to the middle point of the adjoining faces. The length of each is 4·03 Å.U., and the angle between any two, 75° 54′.

In similar ways we may determine the space lattice of any crystal. It is to be remembered that the data on which we depend are the positions of the spectra of the various faces.

Let us now proceed to consider how we may determine the arrangement of the atoms about the representative point. We now work on an entirely different plan, building in fact on a determination of the relative intensities of the reflections of different order and different sets of planes. As has already been said, measurements of this kind are much more difficult than measurements of position; and moreover their exact interpretation has been by no means clear. But in many cases we already know so much from considerations of crystal symmetry, and from measurements of

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* 'Roy. Soc. Proc.,' 89, p. 280.

the angles of reflection, that the very roughest measurements of relative intensity give us all that we want. This is at any rate the case with some of the simpler crystals.*

Let us take one or two examples. The spectra of the (100), (110) and (111) planes of rock salt are shown diagrammatically in fig. 9, the positions of the vertical lines showing the relative magnitudes of the sines of the angles at which the various reflections occur and the heights the relative intensities on an arbitrary scale.

The sines of the angles of the first order reflections are as $1 : \sqrt{2} : \sqrt{3}/2$. Hence we know that the fundamental lattice is that which gives rise to the face-centred cube.

The actual values of these sines agree with the supposition that one atom of Na (or Cl) is associated with each point of the face-centred cube. The calculation has been already published,† and it will not be necessary to repeat it.

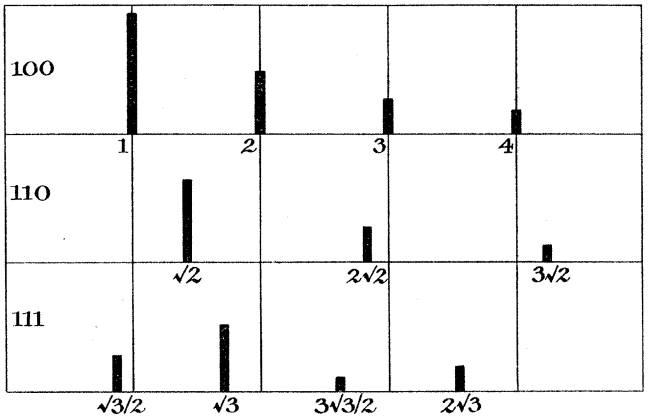

Fig. 9.

We can imagine a face-centred lattice of sodium atoms, and an exactly similar lattice of chlorine atoms which is at first coincident with it, but is then moved out from it in a direction and to an extent which we must gather from the intensity observations. Each chlorine atom is then related to the sodium atom from which it came, as regards distance and orientation, in identical fashion throughout the crystal.

Considering the diagram we see that there is a rapid and steady decline in the intensities of the spectra of the (100) and (110) planes as we proceed to higher orders. From experience of many cases we believe this to be normal, that is to say, it always occurs when all the reflecting planes are similar and equally spaced. We conclude that the chlorine atoms have so moved that they still lie in the (100) and (110) planes of the sodium lattice. But the (111) spectra are not of the same type. A marked alternation of intensity, odd orders weak and even orders strong, is

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* W. L. Bragg, 'Roy. Soc. Proc.,' 89, p. 478.

† 'Roy. Soc. Proc.,' vol. 89, p. 246 or p. 276.

superimposed upon the normal rapid decline. This implies an alternation in the strength of the reflecting planes.

For, suppose the lines a, a, a, in fig. 10, represent a set of reflecting planes, giving the spectra A; and suppose also the lines b to represent a set of reflecting

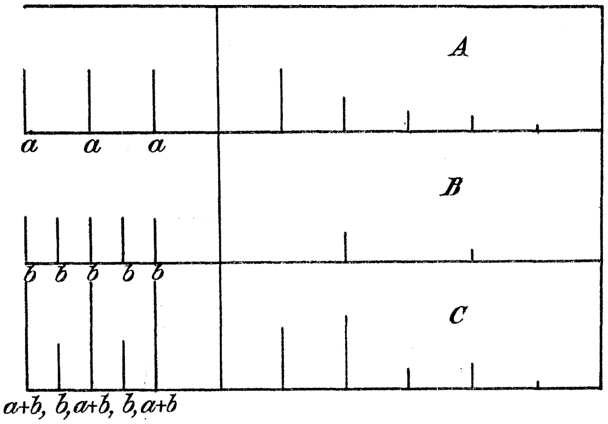

Fig. 10.

planes which have half the spacing of A, and therefore give spectra twice as far apart as in B.

If we combine the two sets of planes, we compound the reflections as in C.

Hence we learn that the chlorine atoms have so moved away from the sodium atoms that their (111) planes lie half-way between the (111) planes of the sodium lattice, for in this way is formed a set of planes of alternating strength like the $a+b$, b, $a+b$, b, of the figures.

The structure shown in fig. 7 is in accordance with these conditions.

Let us take the case of zinc blende, the spectra of which are given in fig. 11.

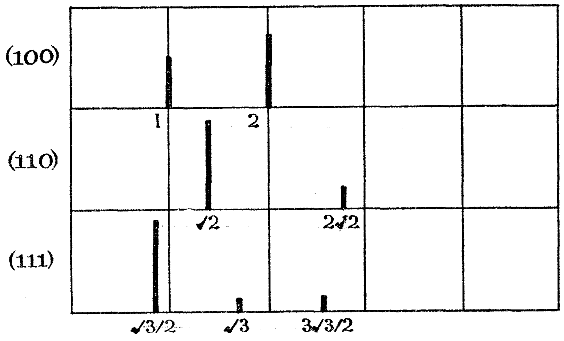

Fig. 11.

Here again the relative positions of the first spectra of the (100), (110), and (111) planes are those of the face-centred lattice; and the actual angles of reflection show that one zinc atom is associated with each point on the lattice.

Again, we may start with a zinc lattice and suppose a similar sulphur lattice to be at first coincident and then to move away to its proper place. The (110) planes are normal, so that the sulphur atoms remain on the (110) planes of the zinc lattice. But the (100) planes show the same sort of alternation as we observed just now in the case of the (111) planes of rock salt. The sulphur lattice must have moved so that its (100) planes lie half-way between the (100) planes of the zinc lattice. Again, the (111) spectra show a new peculiarity in that the second order spectrum is abnormally small. Such an effect is readily explained by supposing that the (111) sulphur planes divide the intervals between the (111) zinc planes in the ratio 1 : 3.

All these conditions are fulfilled by the structure shown in fig. 12, in which the sulphur lattice has moved away from the zinc lattice in the direction of the cube diagonal, the distance of the movement being one quarter of the length of the cube diagonal.

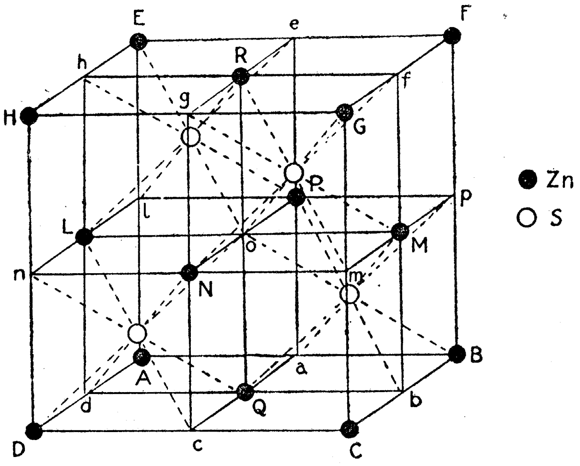

Fig. 12.

Let us take yet one more illustration from the case of the diamond ; the spectra are given in the figure.

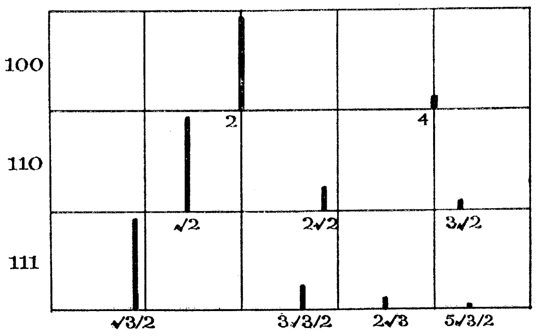

Fig. 13.

In this case it might appear that the relative positions of the first order spectra are not those of the face-centred lattice, but this should be regarded as purely accidental.

The spectra resemble those of zinc blende, except that the odd orders of the (100) spectra and the second order of the (111) spectra are not merely abnormally small, but have entirely disappeared. These facts are very simply explained. The structure is obtained in exactly the same way as that of zinc blende; but the two lattices are alike, both being of carbon, and when their influences interfere, the interference is complete.

Finally, consider the case of fluor-spar (CaF_2) for a special reason.

As regards relative positions and intensities the spectra are exactly the same as those of diamond. If we begin with a face-centred lattice of calcium atoms, we must so move out from it *two* similar lattices of fluorine atoms as to obtain the observed relative intensities. This we do by moving them along the cube diagonal, but in opposite directions, the distance moved being one quarter of the length of the diagonal. This gives a highly symmetrical structure. A fluorine atom lies at the centre of each of the eight cubes into which the large face-centred cube can be divided. The (100) planes of fluorine now lie half-way between the (100) planes of calcium, and we explain the disappearance of the first order (100) spectrum by supposing that *they have equal reflecting powers.* We assume, in fact, that two fluorine atoms of weight 38 are equivalent, within errors of experiment to one atom of calcium of weight 40. This is only one instance out of many; it seems certain that two planes containing equal weights per unit area are equivalent in reflecting power, no matter how the weight is made up nor how it is distributed in the plane. As regards distribution, this is what we should expect: as regards the effect of weight the result is not so obvious, though it cannot surprise us if we suppose the scattering to be due to the cumulative effect of the electrons and nuclei of the atoms.

In the simple cases which we have been considering, the considerations of crystal symmetry, though unable of themselves to determine crystal structure, come so near to doing so that a few plain hints given by the new methods have been sufficient for the completion of the task. The exact positions of the atoms are then known.

But this is not the case with more complicated crystals. As an example we may take the case of iron pyrites. There is a fundamental face-centred lattice of iron atoms, and sulphur lattices are displaced from it in a manner similar to that which has already been described, yet more complicated. The main point, however, is that the extent of the movement cannot be determined from symmetry considerations. In the cases described above the exact movement could be told from these considerations, as soon as the X-ray method had revealed its nature. But in iron pyrites, and probably in the vast majority of crystals, the movement must be calculated from determinations of the relative intensities of the X-ray spectra.

We require, therefore, to determine in the first place how they should be measured, and in the second how they are to be interpreted. In what follows I propose to consider these two points, particularly the latter.

The method of measurement has already been described ('Phil. Mag.,' May, 1914).

A fine pencil of X-rays falls upon a crystal, and the ionisation chamber is set to receive the reflection. The crystal is first set at an angle which is just so far from being correct that no reflection takes place. It is then made to revolve steadily, or rather by uniform small movements at regular intervals; it passes through all the positions in which it can reflect and when the angle has again become such that no reflection takes place, the total movement of the electroscope leaf is observed. In this way the whole reflection effect is integrated. This method is fully discussed in the paper quoted. It is enough to say here that such measurements are really

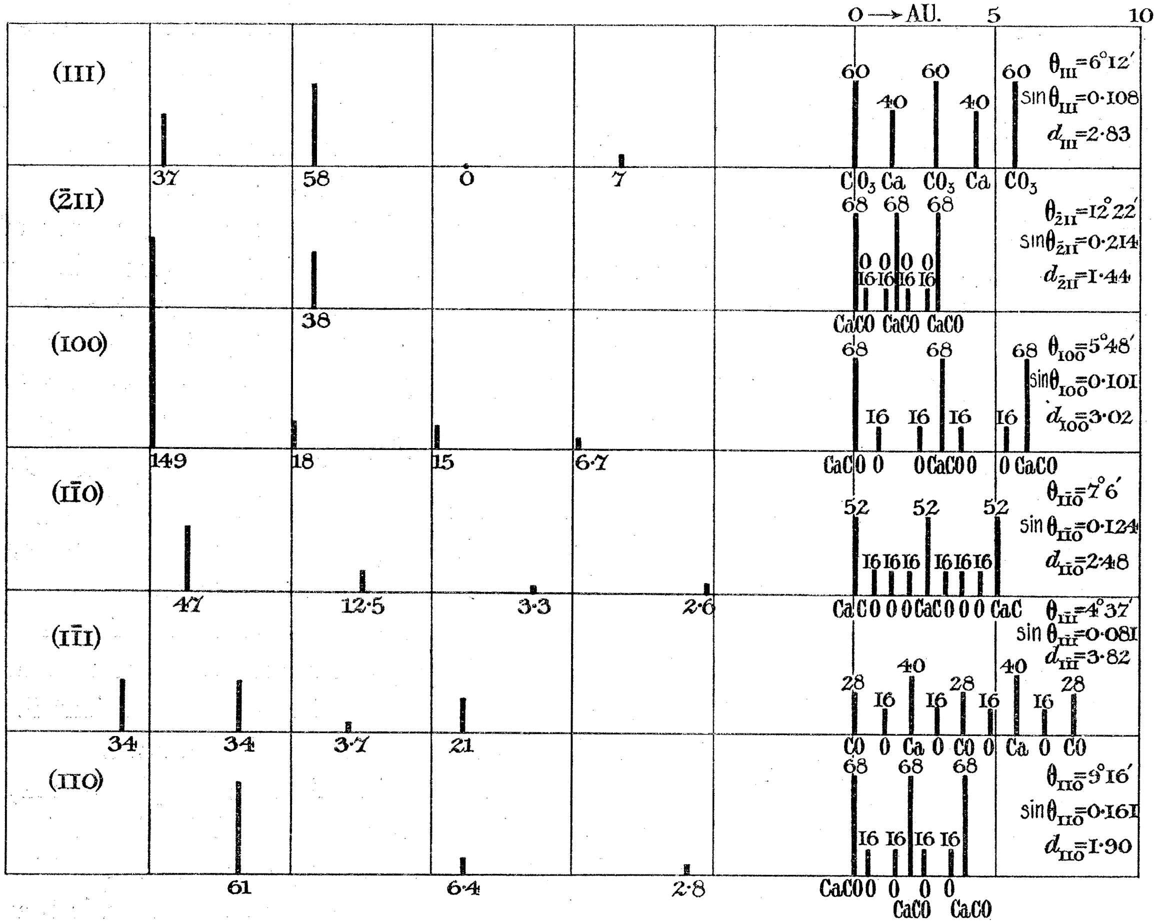

Fig. 14.

comparable with each other, and in particular that the effect of crystal imperfections (sometimes serious) are avoided. A small allowance has to be made for the reflection and scattering of general radiation which enters the slit with the reflected pencil actually measured. This is easily done.

Let us now consider the interpretation of these measurements of intensity. Very useful information on this point is to be gathered from a study of the spectra of various calcite planes. The positions and intensities of the spectra of six of the most important planes are shown in fig. 14. The diagram also shows the spacings of these planes and the angles at which the first order spectra occur. The heights of the vertical lines represent intensities, and their magnitudes are also indicated in figures underneath, in arbitrary units. Their abscissæ represent the sines of the angles of reflection. The numerals placed above the lines on the right of the diagram show the percentages of the molecular weight lying in the various planes.

The structure of calcite has already been investigated by W. L. Bragg,[*] and fig. 15, is reproduced from his paper. In its determination use was made, as in other cases, of a knowledge of the crystal symmetries. The fact that the (111) planes contain alternately calcium atoms only, and groups of CO_3 only was inferred from a comparison of the (111) spectra of the calcite series of crystals. In all cases there is clearly an alternation of composition because, as in NaCl, the odd order spectra are abnormally small. In chalybite $FeCO_3$ the odd order spectra disappear altogether, implying that the alternate planes are now equally weighted. If one plane contains Fe only, and the other CO_3 only, this equality does actually occur. The series being isomorphous we must suppose this structure to be common to them all.

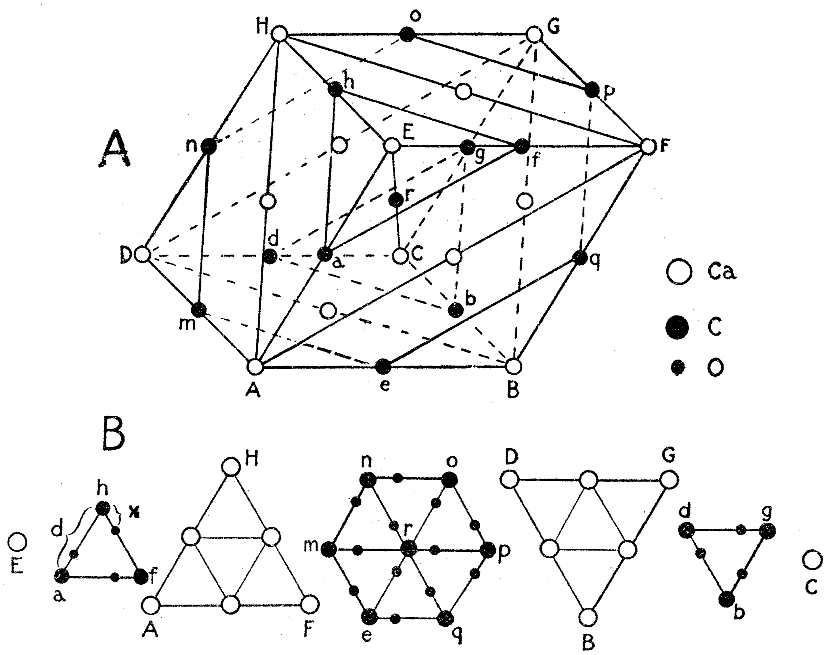

Fig. 15.

Considerations of symmetry show that the arrangement of the carbon and oxygen atoms must be as shown in the lower line of drawings in the figure.

But there is *one* variable which symmetry cannot determine, viz., the distance between the oxygen and the carbon atoms. This can only be found by interpreting the intensity measurements. In the original paper the best measurements available

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[*] 'Roy. Soc. Proc.,' A, vol. 89, p. 486.

were only rough, and the mode of interpretation was not very certain. Nevertheless it was possible to say that x/d (see fig. 15) was about 0·30.

The measurements here shown are much more complete and accurate. They indicate that the value of x/d should be put a little lower, say 0·25 to 0·27. Perhaps this appears most clearly from the $(1\bar{1}1)$ planes. These are of somewhat peculiar structure, as shown in fig. 14. Whatever may be the value of x/d, planes of calcium and of CO alternate with each other; but oxygen planes interleave them. If $x/d = 0{\cdot}25$ they bisect the distances between the Ca and CO planes. This would account for the strength of the fourth order spectrum (21). The smallness of the second order (100) also is in accordance with this view. There can be little doubt that the O atoms are very nearly a quarter of the way from one carbon atom to the next. The figure shows the arrangement of atoms in the planes on this supposition.

Now it is remarkable that in two cases we have different sets of planes with the same or at least commensurable spacings. The second order (111) occurs at almost exactly the same angle as the first $(\bar{2}11)$. This enables us to compare the effects of differing arrangements of atoms apart from the effect of differing angles of reflection.

The first order (111) is due to the full spacing of the (111) planes, viz., 2·83 Å.U.; but the second order is due to half this spacing, viz., 1·41 Å.U. In the former the Ca and the CO_3 in each molecule are in opposition, in the second in concurrence. The whole weight of every $CaCO_3$ unit $(40+12+48 = 100)$ is thrown into the scale in the formation of the latter spectrum. Its intensity is 58.

The first order $(\bar{2}11)$ is due to the same spacing. In this case the planes may be divided into two groups: first, a set of CaCO planes with a spacing 1·44 Å.U.; and, secondly, a set of O planes with a regular spacing of 0·72 Å.U. The latter have no effect at all at the point where the first $(\bar{2}11)$ spectrum occurs. The whole intensity of the latter, viz., 38, is due to the CaCO in each molecule, that is, to a weight of 68 out of the 100. *The intensities of the two spectra are proportional to the weights contributing to them* for $68/100 = 0{\cdot}68$ and $38/58 = 0{\cdot}66$.

It is to be observed that the conditions for this comparison are excellent; the angles of reflection are the same, so that there is no need to consider anything that depends on this angle. Also the number of molecules swept over by the X-rays is the same in each case. The only difference is that in one case the whole molecule is in action, in the other, part of it.

A second opportunity of comparison occurs in the $(1\bar{1}1)$ and (110) spectra. The first order spectrum of the latter is due to the CaCO in each molecule, as in the $(\bar{2}11)$ case, and to a spacing 1·90 Å.U.; its intensity is 61. The second spectrum of the $(1\bar{1}1)$ is due to the same spacing. The Ca and CO planes may be considered to act together, with the O planes in opposition. The mass 68 is acting against the mass 32; the balance 36 may be considered as the origin of the second $(1\bar{1}1)$

spectrum of intensity 34. Here, again, the intensities are very nearly proportional to the amounts of the masses concerned.

Assuming that these cases illustrate a general principle, let us apply it to a case where spacings differ as well as plane composition. Consider the various orders of the (100) spectra. The first order corresponds to a spacing 3·02 Å.U. and is due to CaCO planes only; the remaining oxygen planes are regularly spaced at an interval 0·151 Å.U. and contribute nothing to the first order spectrum. The second order spectrum is due to CaCO planes with the O planes in opposition. The third order is due to CaCO planes only, and the fourth to CaCO and O planes acting in conjunction. Thus the effective masses are in the ratio 68 : 36 : 68 : 100. The normal rate of decline is about 100 : 20 : 7 : 3. When these two causes of variation of intensity are superimposed we obtain the series 68 × 100 : 36 × 20 : 68 × 7 : 100 × 3, which may be expressed as 149 : 16 : 10·5 : 6·6, the first being put equal to 149 for the sake of easy comparison with the experimental figures. It will be seen that, on the whole, there is a good agreement. The third order does not compare very well; but the explanation of the small second and large fourth, as compared with a normal series of spectra, is very clear.

It may be pointed out that the ($\bar{2}$11), (100), and (110) planes must have exactly similar spacings and distributions of weight no matter what value we adopt for x/d. This is obvious when we consider that they all intersect the (111) planes in successive lines such as *nm*, *ore*, *pq* of fig. 15, their inclinations to the (111) planes being the only variables. In the figure the plane *nopqem* is a (111) plane, *nham* a (100) plane, *ngbm* a (110) plane, and EoCe a ($\bar{2}$11) plane. The last contains the axis and is perpendicular to the (111) planes.

Now if we compare the intensities of the higher orders of these planes, we find they are not quite alike. For instance, 149 : 18 : 15 is not the same as 61 : 6·4 : 2·8.

The differences are accounted for in part at least by the effects of temperature which always affect the higher orders more than the lower. The normal decline of 100 : 20 : 7 : 3 is only a rough average for a moderate spacing; if the spacing is small and the spectra are consequently found at higher angles, their decline in intensity is more marked. We should expect the (110) spectra to fall off more quickly than the (100) spectra, although the two sets of planes are exactly similar.

Probably, however, there are other minor causes at work; we shall presently come to a suggestion of one at least. The point is that putting aside these small, but real and perhaps important discrepancies, we do succeed in accounting very satisfactorily for the large differences in the intensities of the different orders. Perhaps this is best seen from fig. 16. Here all the intensities are grouped together in one diagram; the crosses indicating the amounts as transferred from fig. 14. In each case the intensity has also been divided by the fraction of the molecule which contributes to it. For instance, we divide 149 by 68, 18 by 36 in the (100) series; the first 34 in the $(1\bar{1}1)$ series by 12; the second 34 by 36, the 3·7 by 12, and the 21 by 100, and so on. The results are indicated by the dots, which, it will be observed, follow closely a regular curve.* We may be said to have allowed for differences in the masses contributing to the various spectra, and to be free to attack the question of the cause of the rapid change in intensity as we proceed to higher orders.

As far as regards the investigation of crystal structure an explanation is not immediately pressing. We know that it exists, and the law of the decline is not very different in different cases. We can assume it to be expressed by the series 100 : 20 : 7 : 3; and we can interpret the variations from the normal values by means of the principle we have discussed above. Finding in this way the distribution of the atomic masses in the various planes, we have data sufficient for the determination of crystalline structure. But it is of course unsatisfactory from a physical point of view to leave the question at this point.

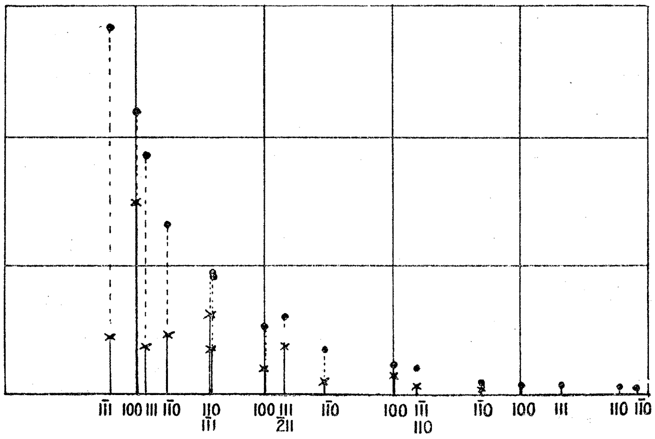

Fig. 16.

I think that an ample explanation of the rapid diminution of intensities is to be found in the highly probable hypothesis that the scattering power of the atom is not localised at one central point in each, but is distributed through the volume of the atom.

We may take the analogy of a diffraction grating. If the transparent portions are very small compared to the opaque, the different orders of diffracted spectra are all equal in intensity. (Rayleigh, 'Phil. Mag.,' 1874, XLVII, pp. 81 and 193.) But if the transparent portions are not relatively small, the higher orders tend to be weaker than the lower. And again, if the transparent portions are not sharply defined, but have "fuzzy" edges, the higher orders are much diminished in intensity, as A. B. Porter has shown by actual experiment ('Phil. Mag.,' Jan., 1905).

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* *Note, June* 7.—I have not been able to account by this principle alone for all the relations between the intensities of the spectra of every crystal hitherto examined: for instance, iron pyrites. But it is most likely that different atoms have different distributions in space and we have not yet taken account of that. Moreover, no case has yet occurred in which the opportunities for comparison are so direct as in calcite, with its different sets of equally spaced planes.

We should expect the scattering centres of the atom to be not only diffused through its volume, but also to be less dense at the edges than at the centre, thus producing exactly those conditions which would reduce greatly the intensities of the higher orders of the spectra.

I have attempted in what follows to make a quantitative estimate of the operation of this principle, but it must be regarded as no more than approximate and provisional. It is based on methods used by Rayleigh, Schuster and A. B. Porter.

Let the density of the scattering centres in a stratified medium be given by $\rho_0+\rho_1 \sin 2\pi \cdot \frac{x}{d}$, where d is the spacing. We might call this a simple harmonic stratification, or for brevity a harmonic medium.

As we know already, reflection of radiation of wave-length λ cannot occur except at angles given by $n\lambda = 2d \sin \theta$.

Let us consider the amount of the reflection at these different angles. The amplitude of the wave reflected to any point P by the stratum dx may be written as proportional to

$$\left(\rho+\rho_1 \sin 2\pi \frac{x}{d}\right) \sin \left(\phi - 2\pi \cdot \frac{2x \sin \theta}{\lambda}\right) dx,$$

where account is taken both of the density of the scattering centres in the layer dx, and of the loss of phase due to the depth of the stratum below the surface.

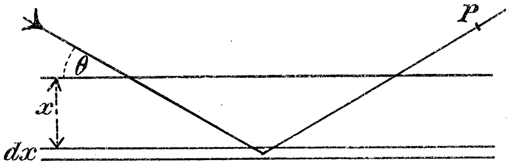

Fig. 17.

It seems to me that we do not contradict our principle that the *intensity* of the reflected pencil is proportional to the mass concerned when we here take the *amplitude* of the reflection by the layer to be proportional to the number of scattering centres or the mass of the layer, although the intensity of a vibration is proportional to the square of its amplitude. The amplitude, here considered, of the reflection is no doubt only one of the factors which determine the intensity. The reflection is not directed strictly in one direction, though it is more and more nearly so the more centres there are in a layer. If we imagine the number of scattering centres in a layer to be gradually increased, the maximum amplitude is increased proportionally, but the intensity of the whole reflection does not increase at the square of this rate, because it is being continuously limited in its divergence from the true direction of reflection. As we know from our experiments, the intensity measured, as we have measured it, is proportional to the mass concerned, other things being the same. In our present discussion we estimate the amplitude of the reflection disturbance at its maximum.

As will be seen presently, we are examining the circumstances when this is zero, and we are at liberty to conclude that when this is zero there is no reflection at all, which is all that we require.

The amplitude of the wave at P, as made up of reflections from all the strata within one period, $x = 0$ to $x = d$, is

$$\int_0^d \left(\rho+\rho_1 \sin 2\pi \frac{x}{d}\right) \sin\left(\phi - 2\pi \cdot \frac{2x \sin\theta}{\lambda}\right) dx.$$

Remembering that $2 \sin\theta/\lambda = n/d$, we see that this vanishes unless $n = 1$. Thus a harmonic medium can reflect at one angle only, not at a series of angles.

If we know the nature of the periodic variation of the density of the medium we can analyse it by FOURIER'S method into a series of harmonic terms. The medium may be looked on as compounded of a series of harmonic media, each of which will give the medium the power of reflecting at one angle. The series of spectra which we obtain for any given set of crystal planes may be considered as indicating the existence of separate harmonic terms. We may even conceive the possibility of discovering from their relative intensities the actual distribution of the scattering centres, electrons and nucleus, in the atom; but it would be premature to expect too much until all other causes of the variations of intensity have been allowed for, such as the effects of temperature, and the like.

There is no harm, however, in ignoring these considerations for the present, in order that we may examine the working of the principle. We believe these disturbing causes to have no great effect.

Let us imagine then that the periodic variation of density has been analyzed into a series of harmonic terms. The coefficient of any term will be proportional to the intensity of the reflection to which it corresponds. This may be justified in the following way.

Suppose the density of the medium to be represented by the ordinates of the harmonic curve in fig. 18; we may look on all the matter represented by the area below the dotted line as inoperative. It is only the part represented by the corrugations above that are effective. The number of effective centres is proportional to the area above the dotted line. If we compare the effect with that of a deeper corrugation as in fig. 19, where the amplitude has been increased, the number of

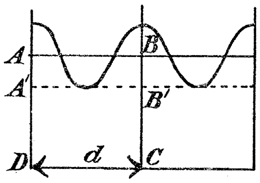

Fig. 18.

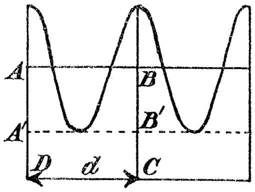

Fig. 19.

effective centres is increased in the same proportion. We suppose the same number of corrugations to be acting in each case.

This is practically the very condition of the comparisons we made in certain cases of calcite.

So also if we compare figs. 18 and 20, where the amplitudes are the same but the spacings are narrower, we may expect the intensities to be proportional to the spacings, when the number of corrugations is the same, because the number of effective centres varies in that proportion.

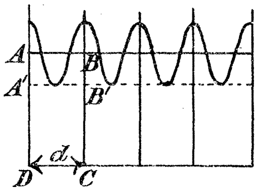

Fig. 20.

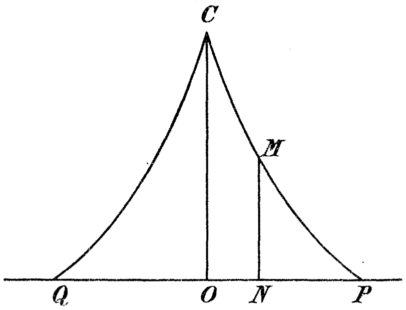

Fig. 21.

Suppose that the density, or the number of the effective centres, in various strata of an atom perpendicular to a given direction is given by the curve in fig. 21, where QOP is drawn in the given direction, and MN represents the stratum density at the distance ON from the centre.

Consider a crystal formed of atoms of one kind, arranged in regularly spaced planes, which all contain the same number of atoms to the unit of area. One atom from each plane will suffice to represent that plane. If, therefore, the density distributions of atoms from the different planes are represented by the curves QCP, Q′C′P′, &c. (fig. 22), the periodic density of the whole crystal is represented by the upper wavy curve formed by adding together the curves of the separate atoms. The distance from crest to crest is what we have called d, the spacing.

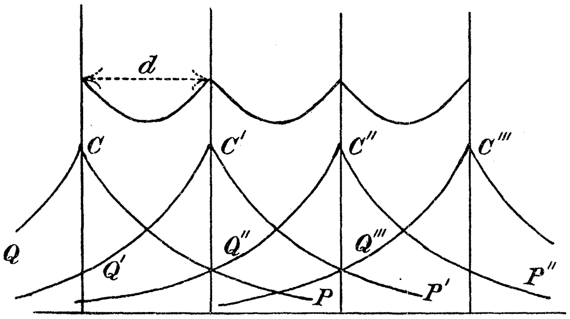

Fig. 22.

Suppose this curve were known and a harmonic analysis made of it. We should obtain a series of harmonic terms having periods d, $d/2$, $d/3$, ...

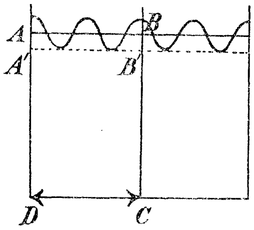

Fig. 23.

Let the curve in fig. 23 represent one of these terms, in fact, the second. The existence of this term implies that the medium, so far as regards the reflection of a wave in the second order, may be looked on as a harmonic medium of amplitude AA′. The rise and fall of the curve above the line AB implies that the medium has a certain distribution of density which will give a second order spectrum if the rays fall on the medium at the proper inclination to the planes. The area ABCD represents the mass of one atom (there being one atom to each spacing); and of the whole, the portion A′B′CD is ineffective so far as this reflection is concerned. The ratio of AA′ to AD represents the fraction of the atom which is effective. Now the X-rays, however they strike the medium, always traverse the same number of atoms. The ratio of AA′ to AD therefore represents that portion of the medium which is effective in the production of the spectrum, and must be proportional to its intensity.

If the distance apart of the planes is not varied the amplitude of the harmonic, that is to say, AA′ must be proportional to the intensity. Experiment shows that after allowing for temperature effects the intensity is nearly proportional to the inverse square of the order. The periodic function which represents the density of the medium must therefore be of the form

$$\text{constant} + \frac{\cos 2\pi x/d}{1^2} + \frac{\cos 4\pi x/d}{2^2} + \ldots \frac{\cos n\pi x/d}{n^2} + \ldots$$

$$= \text{constant} + \frac{(\theta-\pi)^2}{4}, \text{ where } \theta \text{ is put for } 2\pi x/d,$$

that is to say, a series of parabolas arranged as in the upper curve of fig. 22.

We have, therefore, to find such a form of density curve for the individual atom, that when it is combined with others the resulting curve is a series of parabolas, or something very near to it.

Suppose the density of the atom to be represented by $y = ke^{-cx}$ for x positive, and $y = ke^{cx}$ for x negative. Of course, this implies that the atom is of infinite extent, but it will appear that in practice no real disadvantage arises.

The ordinate of the compounded curve is given by

$$y = k\{e^{-cx}+e^{-cx-2ac}+e^{-cx-4ac}+ \ldots e^{cx-2ac}+e^{cx-4ac}+ \ldots\}$$

$$= k\frac{e^{-cx+ac}+e^{cx-ac}}{e^{ac}-e^{-ac}}, \qquad \text{where } 2a = d.$$

This is very nearly parabolic in form, as can be found on trial, except when the individual exponential curves of fig. 22 do not overlap sufficiently.

Proceeding in the usual way, we find that this function from 0 to $2a$ can be expressed by the Fourier series

$$\frac{2k}{ac}\left\{1+\frac{a^2c^2}{a^2c^2+\pi^2}\cos\frac{\pi x}{a}+\ldots+\frac{a^2c^2}{a^2c^2+n^2\pi^2}\cdot\cos\frac{n\pi x}{a}+\ldots\right\}.$$

If a^2c^2 is small compared to $n^2\pi^2$, the harmonic coefficient is nearly proportional to $1/n^2$, so long as a is unchanged. That is to say, the intensities of the various orders for a given spacing are inversely as the square of the number of the order, which means no more than that the exponential curve we chose to express the variation of atomic density was sufficiently correct. It gives a compound curve which is nearly a series of parabolas.

The quantity ac is really a measure of the overlapping of two atoms, because the stratum density of an atom in the plane containing the centre of the next is ke^{-2ac}. If, for example, $e^{-2ac} = 0{\cdot}01$, $ac = 2{\cdot}3$; if $e^{-2ac} = 0{\cdot}1$, $ac = 1{\cdot}15$. Overlappings of this magnitude are quite to be expected, because unless the planes are very widely separated, the atoms of one plane penetrate some distance into the interstices of the next.

If $ac = 1{\cdot}15$ the values of the coefficient $a^2c^2/(a^2c^2+n^2\pi^2)$ for increasing values of n are $\frac{1}{1{\cdot}12}$, $\frac{1}{4{\cdot}08}$, $\frac{1}{9{\cdot}04}$, $\frac{1}{15{\cdot}92}$, or very nearly as the inverse squares of 1, 2, 3, 4.

If $ac = 2{\cdot}3$ the departure from the inverse square law is still not very great. The numbers are then $\frac{1}{1{\cdot}52}$, $\frac{1}{4{\cdot}48}$, $\frac{1}{9{\cdot}41}$, $\frac{1}{16{\cdot}32}$.

Now let us consider the effect of altering the spacing. As we bring the planes together, let us say, the area ABCD of fig. 23 must always represent the weight of one atom because there is one atom to each spacing. The amplitude of any order, say the n^{th}, is

$$\frac{2k}{ac}\cdot\frac{a^2c^2}{a^2c^2+n^2\pi^2}.$$

The effective portion of the atom is therefore

$$\frac{2k}{\text{AD}\times ac}\cdot\frac{a^2c^2}{a^2c^2+n^2\pi^2}$$

of the whole. But AD . $\times a$ = the mass of the atom. Also the mass of the atom

$$= 2\int_0^\infty ke^{-cx}dx \qquad = \frac{2k}{c}.$$

Hence, finally, the fraction of the atom which is effective is $a^2c^2/(a^2c^2+n^2\pi^2)$.

Now we have to explain two things: in the first place, the fact that for a given spacing the intensities of the various orders fall off as the inverse square, in the second the fact that the intensities of two spectra of the same order belonging to different spacings are proportional to the squares of the spacings. For in practice we find that the intensity of any spectrum is proportional to $1/\sin^2\theta$, where θ is the glancing angle, no matter whether the spectra belong to one or to several spacings of the planes. This involves both the facts just stated.

We chose such a form of the density curve for the single atom that we could account for the first fact. The important point is that without further hypothesis we explain the second. The formula we have obtained shows that when a^2c^2 is small compared to $n^2\pi^2$ the intensity varies inversely as n^2 when a is constant, and as a^2 when n is constant.

Thus our hypothesis is self consistent. It does not seem unreasonable. If it turns out to be true, though there is much to be done before its truth can be considered proved, it seems to offer an excellent means of determining the distribution of electrons in the atom.

One or two subsidiary points may be considered very briefly.

I have considered the case of a crystal in which the atoms are all alike and the planes are spaced regularly. It is easy to make the proper changes when more complex cases are considered.

When a^2c^2 is not small compared to $n^2\pi^2$ which would be most likely to happen when $n = 1$, and a or c, or both a and c are large, that is to say for reflections at small angles when there is little overlapping of atoms, then the intensity should be smaller, in comparison with other intensities, than is indicated by the inverse square law. It may be a misleading coincidence, but certainly this effect sometimes appears, for example, in the first $(1\bar{1}1)$ of calcite: perhaps, too, in the first (100) of zinc blende.

An atom for which c is large—a "condensed" atom—should on that account give relatively stronger reflections in the higher orders. The high order intensities can be measured with considerable accuracy, and their comparison should be interesting.