The ionization chamber, however, had to yield to the photographic plate as more complex crystals were tackled, because the number of reflexions to be measured became so large. Accuracy centred on the photometer, or on the uncanny ability of some researchers to get good quantitative measurements by eye estimation with a series of superimposed films. And now, since automation has removed the tedium of ionization measurements on numerous orders, the wheel has turned full circle again and the latest diffractometers are employing just the same principle as we did in 1914 when we turned the spokes on a capstan to the beat of a metronome.

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The Intensity of Reflexion of X-Rays by Crystals

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When a pencil of homogeneous X-rays is incident upon a crystal face it is reflected when, and only when, the angle θ between the pencil and the face satisfies the equation

$$n\lambda = 2d \sin \theta ,^*$$

where λ is the wave-length of the rays, n is an integer, and d is the distance between any plane and the nearest which is similar and similarly placed. In the simplest kind of arrangement, all the planes are similar and equally spaced, and d is then the distance between two neighbouring planes.

If λ and d are given, if, that is to say, a certain X-ray pencil falls on a certain crystal face, several values of θ may be found to satisfy the equation, corresponding to consecutive values of the integer. The reflexions occurring at the angles

$$\sin^{-1}\frac{\lambda}{2d},\ \sin^{-1}\frac{2\lambda}{2d},\ \sin^{-1}\frac{3\lambda}{2d},\ \ldots$$

may be called the reflexions or spectra of the first, second, third order, and so on.

When the planes are equal and equally spaced the intensities of the reflexions decrease rapidly and continuously as n increases; reflexions of an order higher than the fifth or perhaps the sixth have not been observed.

When the arrangement of planes is more complicated this regular diminution in intensity may be greatly modified. Complication may arise in either or both of two ways. The planes may be unequally spaced, or they may be dissimilar. An example of the former effect is to be found in the reflexion from the cleavage face (111) of the diamond. In this case the planes are arranged at distances apart which are alternately as 1 to 3.* In consequence the second order reflexion disappears entirely (*loc. cit.*). The intensity of the third and fifth are normal in comparison with the first, but the fourth is twice as strong as it should be.

An example of the effect of want of similarity in the planes may be illustrated by reference to the (111) planes of rocksalt†. In this case the spacing is uniform but the planes contain alternately sodium atoms only and chlorine atoms only. The result of this unequal loading is that the reflexions of even order are strongly enhanced in comparison with those of odd order: we are taking d to be the distance from one chlorine plane to the next, in accordance with the definition given above, and the glancing angle of the first order to be $\sin^{-1} \lambda/2d$.

When both spacings and loadings are irregular the relative intensities are more complicated still; as for example in the case of reflexion by the (100) or (111) planes of iron pyrites.‡

Since the relative intensities depend so directly upon the spacings and loadings of the planes, and since the manner of dependence can be easily explained, it follows that experimental determinations of the intensities may be used to draw conclusions as to the structure

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* W. L. Bragg, *Proc. Camb. Phil. Soc.* **17**, 43.

* W. H. Bragg & W. L. Bragg, *Proc. Roy. Soc.* **89**, 277.

† W. L. Bragg, *Proc. Roy. Soc.* **89**, 274.

‡ W. L. Bragg, *Proc. Roy. Soc.* **89**, 476.

of the crystal in question. This method has been largely used by W. Lawrence Bragg.*

It is of importance, therefore, that the intensities should be measured with as much accuracy as is possible. It happens that this method of analysis is extraordinarily powerful, and that very rough measurements coupled with general assumptions have been sufficient to lead, in the paper quoted, to definite conclusions. The measurements which were used, and for which I was myself mainly responsible, could only be considered as provisional, under the circumstances. They were sufficient, however, for the determination of several complicated crystals, such as iron pyrites, the calcite series, and so on.

For example, in the case of iron pyrites it appeared that the iron atoms were arranged on a face-centred cube, that is to say, at the corners of a cube and at the centres of each face. A sulphur atom lay in each of the eight small cubes into which the large cube could be divided; it was situated on a diagonal of the small cube which diagonal was to be chosen in a special way, and calculation determined the position as dividing the diagonal in the ratio 1:4. Ewald has now shown (*Phys. Zeit.* April 15, 1914) that by the aid of this determination of the structure of iron pyrites, the Laue photographs of the crystal can be completely unravelled, and the structure is therefore confirmed by an independent method. One small change is all that is required. In order to explain the relative intensities of certain of the less prominent spots in the photograph, it is necessary to suppose that the sulphur atom divides the diagonal, not in the ratio 0·2 to 0·8, as W. L. Bragg had found, but more nearly as 0·224 to 0·776.

If, therefore, it has been possible to find so much from the early and rough measurements of intensity, it ought to be possible to do far more if the measurements are made more accurate.

There are other reasons for attempting to increase the accuracy of the intensity determinations. In the first place, it will be possible in this way to test theories which profess to explain the general process of reflexion of X-rays by crystals. And again, it is important to be able to determine to what extent the intensities are dependent on the temperature of the crystal. The thermal movements of the atoms should affect the reflexion; indeed, Debije has calculated the extent to which they should do so.† Experiment should therefore be of great use in this direction also.

For these various reasons I have endeavoured to increase the degree of accuracy with which intensities can be compared by means of the spectrometer. This paper contains a brief account of the method which appears to be the most suitable, and gives some results of its application to rocksalt and to the diamond. Although much greater accuracy is no doubt still obtainable, the determinations already made seem capable of being applied usefully.

Let us first attempt to give a definite meaning to the term intensity of reflexion.

Imagine a fine pencil of homogeneous* X-rays to proceed from a source at A, to be limited by a slit at B, and to be incident upon a crystal C, so placed that a reflected ray is formed which passes into the ionization chamber D. Let the crystal be so adjusted as to give the maximum value of the reflected ray; and let the ionization current in D be measured in the usual way, the current being allowed to run for a stated time, say t seconds.

We may now remove the crystal and turn the ionization chamber round until the primary beam enters it directly: and we may again measure the ionization current for a given time.

The comparison of these two quantities so obtained does not, however, give us a proper measure of the intensity of reflexion. For, whereas the current in the latter position is proportional to the width of the slit at B, the reflexion in the former case is not proportional to the width of the same slit.

Reflexion takes place only when the angle between ray and crystal is very exactly adjusted. If we consider the rays which come from a single point in the source at A and fall upon a perfect piece of crystal, a very narrow slit at B will let through all the rays which can be reflected at one time, and the reflexion is not in-

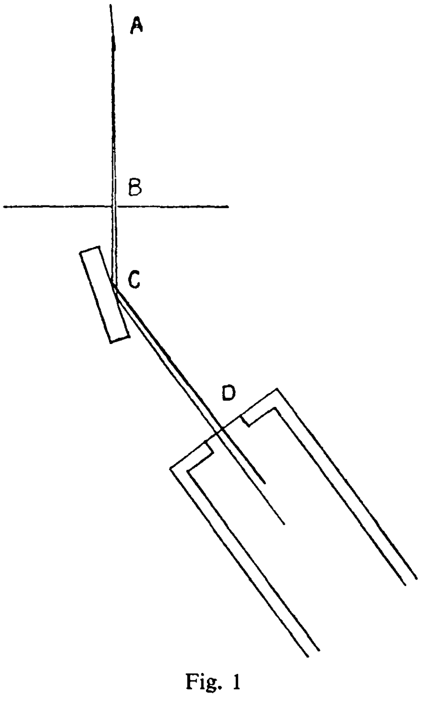

Fig. 1

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* *Proc. Roy. Soc.* **89**, 468.

† *Verh. d. Deutsch. Phys. Ges.* **15**, 678, 738, 857 (1913); also *Ann. d. Phys.* 1914, p. 49.

* Homogeneous pencils have been used in these experiments because they are definite, and can be readliy obtained intense and pure.

creased by opening the slit any wider. The comparison of quantities will therefore bring in the width of the slit, and it cannot be eliminated without a better knowledge of theory than we possess.

But if we turn the crystal by a succession of small steps through the angle at which reflexion takes place, measuring the ionization current at each step, and if we plot the results in a curve, the area of that curve is a measure of the reflexion effect which *does* contain the width of the slit as a factor. If we open the slit at B we prolong in proportion the range over which the crystal is able to reflect. When we compare the quantity obtained in this way with the ionization by the direct primary current the width of the slit disappears. Obviously the height of the slit is of no consequence to a first order of approximation. In fact, the ratio is only affected now by the times during which the current is allowed to run in each part of the experiment, and the magnitude of the steps through which the crystal is turned. As these quantities may be kept constant in different experiments, or altered in known proportions, the ratio is now a true comparative measure of the intensity of the reflexion of an X-ray of given quality by a given crystal face in a given order.*

In some measurements I have found it convenient to observe the ionization current for a given time at each step in the movement of the crystal, and subsequently to add together all the currents observed. This is of course equivalent to plotting the curve and integrating it. At other times I have left the rays in action and advanced the crystal one step at each beat of the clock: the movement of the crystal is begun at an angle at which there is no reflexion, it is taken through the reflexion angle, during which time the leaf of the electroscope moves rapidly, and the rays are turned off when the crystal has ceased to reflect. By this method the integration above mentioned is effected automatically. If it were necessary it would be easy to move the crystal at a uniform rate by clockwork, but in practice the simpler methods are quite sufficient for the purpose. The method of steady revolution has been used by de Broglie* in obtaining photographs of the spectra.

We may now compare the method of the revolving crystal with the methods by which the earlier measurements of intensity were made. The method then used was to move crystal and ionization chamber together, the latter at twice the rate of the former. In this way a 'spectrum' was mapped out, in which the occurrence of 'peaks' marked the existence of homogeneous pencils of greater or less strength; and the height of the peak was taken to represent the strength of the reflexion, and used as a means of comparing the relative strengths of various orders of reflexion. This method would be as good as the other *if crystals were perfect.* But they are not. Rocksalt, for example, is very far from being uniform: it consists rather of an agglomeration of smaller and more perfect crystals put together in imperfect alignment. In consequence, a pencil of X-rays passing through a fine vertical slit and falling on a vertical crystal face, is not reflected simultaneously at all points of the narrow vertical band along which it meets the crystal. It is reflected first in one part, then in another as the crystal turns round, and one piece of it after another presents itself to the rays at the proper angle for reflexion. Since reflexion does not occur within close limits but is spread over a wide range, the highest point of the peak is much lower than it would be if the crystal were perfect, and is no true measure of the intensity of the reflexion.

For example, the curves of Fig. 2 show the result of measuring the intensity of the reflexion of the first order spectrum in the (100) face of rocksalt, the incident rays being limited to a fine pencil. The abscissæ represent the angular positions of the crystal, the ordinates the measured ionization currents. It will be observed how very irregular the curves are; and still more remarkable is the difference between them, for they were obtained from neighbouring portions of the same face. Clearly no measure of intensity is to be obtained from the maximum ordinate of either of these curves. The *areas* of the curves are nearly the same, however. The specimen of rocksalt which was used was very irregular. It is easy to find much better.

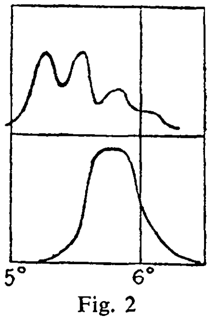

Fig. 2

If a wide pencil of rays is used the results of irregularities are far less obvious. Portions of the crystal

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* W. Lawrence Bragg suggests that this principle is capable of still further development. To turn the crystal round at a definite rate is equivalent to submitting it to radiation from all directions for a given time. Let the intensity of primary radiation within a range $\delta\varphi$ be $R\delta\varphi$, and let $\delta\theta$ be the angle which the slit subtends at the point source. (It makes no difference to the argument that the source is not a point, but must be treated as an assemblage of points.) When the crystal turns round at the rate ω, there will be for a time $\delta\theta/\omega$ a ray making any desired angle with the crystal. If the crystal stood still and were irradiated from all directions in the one plane (to consider one plane only does not affect the generality) for a given time, then there would be *for that time* a ray making any desired angle with the crystal. The experiment therefore is equivalent to submitting the crystal for a time $\delta\theta/\omega$ to radiation R coming from all directions. If k is the coefficient of reflexion, the intensity of the reflected beam may be put equal to $k.R.\delta\theta/\omega$. On the other hand, the measure of the intensity of the primary beam is $R\delta\theta$, if it be allowed to enter the ionization chamber for one second. Hence the ratio of the observed quantities is k/ω; and we find a value for k in absolute measure.

* *C.R.* Nov. 17. 1913.

lying on the narrow vertical band above mentioned may not be reflecting when they should, but other portions which lie off the band are reflecting when they should not. The errors average out. But there is an especial risk in using a wide pencil. When the crystal is set at the fine glancing angles of first order reflexion, five or six degrees it may be, there is danger that some part of the pencil may not fall on the crystal face, unless the latter is very wide. It appears probable that in earlier measurements the magnitudes of several first order reflexions were underestimated on this account.

When, however, the newer method is employed, the effects of crystal irregularity largely disappear even when fine pencils are used. Each piece of the face on which the pencil of X-rays falls gets its chance in turn, and when all is added up, it is as though the differently set pieces had all acted together. This is a very important consideration.

Although the crystal irregularities prevent all parts of it from acting together, the reflected rays from all parts pass through the slit of the ionization chamber even when it is quite narrow. This curious focusing effect has already been explained in the case of a perfect crystal.* It is dependent on the equality of the distances from the crystal to the source and to the slit of the ionization chamber respectively. It may be shown that it holds good to a sufficient extent even when the crystal is not perfect. This is a very convenient circumstance, because the slit of the ionization chamber may therefore be set in position to take in the reflected rays of a given wave-length for all positions of the crystal, and at the same time its width may be limited so that there is no chance of other wave-lengths entering the chamber. For instance, there are two strong rhodium lines, and it is easy to use the one and not the other. The stronger line is really a doublet (see below), and in the higher orders it is possible to use one constituent of the doublet and not the other.

One difficulty, apparently of minor importance, should be mentioned: it is easiest to explain it by a numerical illustration. Suppose the glancing angle is 6°, and the crystal has to be turned through the range from 5° to 7° in order to give all parts of the crystal on which the rays impinge the chance of reflecting. Then it is clear that this area is larger when the angle is small (5°) than when it has the large value (7°). Parts of the crystal are acting in the one case which are not acting in the other. If the crystal were perfect, it must be noticed, this would be quite proper; but an irregular crystal would only give an approximately true value through averaging. It appears probable, however, that this effect is not important. Of course it is well to choose for experiment as good a piece of crystal as is possible.

Some of the crystal faces must be prepared, since natural faces are limited in number. A prepared face should be cut so as to be nearly true, say within half or a quarter of a degree. Want of truth makes very little difference in the determination of the angle of reflexion, but may affect an intensity measurement seriously. This may be seen at once from the Figure.

If the prepared face AA' is not parallel to the crystal planes, whose direction is shown by the dotted line, it will make a considerable difference whether it is set as represented in (*a*) or as in (*b*). The primary pencil IA enters the crystal at A and is reduced to a certain value when it reaches B, B being any point on the path and AB the same length in the two figures. In the one case, however, the reflected pencil has to traverse a much smaller mass of crystal before emerging than it has to do in the other, and the reflexion appears correspondingly greater. This effect is very marked in practice. For example, a (111) face of rocksalt, which reflects the principal rhodium ray at a glancing angle of 11°, was cut 5° out of truth. The intensity of reflexion was then twice as great in the one position as in the other. In the case of a prepared face it is therefore well to measure the intensity effects for both positions and to take the mean, in case the face has not been cut quite truly.

We may now consider some experimental results in the case of rocksalt.

The anticathode A (see Fig. 1) was so placed that the rays left it at a grazing angle in order to pass through the slit at B. The slit was half a millimeter wide, and was placed as close to the crystal as possible. The distance from A to B was 17 cm, from B to C 3 cm, from C to D 12 cm. Although the distances AC and CD were not equal, the focusing was sufficiently good. The crystal was turned by hand, five minutes at a time, one movement for each beat of the clock. About three degrees of total movement was sufficient to take in all the reflexion the crystal could give. The rays used were those constituting the principal line of rhodium. To increase the ionization currect the chamber was filled with methyl bromide.

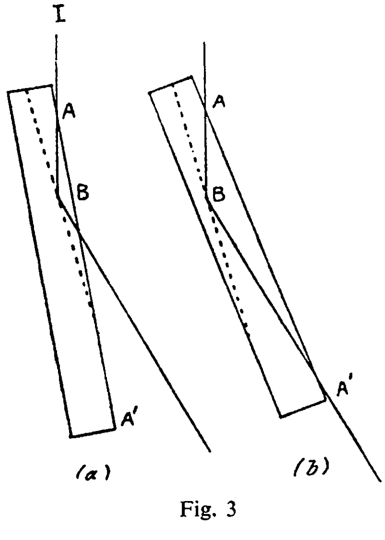

Fig. 3

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* *Proc. Roy. Soc.* **88**, 433.

The measurements were very consistent, consecutive observations differing by not more than one or two per cent. The results are given in the following table, in which the intensity of the first order reflexion is put equal to 100 and the rest are given as percentages.

	1st order	2nd order	3rd order	4th order
Face (100)	100	18·7	6·25	
Face (110)	41	7·05		
Face (111)	16·5	24·4	3·1	4·2

The results for the first two faces show the rapid decline of intensity with increasing order of reflexion which has already been referred to. The planes parallel to the 111 face contain, alternately, sodium atoms only, and chlorine atoms only: as has already been mentioned, the spectra of even orders are therefore much stronger than those of odd orders.

A new experimental fact appears in this, that the intensities of the different faces are comparable with each other. We plot the intensity of each order against the ratio of the sine of its glancing angle to the sine of the glancing angle of the first order of the 100 face. We then find that they all lie nearly on one curve (Fig. 4, lower curve), no matter what face they belong to, excepting, however, the first and third spectra of the 111 face. These last, however, are peculiar, and differ from all the others in that they arise from a difference in atomic weights. In the case of sylvine, where potassium has replaced sodium and the weights of potassium and chlorine are nearly equal, these two spectra do not appear.

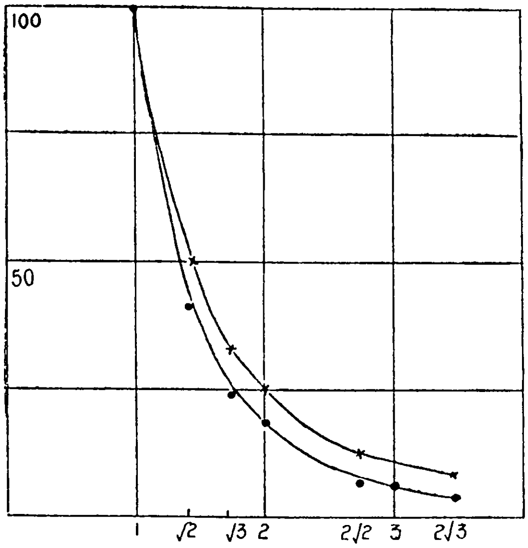

Fig. 4

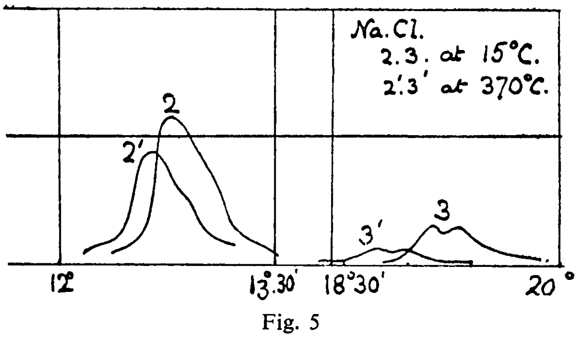

Fig. 5

Considering, therefore, all the reflexions in which the effects of the various atoms add together directly, there is not a different law for each face, but one law for all the faces; and it is of especial interest that those reflexions from the (111) planes, in which the effects of the two kinds of plane add together, fell in with the rest.

It will be observed that the intensities fall away somewhat more rapidly than the inverse square of the sine of the glancing angle. For convenience of comparison, the upper curve in the Figure shows how the observed points would have been placed if the law had been that of the inverse square.

It will be possible eventually to express each of the intensities in the above table in absolute terms, which are independent of all circumstances of the experiment and depend only on the nature of the crystal, the order of the spectrum, or more generally the glancing angle, the temperature, and the wave-length of the rays reflected. This is to be done in the manner explained above (p.5). I have not attempted to do this so far. It will be necessary to use as primary rays a pencil which has been sorted by reflexion. In these experiments the full stream of rays from a rhodium bulb has been used. Some idea of the efficiency of reflexion may be given by the following experimental results.

A sheet of palladium foil was placed over the slit. The foil cut down the intensity of the principal rhodium line to half value and almost destroyed all the radiations of shorter wave-length than the two rhodium lines. A block of aluminium was added, which still further reduced the principal rhodium line to one seventh. When the primary rays had passed through these screens, the principal rhodium line had fallen to one fourteenth of its first value, the lesser rhodium line would be reduced about half as much, and the rest of the radiation would be very largely absorbed. The primary rays entering the ionization chamber directly then caused a leak of 178 in one beat of the clock. The reflexion current of the first order in the 100 face amounted to 676, when the crystal was turned through five minutes of arc for each beat of the clock. If the primary beam had consisted of the principal line of rhodium only, these figures would have been sufficient to give an absolute value. I hope to give such absolute values in a little time.

The effects of temperature upon the intensity of reflexion have been investigated by surrounding the crystal by a small electric oven. Mica windows permitted the passage of the X-rays and stopped convection currents. The results are most conveniently expressed in terms of the ratio of the intensity I at the temperature of the room to the intensity I' at the temperature of the furnace. The temperature was measured with sufficient accuracy by inserting into the oven a thermometer the bulb of which was nearly in contact with the crystal.

The ionization currents were observed for each separate position of the crystal. The Figure shows the second and third spectra of the rhodium line at each of the two temperatures. The diminution of intensity with temperature is very obvious; and the spectrum of higher order is more affected than that of lower order. As the crystal expands, the spacing of the planes increases and the glancing angle diminishes. This effect is also clearly seen.

Sine of glancing angle	Observed values at 15 °C	Calculated, taking $\theta = 200$	Calculated, taking $\theta = 280$	Proportional change on raising to 370 °C	Calculated change
$1 \times 0{\cdot}1097$	100	100	100	1·07	1·075
$\sqrt{2} \times 0{\cdot}1097$	41	46·3	47·6	1·20	1·16
$\sqrt{3} \times 0{\cdot}1097$	24·4	28·5	30·2	—	—
$2 \times 0{\cdot}1097$	18·7	19·8	21·6	1·26	1·35
$2\sqrt{2} \times 0{\cdot}1097$	7·05	7·2	8·9	2·07	1·90
$3 \times 0{\cdot}1097$	6·25	6·0	7·5	1·94	1·92
$3\sqrt{3} \times 0{\cdot}1097$	4·2	3·6	4·9	—	—

The table shows the variation of the effect with the magnitude of the sine of the glancing angle. The latter is expressed in terms of θ, the glancing angle of the first order reflexion by the 100 plane: the value of $\sin\theta$ is 0·1097.

Face	Glancing angle	I/I'
(100)	$1 \times \sin\theta$	1·07
(110)	$\sqrt{2} \times$ –	1·20
(100)	$2 \times$ –	1·26
(110)	$2\sqrt{2} \times$ –	2·07
(100)	$3 \times$ –	1·94

The effects of temperature have been foreseen and calculated by Debije,[*] and the figures of the table may be looked on as measurements of the Debije effect.

It is interesting to compare the results given above with the corresponding figures calculated from Debije's formula. The latter may be written in the form

$$I_\theta = \frac{A}{\sin^2\theta} \cdot e^{-B \sin 2\theta},$$

where A and B are constants, given the crystal, the wavelength, and the temperature, and θ is the glancing angle at which the pencil is reflected. I_θ is the intensity of the reflected pencil.

The constant B contains a quantity which Debije calls the characteristic temperature of the crystal. Its value for rocksalt is not known with certainty, but is believed to be about 240°. In the following table the observed values are set against calculated values. The principal reflexion from the (100) face is always put equal to 100.

The calculated values are slightly modified (become smaller) if we take account of the possible existence of 'Nullpunktenergie' and of an obliquity factor $(1 + \cos^2 2\theta)$, where θ is the glancing angle. The two possibilities are considered by Debije (*loc. cit.*). But the figures are hardly accurate enough as yet to bear discussion in respect to these questions.

On the whole there is certainly a surprising agreement. I find also that fluorspar shows a small temperature effect: this is also in agreement with Debije's theory, for the characteristic temperature is large and the constant B is small.

The diamond is a very perfect crystal, and the intensity curves which are obtained when the crystal is turned round step by step have none of the irregular forms given by rocksalt.

In Fig. 6 the points represent the results (uncorrected for inequality of the electroscope scale) of such a series of measurements. The steps are small, there being twelve for every five minutes of arc, and the regularity of the curve which may be drawn through the points is evidence of the regularity of the crystal. The discontinuity on the right-hand side of the curve is due to the double nature of the rhodium line. Fig. 7 shows the first and third spectra side by side, each being the mean of several experiments. The readings of current

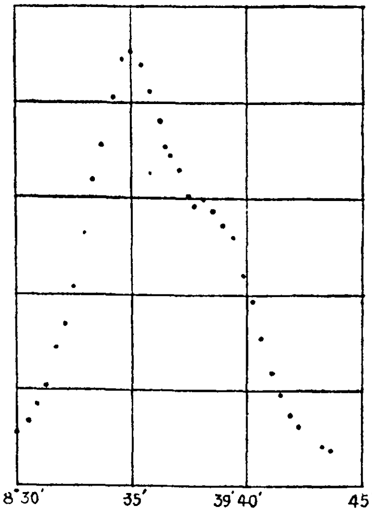

Fig. 6

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[*] *Ann. der. Phys.* 1914, p. 49.

have been corrected for want of uniformity of the readings of the electroscope. The readings of the third order are magnified five times. The separation of the constituents of the doublet is complete in the higher order spectrum. The two constituents are then separated by twelve minutes of arc. In the Figure is shown the result of compounding the two when separated by only four minutes of arc as they are in the first spectrum, and it is seen that the result gives a curve of the experimental form.

The areas of the two curves are to one another as 8·95 to 1. But it must be mentioned that the diamond employed was a thin slip which did not completely absorb the primary rays even when it made an angle with them of only eight and a half degrees. It is not certain therefore that the reflexion obtained was complete; if the crystal had been thicker the reflexion might have been stronger. The point therefore arises as to how the defect is to be calculated.

Let us denote the space absorption coefficient of the rays in the diamond by λ. Let the primary rays enter along *AB* (Fig. 8), and the intensity at *B* be $e^{-\lambda x}$, where $x = AB$ and the primary rays are supposed to have been of unit intensity when they entered. Let $k\delta x \,.\, e^{-\lambda x}$ be the amount reflected while x is increasing to $x + \delta x$. The reflected rays are diminished in the ratio 1 to $e^{-\lambda x}$ while traversing the distance *BC*. Thus the intensity of the reflected pencil is

$$\int_0^{x_1} k\delta x \,.\, e^{-2\lambda x} = \frac{k}{2\lambda}\,(1 - e^{-2\lambda x_1}),$$

where x_1 is the distance which the primary rays move through the crystal. If the crystal is so thick that λx_1 is large, the intensity of reflexion is $k/2\lambda$. If we compare the intensities of reflexion for two different orders, the λ divides out, and the absorption coefficient need not be determined or taken account of. This idea was originally employed by investigators of the scattering which X-rays undergo when passing through ordinary materials.* But if the crystal has a thickness t, and the glancing angle is θ, and if λt cosec $\theta (= \lambda x_1)$ is not large, then the reflected pencil has an intensity

$$\frac{k(1 - e^{-2\lambda t \operatorname{cosec} \theta})}{2\lambda}.$$

If we compare the intensities of reflexion in two different orders for which θ has different values, the absorption coefficient does not disappear. We must find the value of the factor containing the experimental term before we can obtain a true value for the intensity.

The diamond which I have used was very kindly lent to me by Prof. S. P. Thompson. It is a slip about 6 mm square and 0·4 mm thick, its two main faces being cleavage planes. Experiment shows that λt is equal to 0·081. This makes $(1 - e^{-2\lambda t \operatorname{cosec} \theta}) = 0{\cdot}66$ nearly for the first order and 0·33 for the third.

Consequently the true ratio of the intensities of the first and third order reflexions should not be 8·95 to 1, but only half this quantity.

This seems most unlikely, since in the case of all the other crystals experimented upon the ratio is more than 9 to 1. The intensity in general falls off more rapidly than the square of the sine of the glancing angle.

For this reason I sought for some error in the assumptions. It seemed possible that it might be a mistake to assume the absorption coefficient to be the

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* For example, by Barkla, *Phil. Mag.* Feb. 1911.

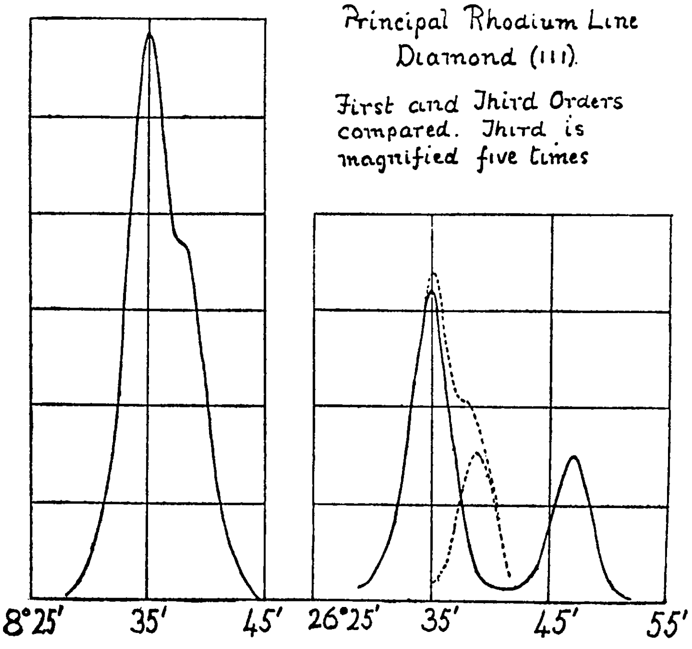

Fig. 7

same when the rays met the crystal at the proper angle for reflexion as when they did not. The strong reflexion which is found experimentally might take place at the expense of the transmitted ray. If this were the case the crystal when reflecting should absorb abnormally; it should be possible to find an absorption band. R. W. Wood found such a band in the analogous case of the reflexion of light by chlorate of potash crystals.

Accordingly the pencil of rays *AB* was made to pass through the diamond *C*, which was mounted on the revolving table of the spectroscope, and afterwards to meet a crystal of rocksalt at *C′*. This was adjusted until it reflected into the ionization chamber through the slit at *D*. The diamond was then turned very gradually through the angles (8°35′ and 8°39′) at which it is itself able to reflect. At the same time the strength of the pencil reflected by the rocksalt was continuously observed. It was found that there was a considerable decrease in the intensity of the pencil transmitted by the diamond and reflected by the rocksalt at exactly the angles mentioned. Thus a special absorption *does* exist, and we understand why the attempt to apply a formula in which the ordinary absorption coefficient is used leads to unlikely results. Fig. 10 shows two curves: the upper records the changes in the intensity of the pencil reflected by the rocksalt as the diamond is turned, the lower the changes in the case of the pencil reflected by the diamond. The two sets of measurements are made by means of the same ionization chamber, placed in different positions, as shown in the figure.

The existence of this special reflexion makes it very difficult to interpret the experimental results. The ratio of 8·95 to 1 given above may be explained on the supposition that there is no appreciable temperature effect in the diamond, which would be in agreement with Debije's theory, that the intensity in such case varies as the inverse square of the sine of the glancing angle, and that for the first and third orders the crystal may be treated as infinitely thick. But there may be other explanations. In any case further experiment is needed.

A useful result of a different nature may be derived from the measurements with the diamond. By averaging the large number of observations an accurate value can be found for the difference between the glancing angles of reflexion of the first and third order. The means of two different sets of observations gave 17°59·8′ and 18°00·9′ respectively: the figures refer to the larger constituent of the doublet. From this we may determine the value of the glancing angle for either order.

When a crystal is mounted on the spectroscope table, it has generally some error of adjustment. This may be corrected by swinging the ionization chamber over to the other side and turning the crystal through 180°. The glancing angle is the mean of the two values observed. It is probably easier to measure with accuracy the difference between the glancing angles of the first and third orders, as the angular movements are simpler and smaller. But there is an entirely different reason for preferring the latter measure to the former. Where the rays fall on the diamond they penetrate some distance into it, as shown in the figure, and the actual point of reflexion is indeterminate. The reflected pencil is broader than the incident. The angle at which the ionization chamber is set to catch the reflected pencil is a little smaller than if the reflexion took place at the surface, the defect being greater at the smaller angles.* In the original paper the series of the glancing

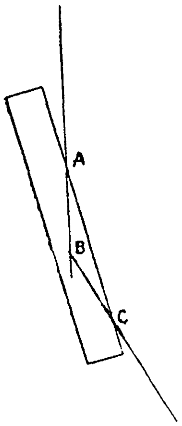

Fig. 8

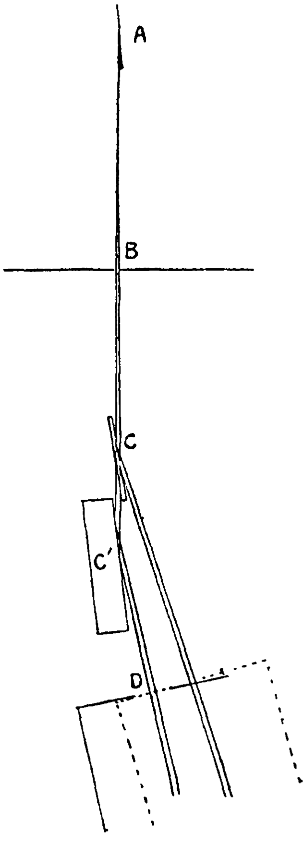

Fig. 9

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* *Proc. Roy. Soc.* **89**, p. 279.

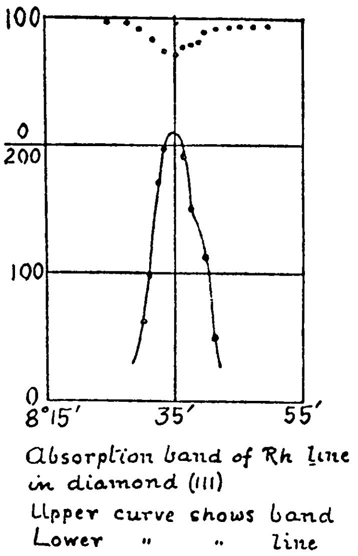

Fig. 10

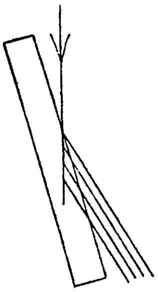

Fig. 11

angles of the first, third, fourth, spectra were found to be 0·1456, 3 × 0·1475, 4 × 0·1485, and 5 × 0·1490. The true value of the glancing angle was assumed to be 0·1495.

When, however, we turn the crystal round to look for the angle of reflexion, the observed values require no such qualification. The angle at which reflexion takes place is determined by the setting of the crystal table, and the place at which the reflexion occurs is of no consequence. By taking the difference of the settings of the crystal table at the reflexions of the first and third order, we eliminate any error in the placing of the crystal.

Let θ be the glancing angle of the first order. We take 18° 00·5′ as the mean of the two angles given above. We then have

$$\sin(\theta + 18°00{\cdot}5') = 3 \,.\, \sin\theta\,;$$

whence

$$\theta = 8°35{\cdot}2' \quad \text{and} \quad \sin\theta = 0{\cdot}1494\,.$$

The density of diamond is 3·520. Let m denote the mass of the hydrogen atom. It has been shown† that there are eight carbon atoms in the elementary cube of side $2a$ (*loc. cit.*).

Hence

$$(2a)^3 \times 3{\cdot}520 = 8 \times 12 \times m$$

$$\therefore\ 2a = 3{\cdot}01 \times m^{1/3}\,.$$

The spacing of the (111) planes

$$= \frac{2a}{\sqrt{3}}$$

$$= 1{\cdot}738 \times m^{1/3}\,.$$

Therefore λ, the wave-length of the larger constituent of the rhodium doublet

$$= 2d \,.\, \sin\theta$$

$$= 3{\cdot}476 \times 0{\cdot}1494 \times m^{1/3}$$

$$= 0{\cdot}5194 \times m^{1/3}\,.$$

If we take

$$m = 1{\cdot}64 \times 10^{-8}\,,$$

we find that

$$\lambda = 0{\cdot}614 \times 10^{-8}\,.$$

Summary

An account is given of experiments in which the intensities of reflected X-ray pencils of various orders are compared with each other, and the results are considered in reference to the recent theoretical discussion by Debije.

It appears that there is a striking agreement between theory and experiment in the case of rocksalt.

The difficulties of experiment with the diamond are also discussed. The existence of an X-ray absorption band in the diamond is demonstrated. The experiments give opportunity for an accurate determination of the wave-length of the rhodium X-rays.

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† *Proc. Roy. Soc.* **89**, p. 282.