

PART A. THE QUANTITATIVE EXAMINATION OF SOME
ELECTRON DIFFRACTION PATTERNS

PART B. AN EXAMINATION OF THE STRUCTURE OF
SOME EVAPORATED METAL FILMS BY
ELECTRON DIFFRACTION

By

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P R E F A C E.

The work described in this Thesis was carried out at the Imperial College of Science and Technology under the direction of Professor G.P.Thomson. It has already appeared in two papers in the Philosophical Magazine, one in November 1935 and the other in November 1936.

Part A is concerned mainly with the investigation of the theory of the diffraction of electrons by a single crystal cleavage face. In connection with this I should like to express my gratitude to Mr. J.W.Harding for the help which he has given in frequent discussions upon the theoretical aspect.

Part B is in the nature of a summary of observations made during an examination carried out with the primary object of discovering the best mode of preparation of evaporated metal films for searchlight mirrors.

In view of the considerable amount of work at present being conducted in connection with the preparation and properties of evaporated metal films, it was felt that any information about the actual crystal structure of such films might be of help and should be published.

I wish to thank Sir Robert Robertson and Professor W.T.Gordon for their kindness in lending the diamonds.

Finally, I wish to express my gratitude to Professor G.P.Thomson, who suggested the main problem dealt with in Part A, for his helpful advice and kindly interest throughout the work.

PART A

THE QUANTITATIVE EXAMINATION OF SOME ELECTRON
DIFFRACTION PATTERNS

THE QUANTITATIVE EXAMINATION
OF SOME
ELECTRON DIFFRACTION PATTERNS.

CHAPTER 1.
INTRODUCTION.

The close analogy between the diffraction of X-rays and of electrons by a crystal lattice was recognised immediately the latter phenomenon was observed. As a result of this similarity, the younger subject, electron diffraction, has probably lost far more than it has gained. The fact that much of the theory was found apparently ready to hand when the new technique was developed, prevented the subject from receiving the attention which it deserved from the theoretician. Although X-ray diffraction theory has been successfully modified to explain many of the observed phenomena of electron diffraction, there are an ever increasing number of unexplained facts and of inconsistencies in our views. This can only be attributed to the non-existence of any satisfactory theory of electron diffraction, free of all limitations which apply only to X-rays, and taking into account such important facts as the readiness with which electrons are inelastically scattered.

In 1928, Bethe^{*} published an account of his dynamical theory of electron diffraction, the immediate aim of which was to explain Davisson and Germer's results for the diffraction of slow electrons by a single crystal of nickel. His treatment is based upon Ewald's theory of X-ray diffraction. He regards the crystal as a periodic variation of potential, which he represents by a three dimensional fourier series. By substituting this expression for the potential in the equation representing a plane incident electron wave train and then seeking a solution in the form of another fourier series, he obtains a solution representing all the possible plane waves which can exist in the crystal lattice. The intensities of all these possible waves are inter-related, but by ignoring all but the strongest ray, which he considers quite justifiable for fast electrons and a good approximation for slow ones, Bethe calculates the range of wavelength over which a certain strong diffracted beam would exist. Davisson and Germer's experiment was not designed in such a way as to make it possible to check the theory at all accurately, but, in spite of this, the theory was quite generally accepted

* Bethe. Ann.Physik. vol. p.55(1928)
Also Handbuch d. Phys.vol.24, p.385.

very largely as a result of Bethe's successful explanation of the discrepancy between the observed directions of the diffracted electron beams and the positions in which diffracted X-ray beams of equal wavelength would be expected to appear, in terms of an inner potential in the crystal.

When a beam of fast electrons is fired upon a single crystal cleavage face at glancing incidence, the resulting diffraction pattern, known as a reflection pattern, differs considerably from the analagous X-ray case in that several diffraction spots may appear at once, and the spots persist over quite a wide range of angle of incidence. The fact that several strong diffracted beams occur simultaneously is at variance with Bethe's assumption that in the case of fast electrons only one really strong beam appears, the others being so weak as to be negligible. Although no accurate observations had previously been made, it was fairly obvious that the range of angle of incidence over which a diffracted spot persisted was much greater than that predicted by Bethe's theory. Attention was first drawn to the phenomenon by Prof. G.P.Thomson, and it has been attributed to lack of penetration due to absorption, i.e. inelastic scattering, of the electron beam. The great objection to this explanation is that the Kikuchi lines from crystals showing

quite considerable persistence of the spots are quite sharp. Since there is no reason for supposing that the diffuse radiation which gives rise to the lines will penetrate **more** than the main electron beam, it is difficult to account for the sharpness of these lines. We should expect their angular breadth to be of the same order as the range of angle of incidence over which the spots are found to exist.

The purpose of this work was to measure the angles over which the spots persisted and also the angular breadth of the corresponding Kikuchi lines, and to compare these with the values to be expected from Bethe's theory. The diamond was chosen as the crystal to be used because it very closely approaches the perfect crystal. This was confirmed by the fact that all the specimens examined gave sharp Kikuchi lines, and sharp lines are an indication of crystal perfection.* An additional reason for choosing the diamond was the fact that it shows the persistence of the spots in a very marked manner. If an electron beam is diffracted by reflection from a natural face of diamond, which is parallel to the (111) planes,

* G.P.Thomson. Phil. Mag. Vol.18, p.640, (1934)

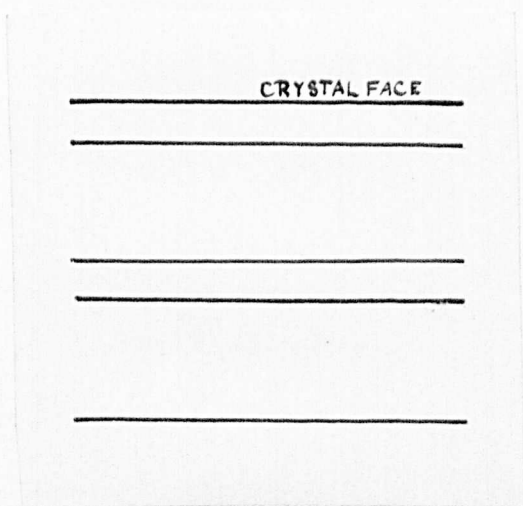


Fig. 1.

a faint spot is visible at all angles of incidence, in the position corresponding to specular reflection. At the Bragg angle the spot becomes much more intense and then as the angle is increased it fades until it reaches a minimum about two thirds of the way between one order and the next. As the angle is further increased, the intensity again rises to a maximum value at the next Bragg reflection.

In this work also, the intensity of the second order reflection from the (111) face was compared with that of the third order. (The first order does not appear on account of the high inner potential of diamond). According to the simple theory, which regards the atoms as spherically symmetrical scattering centres, the second order is forbidden by the structure factor. The reason for this will be immediately obvious from reference to Fig.1. Intermediate planes occur at one quarter of the main spacing, so that for rays scattered in such a direction that the path difference corresponding to the main spacing is two wavelengths, the path difference corresponding to the subsidiary spacing is one half wavelength. Thus there is destructive interference between the rays scattered from each pair of closely packed planes.

This argument applies equally well to X-rays and to electrons. In the case of X-ray diffraction, a faint second order spot does occur but in the case of electrons the second and third orders are of comparable intensity., as Prof. G.P.Thomson has pointed out.

It was hoped also to decide whether it was possible to detect any difference between the electron diffraction patterns from the two types of diamond recently discovered.*

* Sir Robert Robertson, J.J.Fox & A.E.Martin, Phil. Trans. Roy. Soc., vol. 232. p.462. (1934)

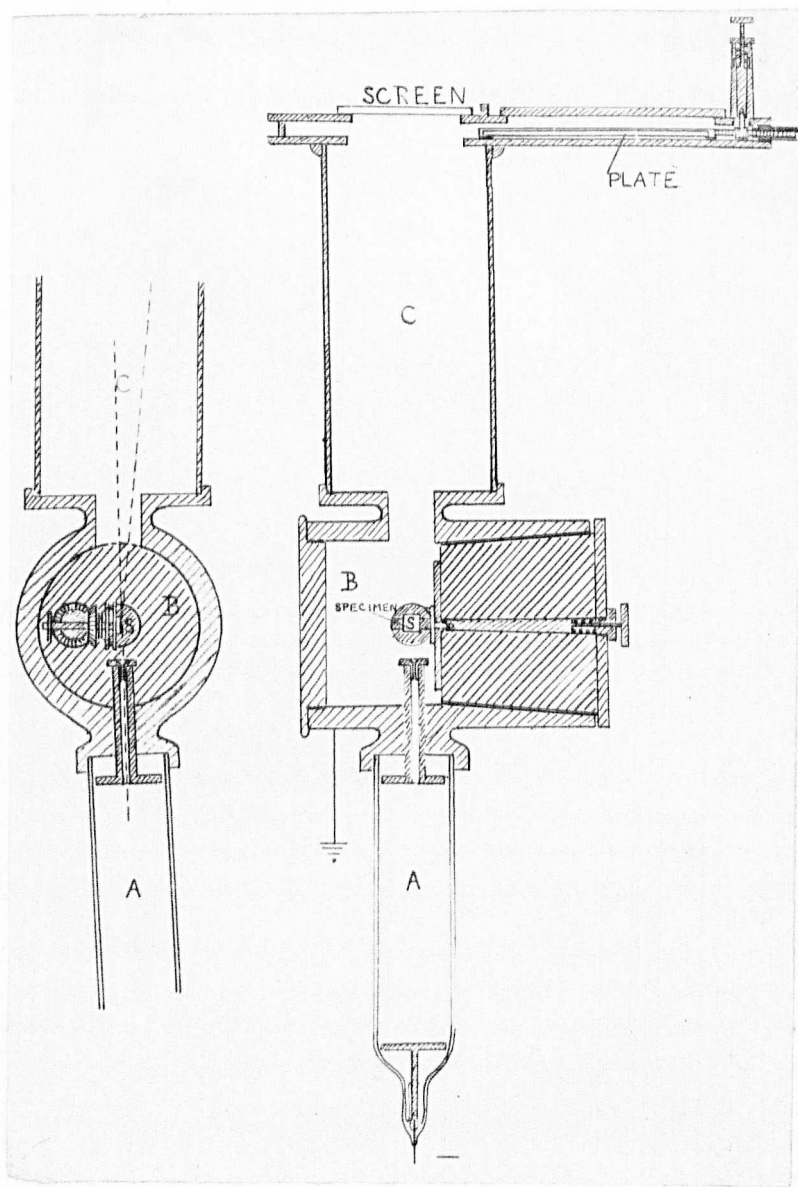


Fig. 2.

Camera length.

Specimen to Plate 37.7 cms
 Specimen to Screen when Plate
 Holder was Removed, 37 cm

CHAPTER 2.THE APPARATUS.

The electron diffraction apparatus used was a modification of that designed by G.P. Thomson. The unmodified form of the camera is shown in Fig. 2. The electron beam was generated in the gas discharge tube A, which was run by an induction coil, the current from the coil being rectified by a diode valve, and smoothed by a condenser. The electron beam leaving the discharge tube was defined by two small holes, one at the bottom and one at the top end of the tube constituting the stem of the anode. These holes were .15mm. in diameter. The specimen S was mounted as shown. By rotating the large ground joint the angle of incidence could be varied, while small ground joints passing through the large cone enabled the specimen to be moved in and out of the beam and to be rotated about the normal to the specimen face. After striking the specimen, the diffracted electrons passed up the chamber marked C and struck either the fluorescent screen or a photographic plate which could be brought in front of it by means of a rack and pinion, operated through a ground joint.

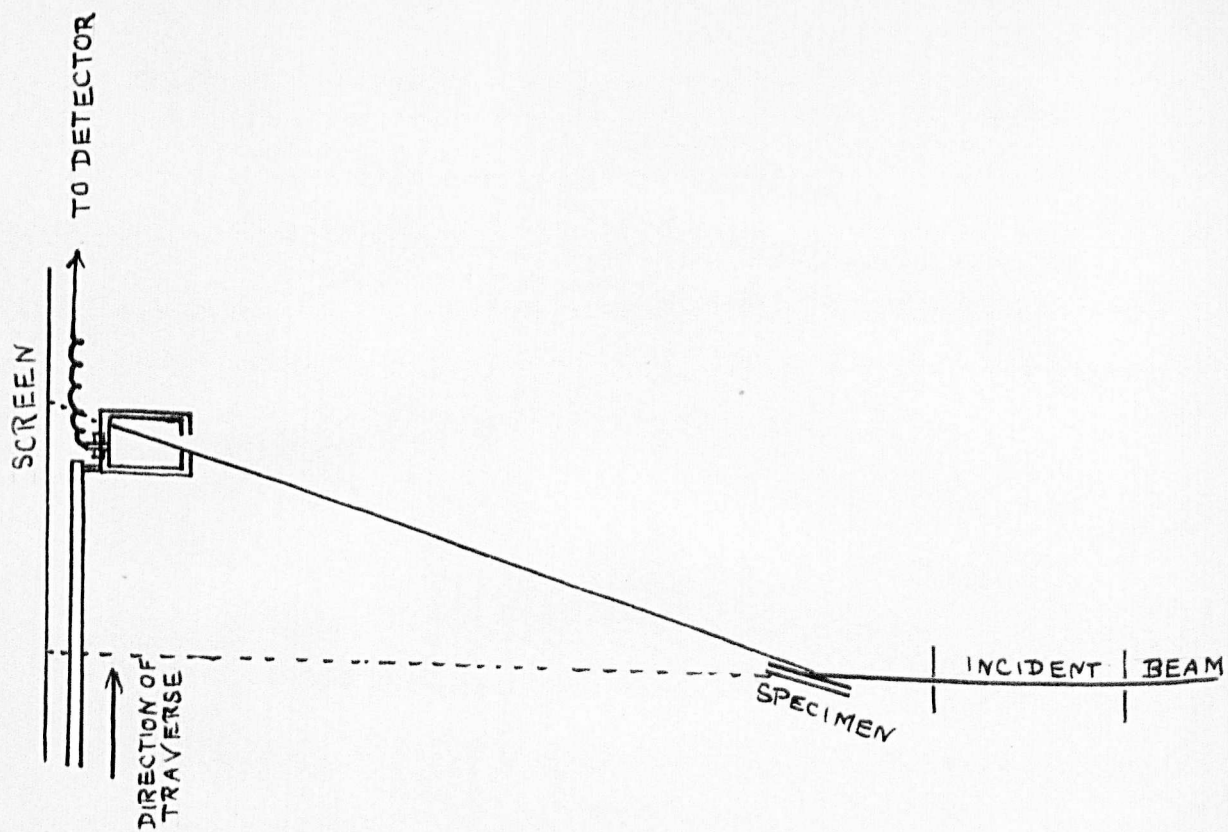


Fig. 3.

For the intensity measurements the apparatus described above was modified in the following way. The casing carrying the plate slide was unscrewed from the top of the tube C and was replaced by a plain brass collar to which a circular fluorescent screen was waxed. A small Faraday cylinder was arranged to traverse across the inside of the camera just below and parallel to the screen, in a direction perpendicular to the line of intersection of the plane of the crystal face and the screen. (See Fig.3.) The cylinder was moved by means of a rack and pinion, operated through a ground joint. The hole in the earthed outer casing of the cylinder was between 3 and 4mm. in diameter, and that in the inner chamber was the same size. The inner cylinder was insulated from the outer by means of an amber bush and was connected by a flexible wire to a terminal passing through an insulating bush in the outer wall of the camera. The connection between this terminal and the detecting system was made by a thick copper wire, enclosed in a glass tube and supported in an earthed brass tube by amber bushes. The charge reaching the cylinder was allowed to leak away through a high resistance of the sputtered chromium type, of the order of 2×10^{11} ohms. The potential drop across this resistance was measured by a Lindemann electrometer.

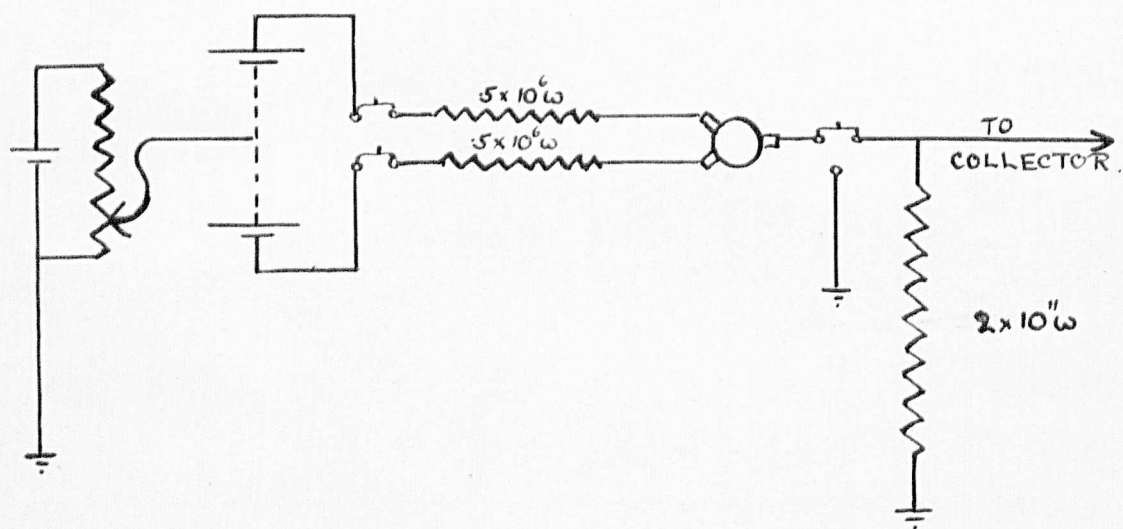


Fig. 4 .

The circuit arrangement is shown in Fig.4. and is one commonly used with such instruments. The whole detecting system was enclosed in an earthed perforated zinc box which provided perfectly satisfactory shielding in spite of the presence of the high tension supply in the room. When the apparatus was first assembled, a few millimetres of the wire from the camera to the detector were left unshielded. This was sufficient to make the whole of the arrangement exceedingly unstable.

Slow changes of intensity of the primary beam and of the leakage resistance caused variation of the readings obtained from day to day, but since absolute measurements of intensity were not required, this slow changing of conditions was of no importance.

THE HIGH TENSION SUPPLY.

A more serious difficulty was the maintaining of the beam at a constant voltage during the course of one set of readings, which might require up to half an hour to obtain. The high tension supply circuit was the one usually used with the Thomson, Fraser type of apparatus and which has already been briefly described, except that the capacity of the smoothing condenser was increased from .002 to .014 microfarads in the later experiments. The discharge tube was run for about half an hour before

readings were commenced, and the spark gap was adjusted so that a spark passed once or twice per minute. A fall of about 1 k.v. in the voltage across the tube, due to a pressure change, was accompanied by an increase in current which was easily detectable by means of a milliammeter connected in the earth lead from the camera. A rise in voltage caused a spark to pass. With this arrangement, a fairly steady potential drop was maintained across the tube. However, the greater part of the uncertainty in this work was due to variations of voltage.

DEFINITION OF THE BEAM.

In the preliminary experiments the length of the anode tube, which determined the distance apart of the two holes which defined the beam, was only 6.5 cm. With this arrangement a number of difficulties were encountered. The beam was slightly divergent on account of the geometrical arrangement. In Fig. 5 is shown the relative intensity distribution across the spot on the screen determined theoretically on the assumption that the electron intensity is uniform over the area of the first hole and also uniform throughout the small solid angle subtended by the second hole at the first. In view of the smallness of this solid angle and of the hole, it is probable that these conditions are satisfied to a close degree of approximation. The minimum width of the beam

is .15 mm, at the point where it leaves the second hole. The further the beam proceeds, the greater its diameter becomes. With the distance between the two anode holes only 6.5 cms., the specimen was about 7 cms. from the top hole, so that the theoretical width of the beam, at the specimen, was about .3 mm. The actual width was probably rather more than this as a result of collisions with the residual gas molecules and possibly some slight scattering by the edges of the second hole. This being so, it was impossible to make the whole beam strike the surface of the diamond, at small angles of incidence, on account of the limited size of the specimens. A further difficulty was caused by the fact that the angle of divergence of the beam was of the same order as the variation of angle of incidence which it was desired to measure.

With a view to reducing these difficulties, the length of the anode tube was increased to 11.5 cms. This had the effect of carrying the top hole to within about 1.5 cms. of the specimen and this, combined with the decreased spread of the beam, made the diameter of the beam where it struck the specimen only about .15 mm. The specimen used most was about 1 cm. long, so even with a glancing angle as small as .02 radians the whole beam struck the face. The calculated intensity distribution

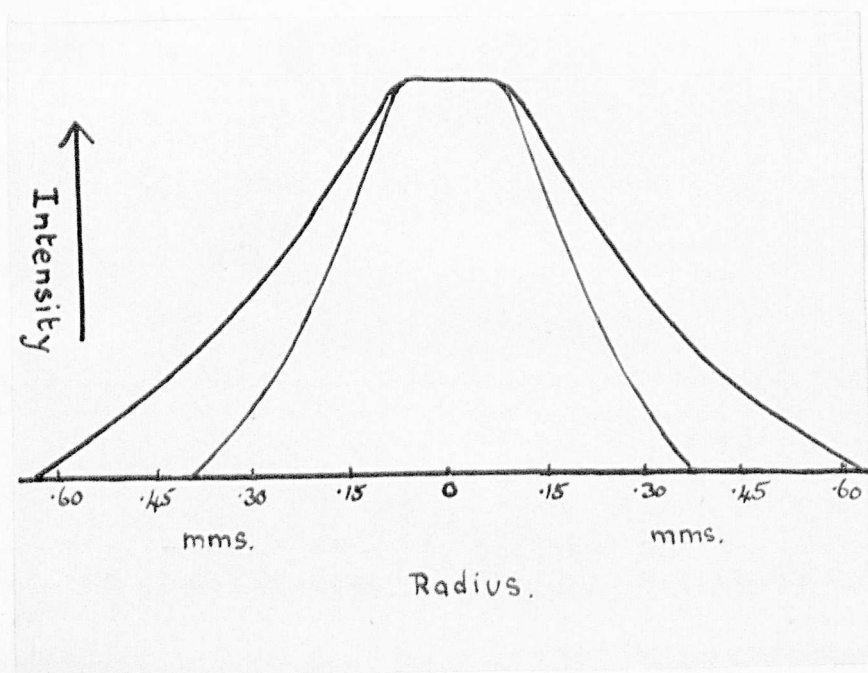


Fig. 5.

in the spot on the screen is shown plotted in Fig.5, the inner curve being that for the longer tube.

MEASUREMENT OF THE ANGLE OF INCIDENCE.

Changes in the angle of incidence of the beam were measured by means of a galvanometer lamp and scale, the spot being reflected from a small mirror on the main ground joint of the camera, to which the specimen was attached. The actual angle of incidence was not required, but could be calculated subsequently if necessary.

THE DIAMONDS.

The diamonds used were kindly lent by Sir Robert Robertson, F.R.S. and by Prof. W.T.Gordon, and the numbers by which they are referred to here are those which they have given them. Detailed descriptions of some of the stones will be found in the paper by Sir Robert Robertson, J.J.Fox and A.E.Martin on the two types of diamond.

Although a considerable number of stones were examined, and although most of them gave very good diffraction patterns at the larger angles of incidence, it was not possible to use many of them for this work as they charged up when struck by the electron beam. As a result of any appreciable charging the pattern is usually completely destroyed.

D.2 "Extraordinary Type": Most of the work was done with

this stone which had a highly polished (111) natural face showing only a few cleavage lines. The face was approximately an equilateral triangle of 1 cm. side.

D.1. "Ordinary Type": This stone had previously been examined by Prof. G.P. Thomson by electron diffraction, and had given a good pattern. When examined for the purpose of this work, it was found to give only a few very blurred spots and much background. This was at the time attributed to some surface contamination resulting from the sputtering of gold on the surface. Washing in organic solvents did not make any improvement. Subsequent to this work the stone was again examined after washing in hydrofluoric acid, on the advice of Prof. Gordon and it was then found to give a good pattern.

D.10 "Ordinary Type": This stone was smaller than the others used, having a natural (111) face which was approximately circular and about 4 mm. in diameter.

D.26. "Ordinary Type": This stone had a natural (111) face which was an equilateral triangle of 1 cm. side. It charged up badly even when mounted in a cell and backed with mercury.

D.27. "Ordinary Type": This diamond had two natural (111) faces. Examination under the microscope showed small equilateral triangular plates on these surfaces.

D.28 "Ordinary Type": This specimen had a triangular natural (111) face of about 1 cm. side. Microscopic examination showed it to be dotted with small pyramid shaped holes of about $1-10\mu$ side. The stone did not give a very good pattern.

CHAPTER 3.

EXPERIMENTAL PROCEDURE

AND

RESULTS OF INTENSITY MEASUREMENTS.

EXPERIMENTAL PROCEDURE.

Davisson & Germer, in their experiments with slow electrons, fired the beam normally on to the crystal face and observed the variation of intensity of a particular diffracted beam as the wavelength of the incident electrons changed. It was to this case that Bethe first applied his theory. In this work, a beam of electrons of constant wavelength was fired on to the crystal face at glancing incidence and the variation of intensity of the diffracted beam with changing angle of incidence was observed. It has already been mentioned that in the case of the diamond, a diffracted spot always appears in the position corresponding to specular reflection.

The adjustment of the Faraday cylinder to receive the diffracted beam was made in the following way. The cylinder was mounted eccentrically at the end of the traversing arm, so that by rotating it about this point

it was possible to adjust it in a direction perpendicular to the line of traverse and to the beam. By trial and error, the cylinder was adjusted to traverse in the plane of incidence, it being necessary to remove the screen to do this. When the camera was in use, the cylinder cast a circular shadow on the screen, but even in the shadow there were still slight traces of the pattern as a result of the phosphorescence of the screen material. The receiver was adjusted so that the persisting image of the spot fell at the centre of the circular shadow of the cylinder, thus ensuring that the diffracted beam entered the collector.

When the discharge was running steadily, having been adjusted as described, the angle of incidence was reduced to less than the Bragg angle for the second order, and the collector was adjusted to receive the faint reflected spot. The angle of incidence was then increased by stages by rotating the main ground joint, and the intensity of the corresponding reflected spot was recorded. In order to eliminate the background, another traverse was taken along a line parallel with the original traverse but about 3 to 4mm. from it. Since it was impossible to move the cylinder perpendicular to the direction of traverse without taking off the screen, which was impossible if conditions were to

be kept constant, it was necessary to move the whole diffraction pattern. This was done by bringing a magnet into a position, about half way up the camera, such that the pattern was displaced through about 3 mms. in a direction perpendicular to the centre line. Although this produced no noticeable distortion of the pattern, some such distortion was undoubtedly present. However, this method gave a curve which was certainly a good approximation to the background distribution of intensity.

When calculating the variation of intensity of any one diffracted beam, Bethe assumes that it is the only strong beam. As has already been mentioned, this is by no means true, even in the case of fast electrons. In order to satisfy the condition as far as possible, however, the azimuth setting of the crystal was always arranged so that any spots appearing during the traverse, other than those in the plane of incidence, were always far out from the central spot. These spots were of lower intensity than those near the central spot, and less likely to have a strong interaction with the spots in the plane of incidence.

RESULTS OF INTENSITY MEASUREMENTS.

From the sets of readings obtained, curves were plotted showing intensity in arbitrary units against change in angle. The curve for the background intensity was

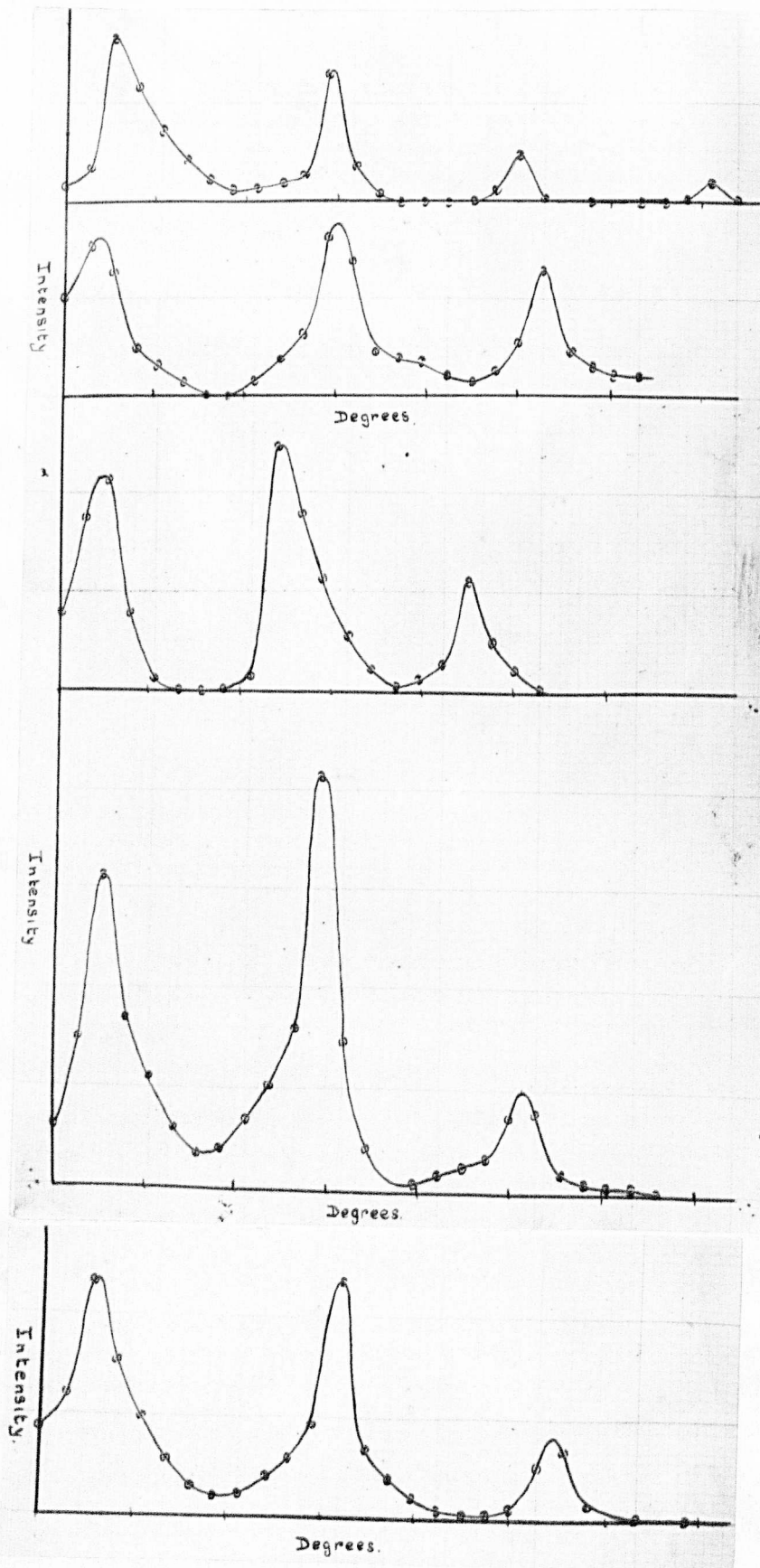


Fig. 8.

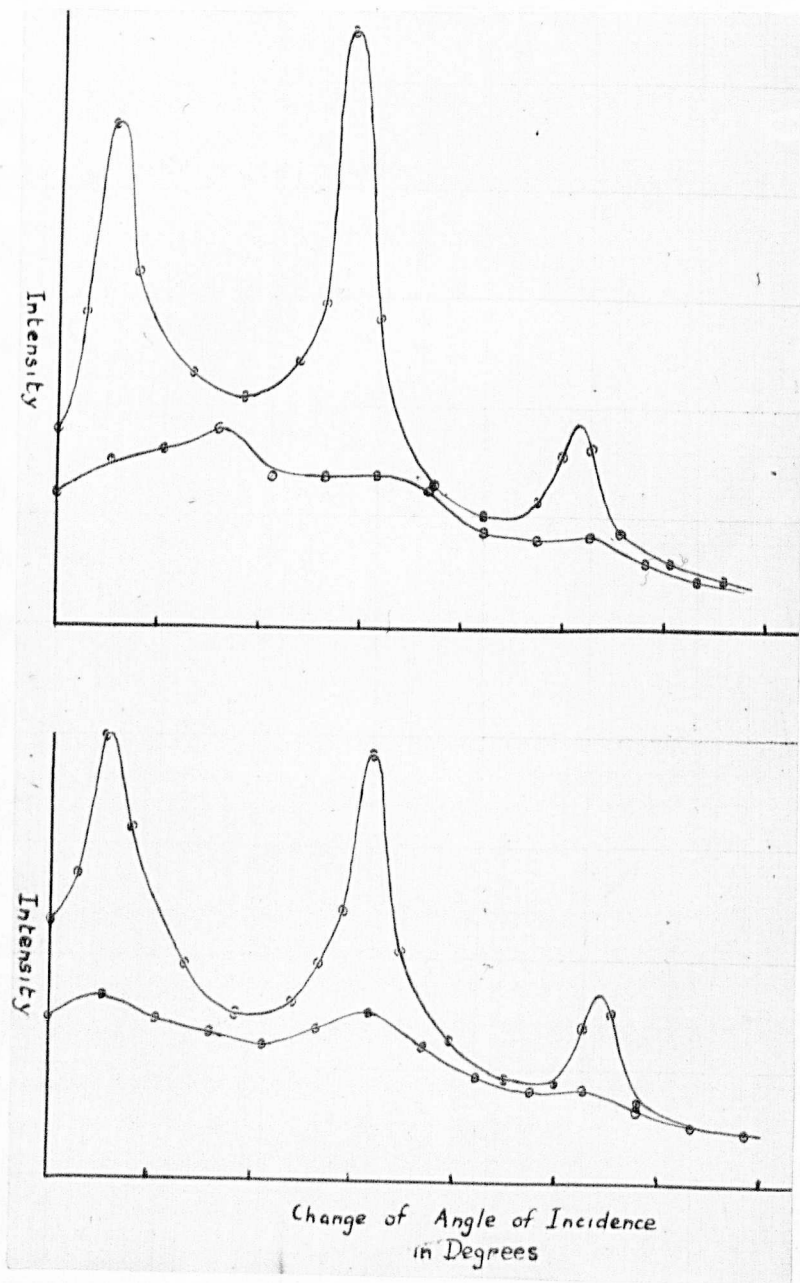


Fig. 7.

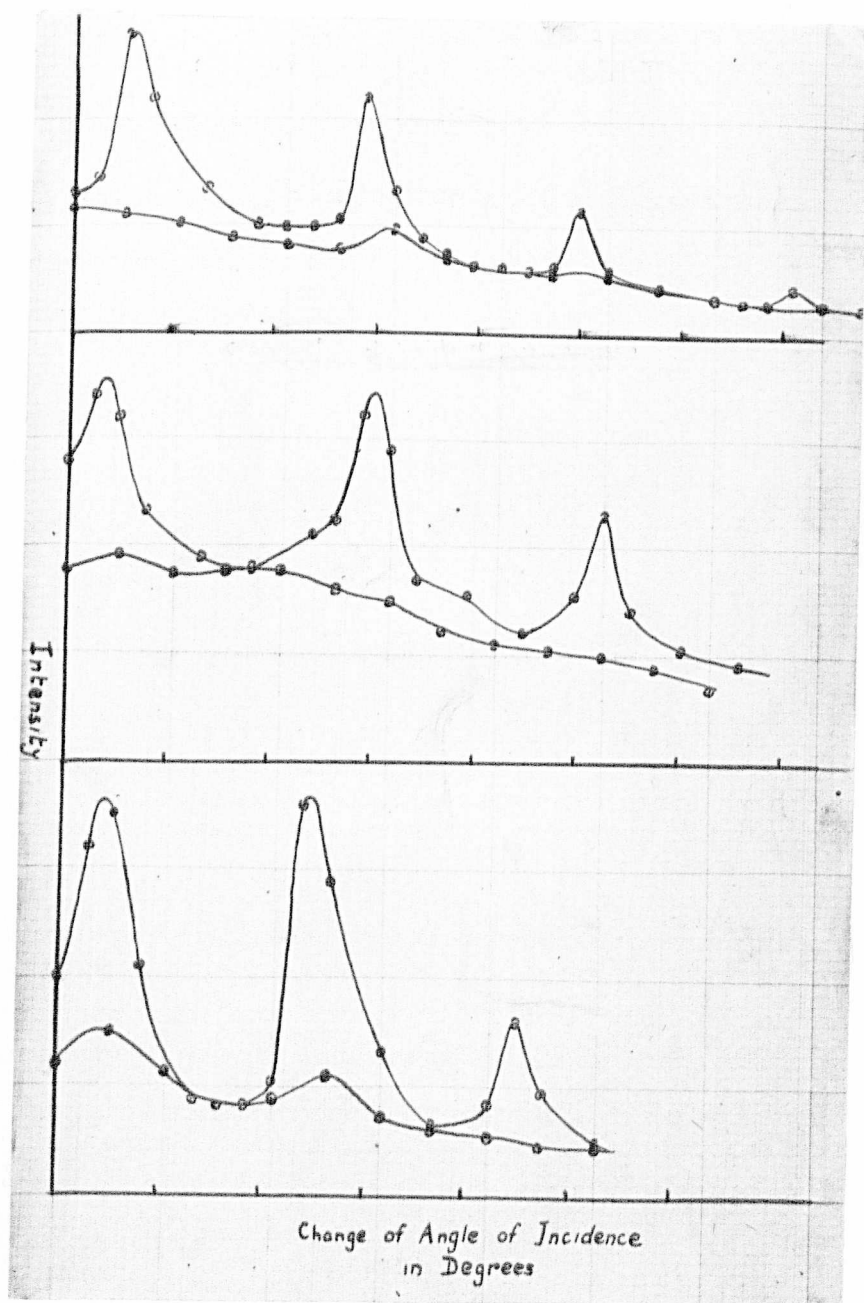


Fig. 6.

plotted on the same graph, and from these pairs of curves, curves showing the difference in intensity between the spots and the background were plotted. Five sets of curves obtained in this way are shown in Figs. 6, 7 & 8, while the relative intensities and half intensity spreads of the various orders are shown in Tables 1 & 2. The values of the spread shown in the Table are the sums of the deviations on either side of the Bragg position, which reduced the intensity to half the maximum.

TABLE 1.

SHOWING THE HALF INTENSITY SPREADS OF VARIOUS ORDERS.

Wave Length	Half Intensity Spread			Spread calculated for a wave length of .06A.		
	2nd.	3rd.	4th.	2nd.	3rd.	4th.
.067	33'	23'	18'	27'	18.5'	14.5'
.072	43	29	19.5	30	20	13.5
.060	38	36.5	25	38	36.5	25
.069	23	29.5	23	17.5	22	17.5
.072	38	21	23	27	15	16
Mean				30 $\pm$ 3	22.5 $\pm$ 4	17.3 $\pm$ 2

TABLE 2,
SHOWING THE RELATIVE INTENSITIES OF THE
SECOND, THIRD & FOURTH ORDERS.

TABLE 2.

<u>RELATIVE INTENSITIES.</u>		
<u>Wave Length</u>	<u>3rd Order/2nd Order</u>	<u>3rd Order/4th Order</u>
.067	.77	2.6
.072	1.12	1.39
.060	1.26	1.32
.069	1.46	3.95
.072	1.02	2.58
Mean	1.1 $\pm$.1	2.4 $\pm$.5

All the curves were not taken at the same voltage but it may be shown from Bethe's theory that the spread is directly proportional to the square of the wavelength. On this basis, the spreads of the various orders have been reduced to spreads corresponding to a wavelength of .06 Å. These values and their mean are shown in Table 1.

A number of preliminary curves were obtained with the apparatus before the anode was lengthened and with only .002 microfarads smoothing in the high tension supply circuit.

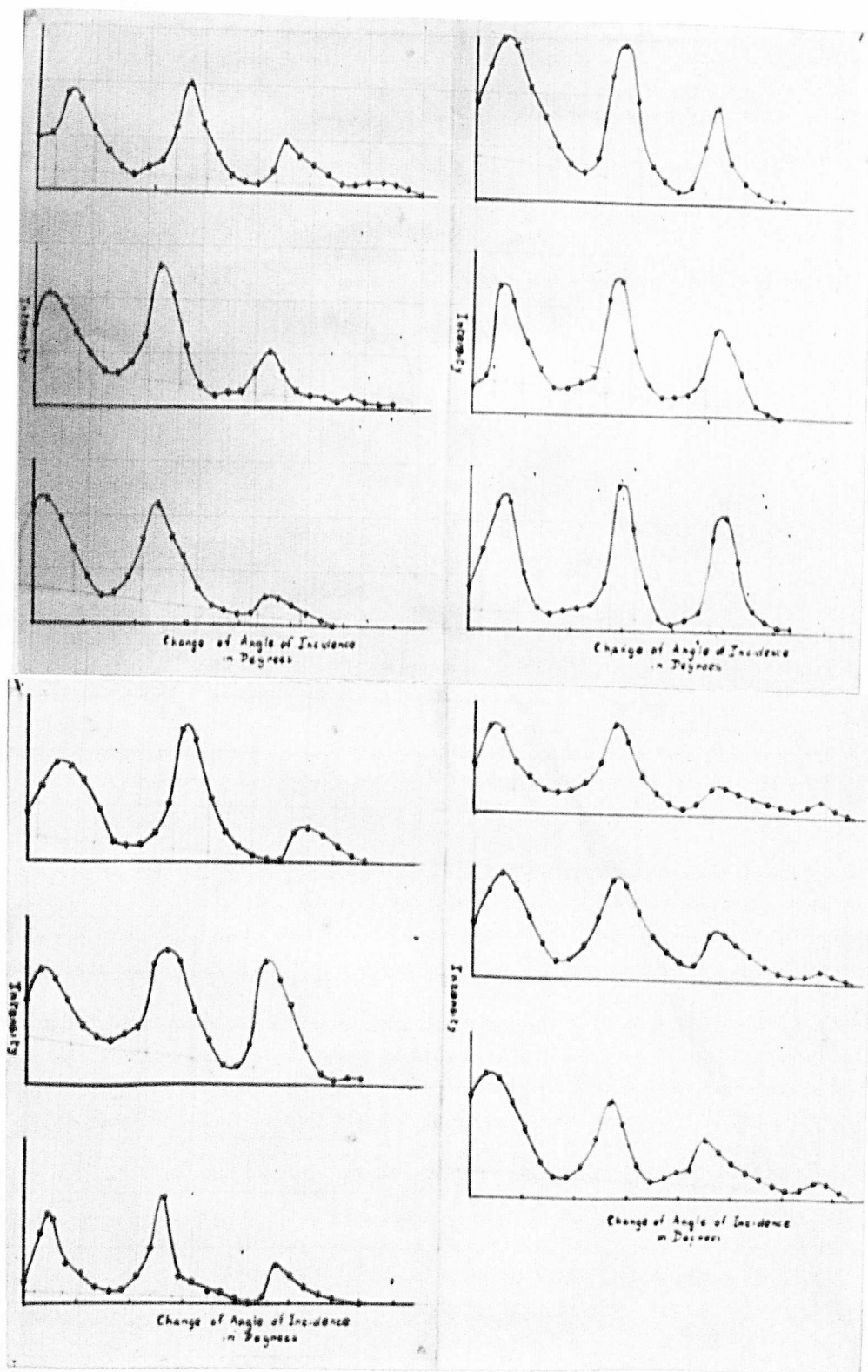


Fig. 9.

The curves showing the intensities of the spots, with the background subtracted, are shown in Fig.9, while the values of the half intensity spreads and the relative intensities of the different orders are shown in Table 2. All these curves were obtained with electrons having a wavelength of about $.06 \text{ \AA}$.

TABLE 3.

ANGLE OF HALF INTENSITY SPREAD.			RELATIVE INTENSITIES.	
2nd. Order	3rd. Order	4th. Order	<u>3rd.Order</u> 2nd.Order	<u>3rd.Order</u> 4th.Order
41.5 '	39'	61.5 '	1.21	2.66
61.5	53.5	48.5	1.07	2.00
75	38	48.5	.81	1.68
47	36	39	1.17	2.09
51	36	35	1.50	2.47
63	50	50	1.09	3.70
67	40	29	1.11	1.49
63	38	45	1.52	.98
51.5	53.5	48.5	1.58	3.84
34	29.5	39	1.21	1.50
44	29.5	36	1.22	1.22
33	26	56	1.28	2.55
Mean 53 '	39 '	45 '	1.23	2.18

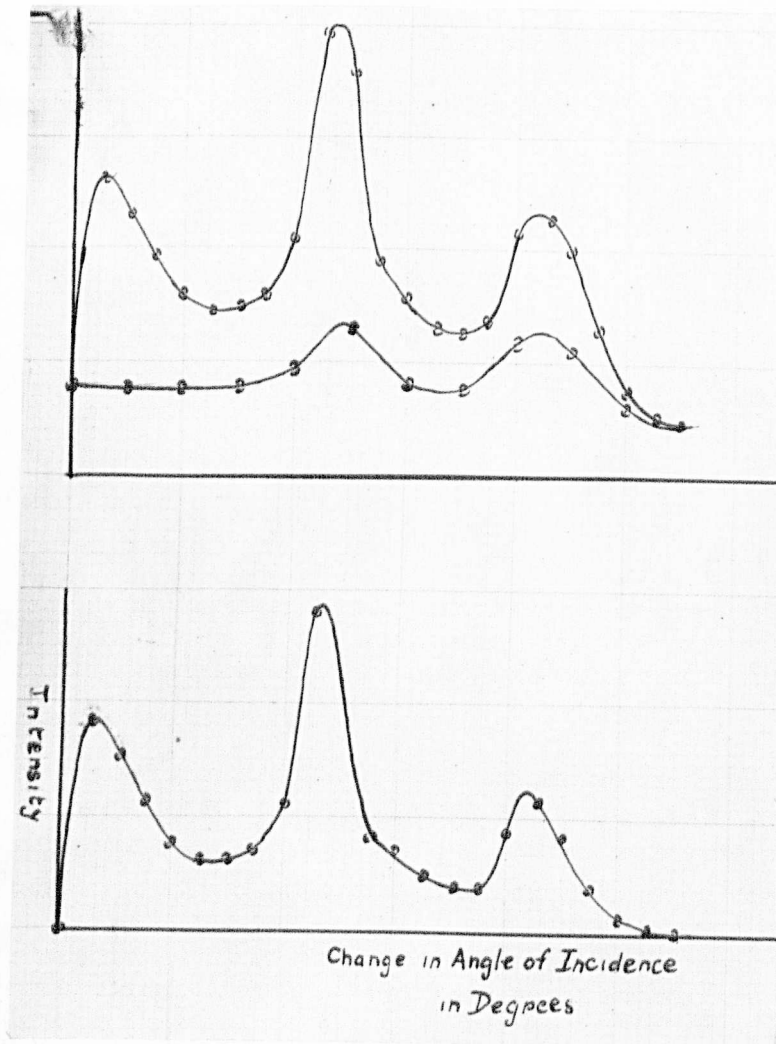


Fig. 10 .

It will be seen that the values for the relative intensities of the orders agreed very well with those obtained under the final conditions, but the spreads were 20 - 30 per cent larger. This was probably largely due to slight inhomogeneity of the beam, resulting from the inadequate smoothing.

A few curves were taken with D.10, which is the ordinary type of diamond, under the original conditions. The curves, one of which is shown in Fig.10, were of the same general shape as those with D.2, except that the second order was about 20 per cent less intense and its spread uncertain due to charging up.

EXAMINATION OF THE KIKUCHI LINES.

In the first case, an attempt was made to measure the intensity distribution across the Kikuchi lines by means of a Faraday cylinder with a fine slit in it parallel to the line. It was found possible to detect the lines in this way, but owing to the fact that they were only about 5 per cent more intense than the background, it was impossible to measure the distribution of intensity. Quite apart from the difficulty resulting from the low relative intensity of the lines, it would have been difficult to devise a method of moving the Faraday cylinder through

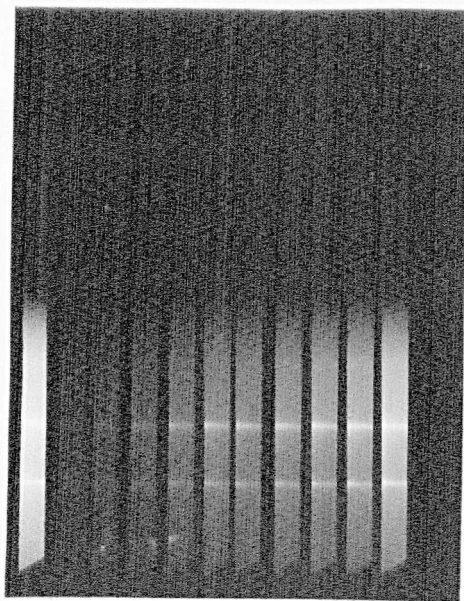


Fig. 11.

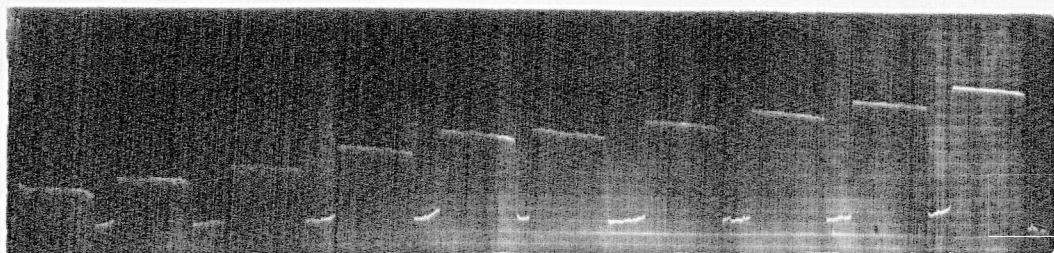


Fig. 12.

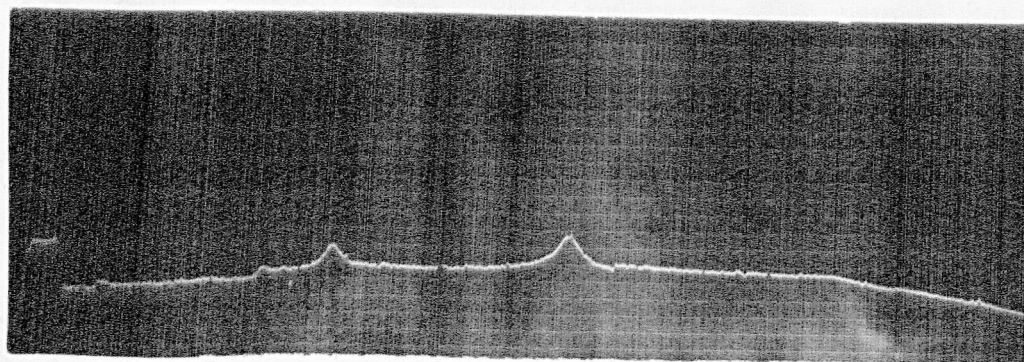


Fig. 13.

distances of the order of .1mm. inside the vacuum, and it would have been necessary to do this in order to study the intensity distribution across the lines. This method was, therefore, given up in favour of a photometric method.

For this purpose, the plate attachment, which had been removed for the first part of the work, was replaced. The part of the plate to be exposed at any one time was limited, by means of a mask of sheet brass to a strip 3mm. wide, perpendicular to the shadow edge, (i.e. to the line in which the plane of the crystal met the screen), and slightly to one side of the central line of the pattern. The specimen was adjusted so that several orders of the lines parallel to the shadow edge were seen crossing the strip. A number of exposures were then made on one plate, by racking the plate down in a series of steps, the time of the first exposure being one second and those of succeeding exposures increasing by intervals of a second. From seven to eleven exposures were made on each plate, the strips being parallel side by side. A typical plate of this sort is shown in Fig.11.

In order to obtain intensity curves from the photographic records, the plates were micro-photometered by means of a Cambridge recording microphotometer. A traverse was made along the one-second exposure strip and a second traverse was made at right angles to the strips.

The two records from the plate shown in Fig. 11 are shown in Figs. 12 & 13. The readings from such an instrument bear no direct relation to either the blackening of the plate or to the intensity of the incident electron beam. The following method of deducing the electron intensities was therefore employed. From the second record, which presents the appearance of a series of flat-topped humps, a curve was plotted showing the instrument reading against the corresponding value of (It) , where (I) is the electron intensity, which was of course the same at corresponding points on all strips, and (t) , the time of exposure. It has been shown by Chadwick that in the expression for the blackening of a plate by electrons the intensity and the exposure time always occur together as the product (It) . It was possible, therefore, by means of this curve, to convert the photometer record for the traverse along the strip, into a curve showing intensities against distance along the strip.

This method, which, as far as is known, is used here for the first time, provides a very easy and convenient method of deducing the relative intensity of electron and X-ray beams from photographic records. It has the advantage of eliminating the peculiarities of the plate and of the instrument in one operation. Since the micro-photometer is of the recording type it is possible to carry out the experimental work with much less trouble

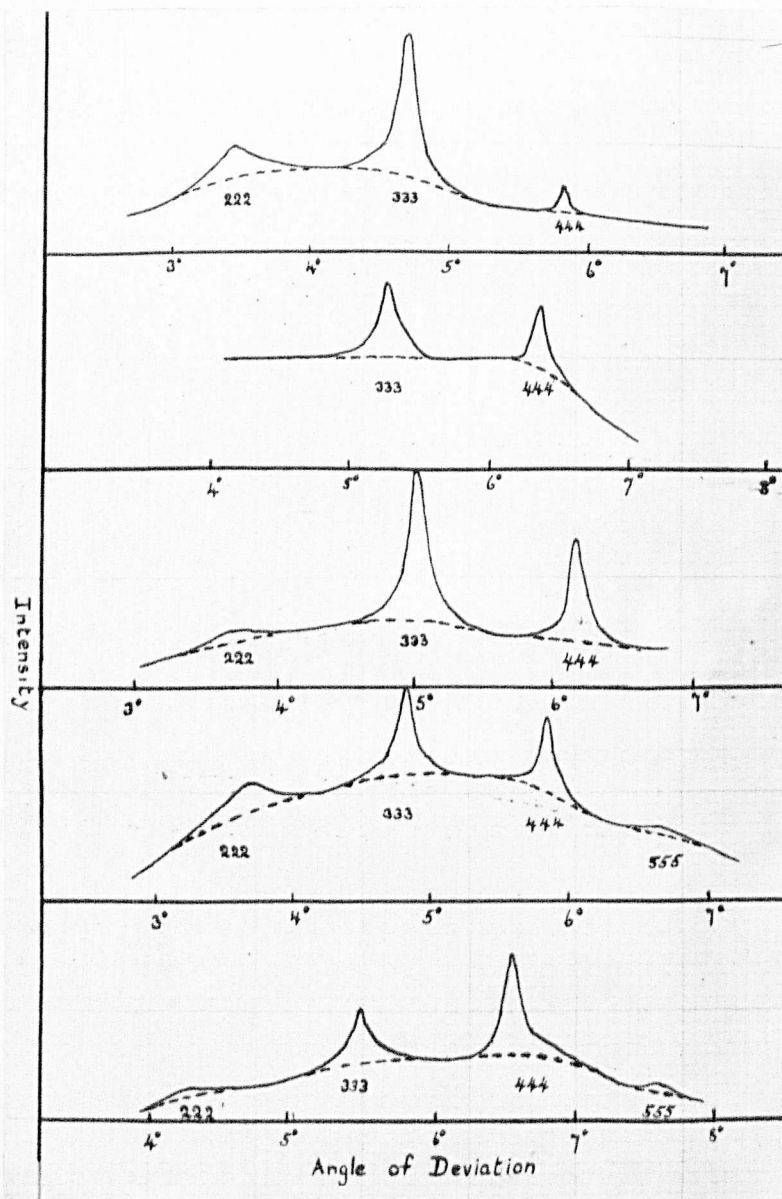


Fig. 14.

The intensity curves derived from the photometer records show the Hikuichi lines to have about twice the intensity of the background. This is not in agreement with the observations on the lines, made by means of the Faraday cylinder. The discrepancy is probably due to the fact that many of the electrons recorded by the electrometer were slow secondaries and these would have little effect upon the photographic plate.

and much more quickly than with the usual compensating wedge type of instrument which gives direct readings of plate blackening, but which is non-recording. Three curves were obtained in this way from D.2 and two from D.27.

RESULTS OF THE KIKUCHI LINE MEASUREMENTS.

Five typical intensity curves are shown in Fig.14. The intensity in arbitrary units is shown plotted against the angle between the main and scattered rays. The half intensity spreads of the lines are shown tabulated in Table 4.

TABLE 4.

KIKUCHI LINE MEASUREMENTS.

Curve	Wave Length	Angle of Half Intensity Spread			Spread calculated for a wave length of .06A.		
		2nd. Order	3rd. Order	4th. Order	2nd. Order	3rd. Order	4th. Order
D ₂ 1	.071	15'	9'	5.5'	10.5	6.5	4
2	.071	--	11	7.5	-	8	5.5
3	.072	20	10	6.5	14	7	4.5
D ₂₇ 1	.061	16.5	10.5	5.5	16	10	5.5
2	.067	-	8	7.5	--	6.5	6
Mean					13.5	8	5

The values should all be reduced by about 2' to allow for the finite width of the spot, as also should the values given previously for the spread of the spots. The relative intensities of the lines depend upon the distribution of intensity in the diffuse radiation producing them and hence upon their proximity to a diffracted spot. This effect will be readily appreciated when it is explained that in the first case the diffracted spot was between the (222) and the (333) lines, but much closer to the latter. In case two, the diffracted spot was about mid-way between the (333) and (444) lines, while in case three it was between the same pair of lines, but nearer the (333) line. The diffracted spot was in about the same position in case four as in case three, while in case five it was between the (333) and the (444) lines but much nearer the (444). In no case was the diffracted spot actually on one of the Kikuchi lines observed and in all cases the line was examined at some distance from the centre. Thus, as will be explained later, the relative intensities of the lines should not have been affected in any way by the proximity of a spot if they are produced in the manner supposed by the commonly accepted theory. For this reason, values of the relative intensities of the Kikuchi Lines have little meaning until more is known about the diffuse radiation.

CHAPTER 4.THE INNER POTENTIAL OF DIAMOND.

As has been mentioned in the introduction, Bethe suggested that the discrepancy between Davisson & Germer's results and those to be expected by analogy with X-rays, was due to a variable refractive index resulting from a constant "inner potential" of the crystal. Bethe calculated this refractive index for nickel on the basis of an atomic model deduced from spectroscopic data. This calculated value was found to agree quite well with that necessary to rectify the existing discrepancy between the experimental and theoretical position of the diffracted rays. Since then, a number of authors have determined the inner potential for many crystals, both by means of slow and fast electrons.

As has already been pointed out, the first order reflected ray from the (111) face of diamond does not appear on account of the high inner potential, a fact which was first demonstrated by Prof. G.P.Thomson, who found an inner potential of about 20 volts. It was decided to determine the value for the inner potential for both the ordinary and the extraordinary type of stone to see whether there was any detectable difference.

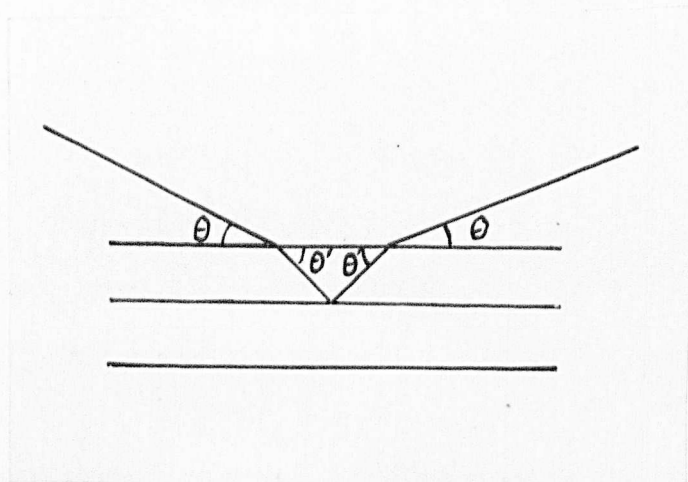


Fig. 15.

THE EFFECT OF INNER POTENTIAL ON THE POSITIONS
ON THE
DIFFRACTION MAXIMA.

The effect of the inner potential on the spots reflected from the specimen surface may be determined quite simply in the following way. Suppose a beam of electrons makes an angle θ with the crystal face, and suppose the refracted ray in the crystal makes an angle θ' . (Fig.15).

Then the refracted index μ is given by:-

hence
$$\mu = \frac{\sin\left(\frac{\pi}{2} - \theta\right)}{\sin\left(\frac{\pi}{2} - \theta'\right)}$$

 hence
$$\mu^2 - 1 = \frac{(\cos^2 \theta - \cos^2 \theta')}{(1 - \sin^2 \theta')}$$

 Since
$$\mu = \sqrt{1 + \frac{V_0}{P}}$$
 where V_0 is the inner potential and P the voltage of the incident electrons

$$\frac{V_0}{P} = \frac{(\sin^2 \theta' - \sin^2 \theta)}{(1 - \sin^2 \theta')}$$

If θ corresponds to a diffraction maximum, we know that $2d \sin \theta' = n\lambda$ if the change in wavelength is neglected.

So that:
$$\sin^2 \theta' = \frac{n^2 \lambda^2}{4d^2} = \frac{150 n^2}{4 d^2 P}$$

where, as usual, $\sqrt{\frac{150}{P}}$ has been substituted for λ

Substituting in equation (1) we get:-

$$\frac{V_0}{P} = \frac{\left(\frac{150 n^2}{4 P d^2} - \sin^2 \theta\right)}{(1 - \sin^2 \theta')}$$

Since θ' is always small $(1 - \sin^2 \theta')$ may be

taken as unity.

Thus
$$P \sin^2 \theta = \frac{150 n^2}{4 d^2} - V_0$$

where P and V_0 are expressed in volts, and d in angstroms.

In this analysis, no account has been taken of the relativity change of wavelength. To correct for this the value of P should be changed to: $P(1 + e^2/600m_0c^2)$

It will be noticed that if V_0 is large enough, some of the lower values of n do not satisfy the equation so that no corresponding diffracted beam appears. This is the case with the first order (111) reflection of diamond.

METHODS FOR DETERMINING THE INNER POTENTIAL.

As will be seen from equation (2), the inner potential may be determined from a knowledge of the positions of the various orders of reflection, by plotting $P \sin^2 \theta$ against the squares of the order numbers n . This method, which was first adopted by Yamaguti, has been used to determine the inner potential of diamonds D.2 and D.26. The necessary measurements were made on the fluorescent screen.

A second method, due to Shinohara, and used subsequently by Tillman, depends upon the determination of the values of θ in equation (2) by observation of the positions of the Kikuchi lines parallel to the shadow edge. The angles are determined by dividing the distance between the Kikuchi lines and the shadow edge by the distance from specimen to plate or screen. This method was used in the

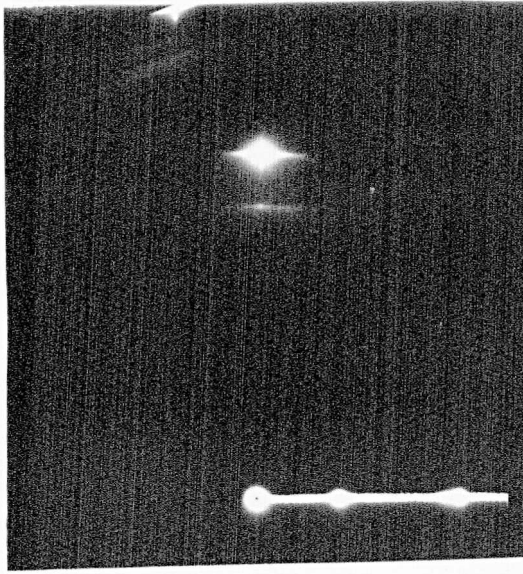


Fig. 16.

case of diamonds D.2 and D.27, some of the measurements for this purpose being taken from the photographs used to determine the intensity of the Kikuchi lines and others being taken from photographs similar to Fig. 16.

RESULTS OF THE INNER POTENTIAL MEASUREMENTS.

The values of the inner potential for the various specimens examined are shown tabulated below.

TABLE 5.

"ORDINARY TYPE"		"EXTRAORDINARY TYPE"	
Rotation Method	Kikuchi Lines	Rotation Method	Kikuchi Lines
<u>Volts</u>	<u>Volts</u>	<u>Volts</u>	<u>Volts</u>
24.3 D.26	20.1 D.27	23.4 D.2	20.7 D.2
20.4	17.9	19.4	17.5
24.0	20.7	21.4	21.0
	20.7	19.4	20.6
Mean 21.1 $\pm$.7		Mean 20.4 $\pm$.6	

The mean value for all specimens
is 20.8 $\pm$ 5 Volts

As will be seen, the difference between the inner potential determined for the two types is less than the probable error, and it is felt that there is, in fact,

no difference between the two types in this respect.

It is interesting to note a value for the inner potential of diamond calculated by ^{*}Lasckarew and Tsachaban. They assume a spherically symmetrical atomic model designed to give the observed X-ray F curve. Using such a model they arrive at a value of 13.7 volts as the inner potential of diamond. This method, in common with others like it, suffers from the weakness that the F.curve is relatively insensitive to the actual configuration of the charge in the atom.

*W.E.Lasckarew, Zeits.Phys., Vol.86, p.697 (1933),
& Vol.89, p.820 (1934). Trans.Faraday Soc.Sept.1935.

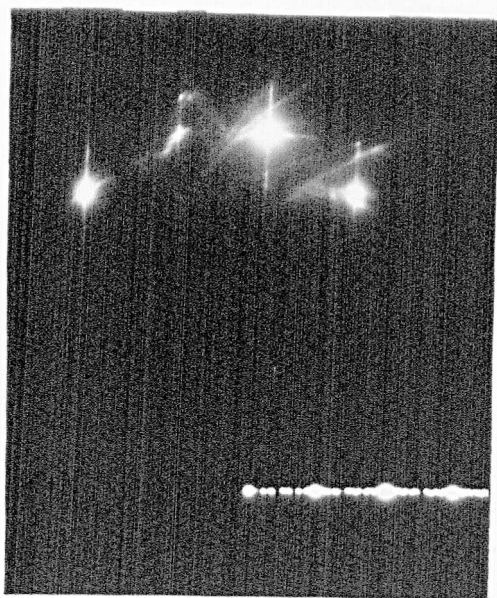


Fig. 17.

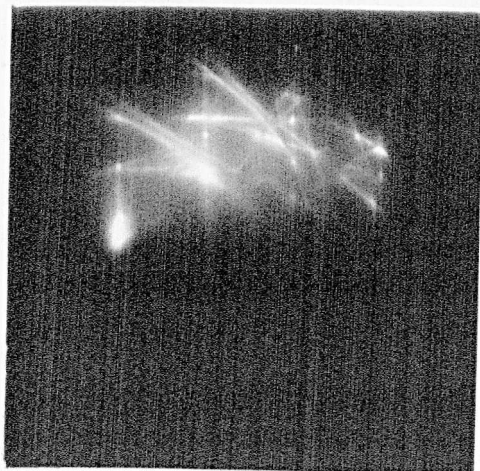


Fig. 18.

CHAPTER 5.QUALITATIVE EXAMINATION OF THE DIAMOND PATTERN.

A number of ordinary electron diffraction photographs were taken from D.2, D.27 and D.28; also, rotation photographs were taken with D.2 and D.27. The latter specimen charged up slightly at small angles of incidence, but the rotation pictures showed the persistence of the spots over a considerable range of angle of incidence and also the asymmetry of spread mentioned in the Introduction.

VERTICAL BLACK & WHITE LINES.

In the case of D.2 it was found that for all settings of the azimuth a faint, fine line similar to a Kikuchi line always appeared, passing through the spots in the plane of incidence, and perpendicular to the shadow edge. In symmetrical or nearly symmetrical settings of the crystal, as many as five similar vertical lines appeared, passing through the various side spots. In such settings the lines were much more intense. (Figs.17,18)

With none of the other stones were lines of such intensity observed, but several of the others showed the lines faintly. The broad bands which are normally observed with other crystals under similar circumstances were not found with any of the stones.

It has not yet been decided to what these lines are due. With many crystals, elongation of the spots in a direction perpendicular to the shadow edge is observed and may usually be attributed to one of two causes:

- (1) Part of the crystal surface being broken into small blocks, tilted slightly with respect to one another.
- (2) Part of the crystal surface being composed of very small blocks which have maintained their alignment but which are separated by fine cracks.

The effect of crystal imperfection of the first type would be to produce a rotation pattern superimposed upon the ordinary spot pattern. The lines should, therefore, show minima at certain places, but they do not. The elongated spots produced would be rather broad, since the normals to the small crystal facets will not necessarily be in the main plane of incidence. Actually the lines are very sharp. Also, this theory would not account for the greatly increased intensity of the lines in all symmetrical settings of the azimuth.

The objections to an explanation based upon a supposed imperfection of the second type are very similar. The way in which elongated spots are produced by such imperfection is by relaxation of one of the diffraction conditions described by Kirchner^{*} as a result of the small extent of the crystal blocks in the direction of the beam.

* F. Kirchner & H. Raether, vol. 30, p. 510 (1932). Phys. Zeit.

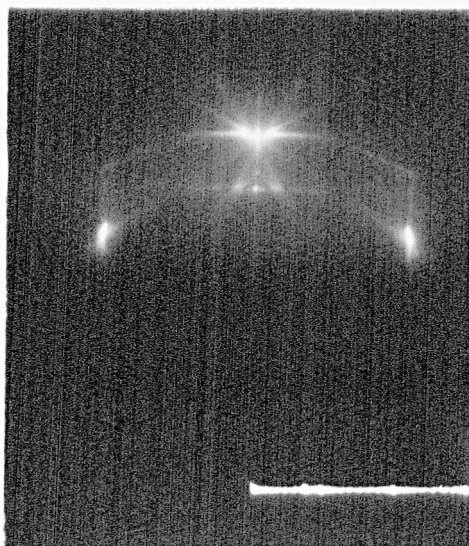


Fig. 19.



Fig. 20.

The pattern produced will resemble a rotation picture superimposed on the ordinary pattern. As has already been pointed out, the lines from diamond do not show the features to be expected in a rotation pattern.

For the reasons given, it seems that the observed lines cannot be attributed to the causes mentioned. Many crystals, when set in symmetrical or nearly symmetrical positions with respect to the electron beam, give rise to a pattern of dark bands, an effect first mentioned by

* Shinohara. As has already been mentioned, no such bands were observed with any of the diamonds examined, in any azimuth, and it seems probable that the vertical lines are a modified form of band. The supposition that they are of the same nature as Kikuchi lines, (the bands observed with other crystals are a modified form of Kikuchi line), is supported by the fact that in many of the patterns, vertical white Kikuchi lines also appear. These do not show very well in the reproductions, but they are quite clear upon some of the plates. One is faintly visible in Fig. 18.

THE APPARENT SUPPRESSION OF A DIFFRACTED SPOT

BY KIKUCHI LINES.

With all the specimens which gave good patterns it was possible to find a symmetrical setting, such that the fourth order reflected spot was flanked on either side by an intersection of Kikuchi lines. Under these circumstances,

* K. Shinohara. Sci. Pap. I. P. C. R. Tokyo, vol. 18, p. 223 (1932).

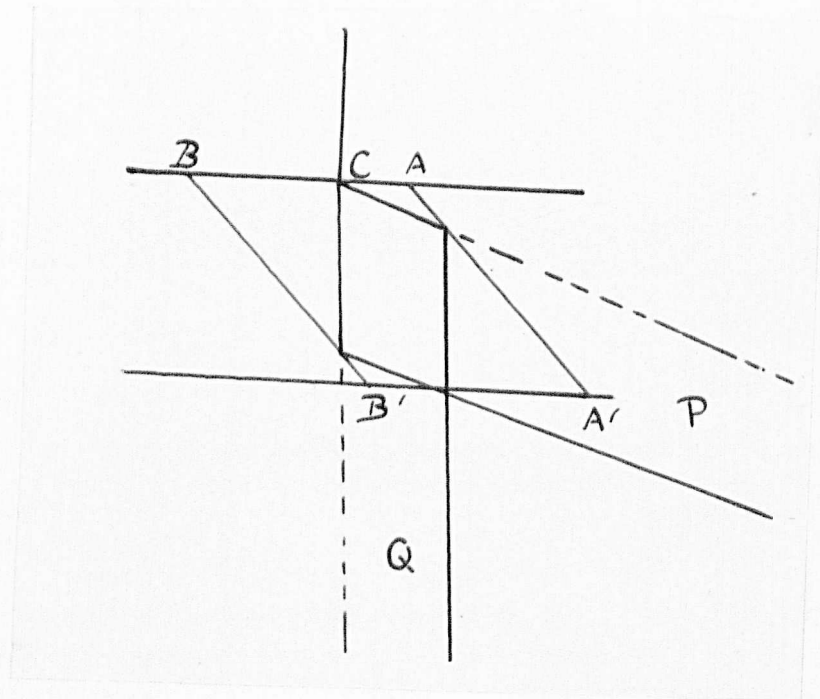


Fig. 21

the spot was noticeably diminished in intensity by the proximity of the lines. This effect is shown in Figs. 19 and 20. Fig. 19 shows the general appearance of the pattern while Fig. 20 shows the spot when normal and when partially suppressed. The two exposures were made on the same plate for the same time.

This suppression of the spot would seem to indicate interference between the spots and the Kikuchi lines.

THE COMMONLY ACCEPTED THEORY OF THE PRODUCTION OF KIKUCHI LINES.

Kikuchi's explanation of the occurrence of the lines, which is the generally accepted one, is as follows: He supposes that when the electron beam enters the crystal, there will be a certain amount of diffuse scattering. The scattered rays will be reflected from various sets of planes with which they make the Bragg angle. Thus in Fig. 21 suppose AA' and BB' be crystal planes, and suppose the incident ray to be diffusely scattered at C, then AA' reflects towards Q rays which would have gone to P, while BB' reflects towards P rays which would have reached Q. The intensity of the rays scattered towards Q will presumably be greater than the intensity of those scattered towards P, since the angle of scattering is less. Thus, as a result of the reflection at BB', Q will lose more than it gains from the reflection from AA'. Thus Q will lose intensity while P will gain.

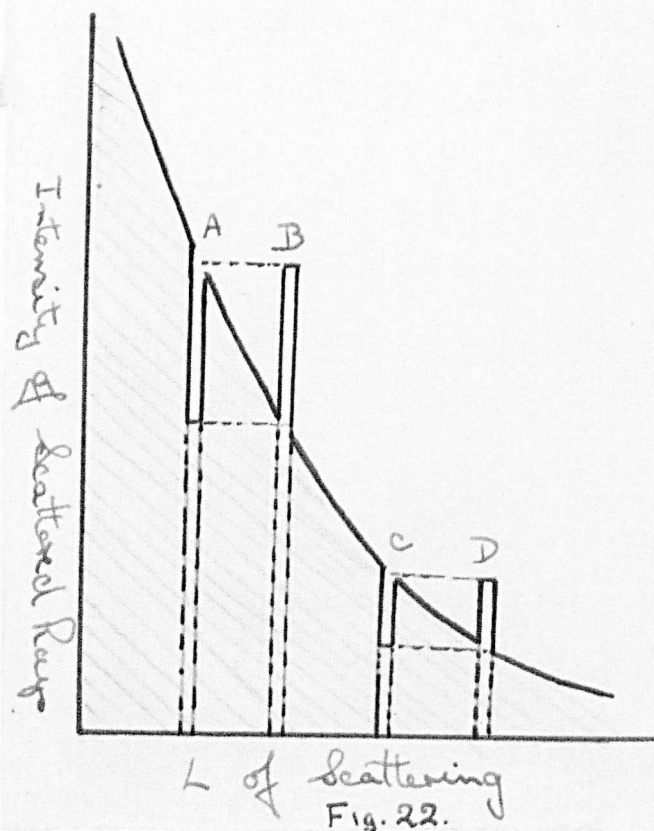
When the planes producing the lines are symmetrically disposed about the incident beam, the amounts gained and lost by the P and Q will be equal. Under such circumstances, the result is not a complete disappearance of both black and white lines as one might suppose, but the lines are replaced by a band of the type already mentioned.

DISCUSSION OF THE THEORY

IN THE LIGHT OF THE OBSERVED FACTS.

Although the explanation given by Kikuchi as to how the lines arise from the diffusely scattered electrons is undoubtedly right, the theory is incomplete insofar as it does not account for the production of diffuse scattering. Opinion is divided as to whether the diffuse scattering results from elastic or inelastic collisions. If the former is the case, it is necessary to consider some irregularity in the crystal lattice, such as the heat motion of the atoms, to account for it. On the other hand, if the electrons are inelastically scattered, and we suppose no phase relationship between those scattered by any atom and by its neighbours, then it is immediately obvious how the diffuse scattering may arise.

If the diffusely scattered electrons are produced in the manner last described, it is reasonable to suppose that their intensity falls off with angle of scattering in much the same way as if the atoms were free, since we are supposing no phase relationship between the electrons from



A and C are two white Kikuchi lines, while B and D are black lines (on the plate). The form of intensity distribution shown above is of the type commonly associated with the scattering of electrons by free atoms (either elastic or inelastic scattering). Assuming such a curve and assuming that all electrons making the Bragg angle with a set of planes are reflected, the relative intensities of the lines would be as shown. Even if the reflection were not complete, a similar distribution of intensity in the lines would result.

neighbouring atoms, and hence no strong linkage between the atoms. This being the case, the curve showing intensity of scattering against angle would be of the general form shown in Fig. 22. Since the slope of the line decreases with increasing angle, the intensity of the bright Kikuchi lines, (i.e. the black lines on the plate), would decrease steadily with increasing angle. This is not in agreement with the measurements of the intensity of the Kikuchi lines described in Chapter 3 as it does not account for the variation of the relative intensity of the Kikuchi lines with the proximity or otherwise of a diffracted spot, nor the partial suppression of a spot by the proximity of Kikuchi lines.

If the diffuse scattering is elastic in nature and due to heat motion or some other irregularity in the lattice, then we should expect some relationship between electrons scattered from neighbouring atoms and, therefore, it is to be expected that there would be an interaction between the Kikuchi line and spot patterns.

There is one other possible explanation which might also account for the facts. The scattering may be inelastic and there may be sufficient interaction between the various atoms of the lattice to cause a phase relationship between electrons scattered from neighbouring atoms. If this were so, there could still be no interference between the elastically and inelastically scattered electrons.

However, if such were the case, the spot pattern might be partially due to inelastic scattering and this would account for the interaction between the spot and line patterns.

CHAPTER 6.THE DISCUSSION OF THE MEASUREMENTS OF THE INTENSITY DISTRIBUTION
IN THE SPOTS AND LINES.

The quantitative results are not in agreement with any existing theory. Bethe's dynamical theory predicts that over a small range of angle, the reflection be total, while outside this range the intensity will fall off very rapidly.

The range of angle over which the spot produced by the cleavage planes persists is given by 2τ where:

$$\tau = \frac{v_{nnn}}{k^2 \sin^2 \theta}$$

v_{nnn} is the fourier co-efficient of potential in the reciprocal lattice corresponding to the n^{th} reflection, k is the wave number, and θ the Bragg angle. In the case of electrons of the velocities used the range of total reflection predicted is of the order of 2 to 3' for the (333) reflection and less for higher orders. Actually the diffracted spots are found to have an intensity of only about 1% of the primary beam, and the third order has a half intensity spread of about 20'.

Recently, Kikuchi* has arrived at a result similar to that of Bethe by a somewhat different method. He has also measured the spread of the spots from zinc blende by photometric

* S.Kikuchi. Sc.Papers. Tokio Inst.Phys.Chem. Res.Vol.XXVI
p.225(1935).

measurements on a rotation photograph and he finds the actual spreads are about twenty times those predicted by theory. This is in good agreement with the results obtained from diamond. Kikuchi suggests that the discrepancy between the theoretical and practical results is due to the fact that absorption has not been taken into account in the theory, while in practice it limits the depth of penetration of the electron beam. As has been pointed out in the Introduction, this is the view that has been advanced many times to explain the spread of the spots but it does not account for the comparative sharpness of the Kikuchi lines, which should have an angular width equal to the angle over which the spots persist.

From the thickness of poly-crystalline metal film which an electron beam will penetrate before falling to half intensity, (i.e. about $500 \text{ \AA}^\circ$), it is often concluded that at the small glancing angles employed in reflection work, the effective depth of penetration of the beam will be of the order of five or six planes. This is sometimes advanced as an argument in favour of the theory that the spread is due to lack of penetration, and since the observed order of spread would result if only about four or five planes were effective, the agreement seems to be good. It is questionable, however, whether the value of penetration determined on the basis of transmission through poly-crystalline films, may be applied

to the case of reflection from a single crystal at glancing incidence.

In the case of reflection from some types of crystal, a so called "Surface pattern" occurs, consisting of two or more semicircles of spots, which occur simultaneously and persist over a wide range of angle of incidence. Such patterns satisfy the condition for diffraction by a plane cross grating (as formed by the top net plane) at grazing incidence. The appearance of such patterns is usually explained in terms of lack of penetration. This type of pattern might, however, be equally well explained by supposing that the top few planes differ from the bulk of the crystal in some respect.

J.W.Harding has suggested that the observed effects may be due to an expansion or contraction of the spacing between the surface planes. He is at present working further upon this idea, and until the theory has been fully considered it is impossible to say whether it will explain the experimental results, but it promises to do so.

The appearance of the (222) reflection is forbidden on the simple theory, but Bethe's dynamical theory predicts such a beam as a result of interaction between the (111) and (333) beams in the crystal. Bethe has suggested that the weak (222) beam found with X-rays may be due to a

similar effect. It has been shown that the relative intensity of the (222) reflection is less the harder the X-rays and the less perfect the diamond, which suggests that it is dependent upon the magnitude of the interaction between the waves and the crystal. In the case of electron waves which are easily scattered, we should expect the relative intensity of the forbidden order to be far greater than in the case of X-rays.

The appearance of a (222) order from diamond with X-rays is often attributed to the distortion of the carbon atom by its neighbours, so that it can no longer be regarded as spherically symmetrical as it is in the simple theory. Since in the case of electron waves the greater part of the scattering is due to the nucleus, we should expect the effect of such distortion to be much less than for X-rays, since it is likely to affect only the outer shells of the atom. It has already been pointed out that the (222) order is relatively far more intense in the case of electrons than for X-rays, so that it seems highly improbable that the appearance of the forbidden orders can be attributed to distortion in the electron case.

The second order cannot be due to a purely surface effect, since a fairly sharp (222) Kikuchi line appears. It would seem fairly likely, therefore, that the forbidden maximum is produced in the manner suggested by Bethe.

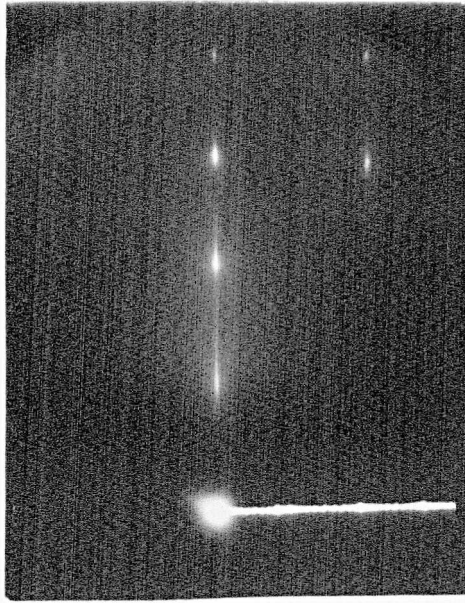


Fig. 23 .

Attention has been drawn in the Introduction to the fact that the intensity of the reflected spots does not fall off symmetrically on either side of the Bragg angle. The intensity falls off more slowly on the side of large angle. This effect, which was clearly visible on the screen, is shown in the rotation photograph, Fig.23 and is also noticeable as a tendency in the intensity curves. The asymmetry is in the opposite sense to the asymmetry observed by Yamaguti, in the case of a natural face of pyrite.

*Kikuchi has offered an explanation of the effect observed by Yamaguti. He attributes the asymmetry to the effect of intermediate crystal planes. He considers first of all a single crystal with equally spaced planes parallel to the surface, and by assuming that each plane scatters the same amount of the incident wave he arrives at the solution:

$$|S_0|^2 = \sin^2 \left(\frac{2\pi}{\lambda} n d \sin \theta \right) / \sin^2 \left(\frac{2\pi}{\lambda} d \sin \theta \right)$$

where $|S_0|^2$ is the intensity of the scattered beam, n the number of planes and d the plane spacing.

In the case where there are intermediate planes distance x from the original plane, this expression becomes:

$$|S|^2 = 4 |S_0|^2 \cos^2 \left(\frac{2\pi}{\lambda} x \sin \theta \right)$$

where $|S|^2$ is the new intensity of the scattered beam and

S_0 has the same meaning as before. Since $|S_0|^2$ represents

* S.Kikuchi. Sc. Papers. Tokio Inst. Phys. Chem.
Res. Vol. XXVI p.225 (1935)

a symmetrical distribution in the spots, the asymmetry is introduced by the $\cos^2 \left(\frac{2\pi}{\lambda} x \sin \theta \right)$ term.

In the case of diamond x is $d/4$ so that this term becomes: $\cos^2 \frac{\pi \lambda}{4}$

On this theory, the second order is missing, the third order falls off more slowly on the side of large angle, the fourth order is symmetrical, while the fifth order falls off more slowly on the side of small angle. Actually, all the orders fall off more slowly on the side of large angle, so that this theory certainly does not hold in the case of diamond.

The suggestion made by Harding that the spread of the spots may be due to contraction or expansion of the spacing between the surface planes would probably also account for the asymmetry of spread.

THE TWO TYPES OF DIAMOND.

This work has shown no definite differences between the electron diffraction patterns obtained from the two types of diamond. It is felt that no importance can be attached to the fact that the second order reflection appeared to be slightly less intense in the case of the ordinary type, since the specimen used charged up badly. All the specimens of the ordinary type used showed this charging up, while D.2 only charged at very small angles of incidence indeed. Since D.2 was the only stone of the ordinary type

examined, it is impossible to say definitely whether this difference is a feature of the two types. However, it seems quite probable that this difference is real in view of the fact that Sir Robert Robertson and his collaborators have shown that the extraordinary type of diamond has generally a greater photo-conductivity than the ordinary type. The photo-conductivity of D.2 is about ten times that usually associated with the ordinary type.

D.2 showed the vertical lines in a much more marked manner than the other specimens, although D.27 showed the effect quite noticeably.

The fact that no difference has been detected between the electron diffraction patterns from the ordinary and extraordinary types is not surprising after consideration of the known difference between the two types. The main distinguishing feature, and the one which probably gives rise to all the others, is that, while the ordinary type is usually under strain, in the extraordinary type this strain has been relieved by slip, resulting in a laminated structure. These laminae, which have faces parallel to the cleavage face, have thickness estimated to be of the order of $1-10\mu$. From the point of view of electron diffraction, such lamination would be of no importance since the electrons certainly do not penetrate to a depth comparable with 1μ .

In the case of X-ray diffraction where the penetration is far greater, the lamination is of importance. As a result of it, the intensity of the second order reflection from the cleavage face is several times more intense, relative to the other orders, in the case of the ordinary type than in that of the extraordinary type. This would not be accounted for by supposing the second order to result from the distortion of the carbon atom, but might be accounted for if the forbidden orders arise in the manner suggested by Bethe, namely by interaction between the (111) and (333) orders.

S U M M A R Y.

Intensity measurements have been made on the electron diffraction patterns obtained from a (111) natural face of diamond. The relative intensities of the reflected spots have been determined and the tolerances in the Bragg angles have been measured and compared with the widths of the corresponding Kikuchi lines, and with the values predicted by Bethe's theory. The inner potential has been measured and various qualitative observations have been made. A case where a spot has been partially suppressed by Kikuchi lines has been observed.

The general conclusions arrived at are, that there is no really satisfactory theory to account for the diffraction of electrons by the crystal lattice, at present. Bethe's theory suffers from the great disadvantage that it does not take into account the absorption due to inelastic scattering. The explanation of the persistence of the spots, based on lack of penetration, is considered unlikely as it does not account for the Kikuchi lines. An alternative possible explanation suggested by J.W.Harding is mentioned.

The origin of the diffuse radiation giving rise to the Kikuchi lines is discussed in the light of the

observed interaction between spot and line patterns and is considered to be due either to diffuse elastic scattering resulting from the heat motion of the atoms or some irregularity in the lattice, or to inelastic scattering by the crystal as a whole and not by individual atoms.

SUPPLEMENT.DIFFRACTION PATTERN FROM A POLISHED DIAMOND FACE.

Two small cut diamonds, which had been exposed to a radio active source, were sent to the author with a request to examine them to see whether the structure was in any way changed. One, which was initially a yellow stone, had turned brown, while the other, which had been white, had turned a green colour. Although it was not anticipated that any change of structure would be found, the stones were examined by electron diffraction to see what the effect of the cutting process was. The result was rather surprising in that the pattern produced was in each case of the type to be expected from a cleavage or natural crystal face. Typical patterns obtained from the two stones are shown in Figs. 24 & 25. In Fig. 24, Kikuchi lines are clearly visible as well as a diffracted spot, while in Fig. 25 three diffracted spots appear.

The stones were very small and difficult to clean and examine. In addition, the co-ordinates of the cut faces were not known, nor how they had been prepared except that presumably they had been polished by diamond dust in the usual way. In order to examine the matter further, a stone which was polished to a known face was required. Prof. W.T. Gordon very kindly provided a stone which had originally had two natural faces.

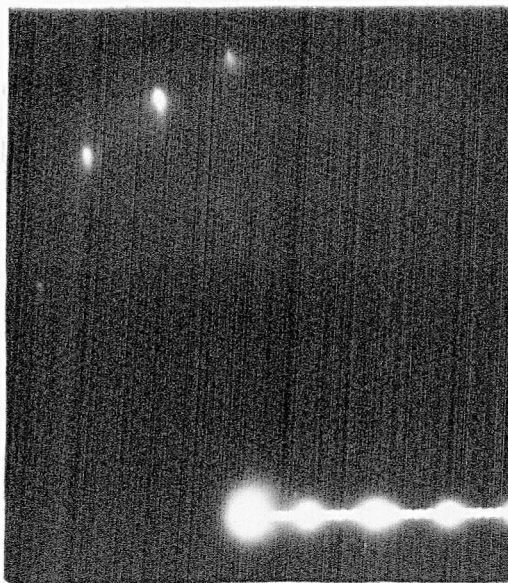
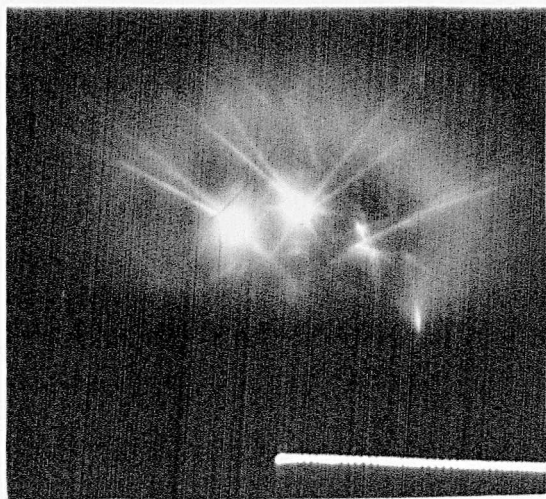


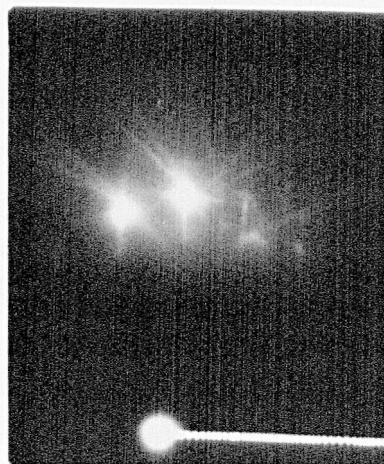
Fig. 24.



Fig. 25.



Natural Face. (a)



cut Face. (b)

Fig. 26.

One of these had been polished off, efforts being made to keep the polished face as nearly parallel to the original face as possible. The polished face gave exactly the same type of patterns as the natural face. For the purpose of comparison, two patterns are shown, (Fig. 26), taken one from each face in almost exactly the same azimuth. The fact that the two azimuths are unfortunately not precisely the same causes slight differences in the pattern but it is obvious that the pattern from the polished face is of just the same type as that from the natural face. It will be observed, however, that the line joining the central spot to the reflected spot is not quite perpendicular to the shadow edge in the case of the polished face, thus showing that the polished face is not quite parallel to the (111) planes.

Diamonds are polished by being pressed down on to a steel wheel sprinkled with diamond dust. The process resolves itself into grinding with finer and finer particles as the dust itself gets broken down. It would appear that the polish ultimately arrived at results solely from the removal, at each stage of grinding, of the projection left by the previous stage so that ultimately a flat surface is left. No glass-like film, of the Beilby layer type, can be formed or the pattern observed would not appear.

PART B

AN EXAMINATION OF THE STRUCTURE OF SOME EVAPORATED METAL FILMS BY ELECTRON DIFFRACTION

THE STRUCTURE OF
ALUMINIUM, CHROMIUM AND COPPER FILMS
EVAPORATED ON TO GLASS.

INTRODUCTION.

During the course of research, conducted with a view to establishing the best method of preparing evaporated metal films for mirrors, specimens of aluminium, chromium and copper films on glass were examined by electron diffraction. Several interesting features in their structure were observed, although, owing to the necessity for keeping the immediate practical object in view, it was not possible to examine some of the effects in detail.

PREPARATION OF SPECIMENS.

The evaporation, which was not performed by the author, was carried out in a metal chamber, the initial pressure in which was of the order of 10^{-4} mm. of mercury. When the evaporation was begun, there was a momentary drop in pressure, followed by a rise to two or three times the initial value. After the evaporation was over, the pressure was lower than at the beginning, which suggests that the evaporating process has a "gettering" effect.

In order that specimens of suitable dimensions for electron diffraction examination might be prepared with

minimum handling, the metal was evaporated on to glass strips about 1 cm. wide and about 5 cm. long. These were divided into six parts by diamond scratches on the face, upon which the metal was to be evaporated. A sharp tap with a file on the back face was sufficient to break the strips into pieces. The metal was evaporated from a filament placed slightly to one side of the glass strip, so that one edge of the strip was coated as well as the face to be examined. This was done in order to enable contact to be made with the metal film, to prevent charging up when the electron beam was incident upon the specimen surface.

A standard method of cleaning the glass was adopted. The strips were washed in aqua regia, then in distilled water, rubbed hard with clean cotton wool soaked in hydrogen peroxide solution, and finally dried on dry cotton wool. In order to prevent contamination from handling, rubber gloves washed with ammonia were worn. This method of cleaning is that recommended by Mr. E.W.Foster of The Imperial College of Science, for the preparation of sputtered silver films, where conditions of cleanliness are of extreme importance. The cleaning procedure was probably more stringent than was necessary, but was adopted to eliminate uncertainty in the results as far as possible.

ALUMINIUM FILMS: SCHEME OF EXAMINATION.

It was decided first of all to vary the thickness of the films, then the path from heater to mirror; also the speed of evaporation and finally the vacuum conditions. Under each set of evaporating conditions, three strips of specimens were prepared. One of these was examined without further treatment, one was heated to 250°C in an air oven, and one was washed with methylated spirits before examination. One strip was washed with methylated spirits because it had been suggested that this treatment hardens the film. It is difficult to imagine a possible mechanism for such hardening, and, in fact, no such effect was observed. Electron diffraction examination showed no change in structure, and the washed specimens were found to scratch as easily as the unwashed ones.

CHANGE OF THICKNESS OF THE FILM.

The structure of the evaporated films was found to vary in a very marked manner with increasing thickness. Very thin films about $100\text{-}200\text{\AA}$ thick, (i.e. films which were barely visible by transmitted light but which appeared to reflect quite well and had a metallic lustre by reflected light), gave electron diffraction patterns which showed no trace of aluminium metal. A considerable number of plates of this pattern were taken, and the mean crystal spacings calculated from them are shown in Table 1.

(4)

The intensities of the rings are not given as these were found to vary from specimen to specimen. A typical pattern is shown in Fig. 1.

TABLE 1.

Plane.	Observed Spacing.	Spacing of $\gamma\text{Al}_2\text{O}_3$
111	4.56 $\text{\AA}^\circ$	4.49 $\text{\AA}^\circ$
200	3.87	3.88
211	3.20	3.17
220	2.73	2.74
311	2.33	2.34
222	--	2.24
400	1.98	1.94
331	--	1.78
420	--	1.74
422	1.65 ? very faint.	1.58
511)	--	1.49
333)	--	1.49
440	1.39	1.37
531	--	1.31
442)	--	1.29
600)	--	1.29
620	1.22	1.23
533	--	1.18
622	--	1.17
444	1.12	1.12

Cube Side "a" = 7.82 $\text{\AA}^\circ$

"a" = 7.77 $\text{\AA}^\circ$ Steinheil *

A. Steinheil . Ann. Physik. (5) 19, (1934)

The compound producing these rings is almost certainly some form of aluminium oxide, (Al_2O_3).

There are several reasons for supposing this. Firstly, the residual gas in the apparatus was air and since no known form of aluminium nitride exists, the oxide seems the obvious choice. Added to this, the diffraction pattern shows the compound to have a crystal structure with a face centred cubic lattice of cube side " a " = 7.82A. In this respect, the structure is similar to that of $\gamma\text{Al}_2\text{O}_3$, which has a face centred cubic lattice, the cube side of which has been given as 7.77 Å and 7.90 Å^u by different workers. The ring intensities in the pattern from thin films were, however, quite different from those in the $\gamma\text{Al}_2\text{O}_3$ pattern. According to Verwey* the structure of $\gamma\text{Al}_2\text{O}_3$ is a face centred cubic lattice of oxygen, with aluminium atoms distributed at random, in certain proportions, over a limited number of possible positions in the cell. In the case of another form of the oxide, $\gamma'\text{Al}_2\text{O}_3$, Verwey† suggests a similar structure with even less constraints upon the positions of the aluminium atoms. It would seem quite probable, therefore, that the compound giving rise to the patterns obtained from very thin films of aluminium is some form of Al_2O_3 related to the γ form. The supposition that the compound is Al_2O_3 is strengthened by the fact that films of evaporated chromium give a similar pattern

* Verwey. Zeit.f. Krist, vol.91.p.65 (1935)

† Verwey. Laboratoria N. & V. Phillips Glouhampenfabrieken Eindhoven, Holland (1935)

when heated. The only oxide of chromium which would be expected to have a crystal structure similar to that of an aluminium oxide is Cr_2O_3 .

Thicker films of aluminium, about $500-1000\text{\AA}$ thick, (i.e. films which are quite blue by transmitted light, but which are too thick to allow print to be read through them), give patterns showing both oxide rings and the ordinary aluminium pattern. Usually only one or two oxide rings appear, and as a rule the aluminium rings tend to be rather diffuse, indicating small crystal size. In some cases the pattern consists of very diffuse aluminium rings, with no oxide rings. A probable explanation of these patterns is that in some cases the upper surface of the film consists of aluminium and oxide mixed, while in others the oxygen prevents the formation of large crystals without actually going into combination. (Large crystals, as referred to here, mean crystals of over $100\text{\AA}$ side, while crystals so small as to give really diffuse rings have dimensions of about $20\text{\AA}$).

Still thicker films of aluminium, (i.e. films which are almost or quite opaque), give sharp ring patterns due to crystals of aluminium more than about $100\text{\AA}$ square. In nearly all cases, these patterns show a tendency for the aluminium crystals to orientate with a cube face parallel to the glass surface. A further account of the orientation of these films will be included later.

VARIATION OF THE DISTANCE FROM HEATER TO MIRROR.

Variation of the distance from heating filament to the specimen surface appears not to affect the film, provided the thickness of the film is about the same in each case, except that films prepared at about 8 cm. from the heater, which was the shortest path used, tended to contain oxide rather more than the others.

THE SPEED OF EVAPORATION.

The speed at which a certain thickness of film may be reached depends upon the distance from the heater to the specimen and upon the rate of evaporation. In the case of fast evaporation, it took from 5-10 seconds to prepare a film, while a film prepared very slowly might take a minute or more to deposit. The slower the evaporation, the poorer the electron diffraction pattern produced insofar as the intensity of the rings, compared with the diffusely scattered background becomes less and the rings themselves tend to be diffuse. When the rate of evaporation is very slow, even an opaque film, such as would normally give a sharp ring pattern, gives only two diffuse rings. There are two possible explanations of this effect. Either the crystals in the surface are very small, or the surface is so flat that there are no fine projections through which the electron beam can penetrate. Since it seems unlikely that a very flat surface will result in this particular case only,

the first explanation is the more probable. One would normally expect larger crystal size to result from the slower crystal growth consequent upon slower evaporation. This effect is probably offset by the fact that more gas is trapped in the metal during a slow evaporation.

EFFECT OF POORER VACUUM CONDITIONS.

A number of specimens prepared under poorer vacuum conditions, the initial pressure being of the order of 10^{-3} mm. were examined. The effect of the increased pressure appeared to be similar to that due to the slowing down of the evaporation. The diffraction rings were diffuse, and in one or two cases oxide rings were observed in the patterns from quite thick films. These films became cloudy when heated to 250°C , and this will be discussed further under the next heading.

THE EFFECT OF HEATING THE FILMS TO 250°C .

The effect of heating all the types of specimen so far discussed was investigated. In the case of the very thin films, which already showed an oxide film, there was no change either in the appearance or the structure of the film when it was heated to 250°C . Those thicker films which were partly aluminium and partly oxide, gave a pattern which showed no aluminium rings at all after heating. The pattern obtained was such as would be produced by a face centred cubic lattice of side " a " = $5.53\text{\AA}$. As this spacing is equal

Part.B.

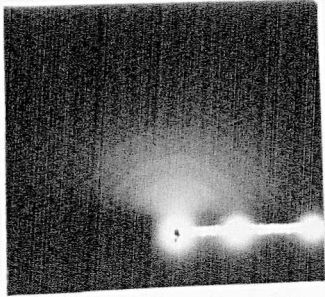


Fig. 1.

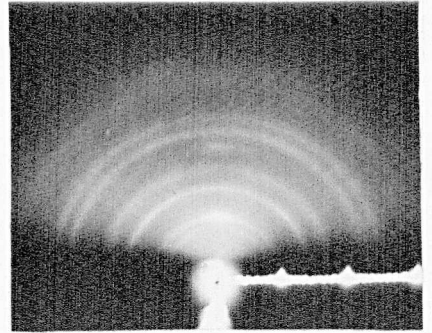


Fig. 2.

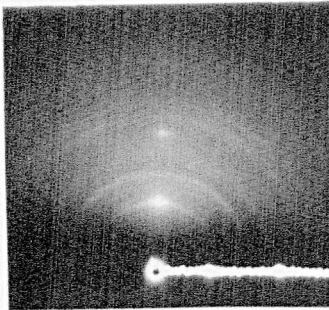


Fig. 3.

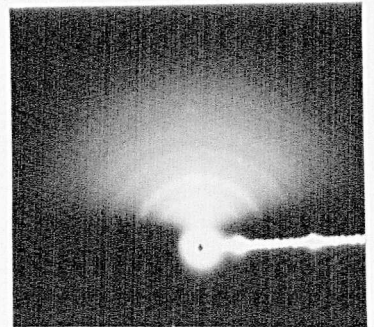


Fig. 4.

to half the face diagonal of the $\gamma\text{Al}_2\text{O}_3$ cube, the ring spacings are common to the two patterns. This is shown in Table 2 while the actual pattern is shown in Fig. 2.

TABLE 2.

Plane.	Observed Spacing.	Calc. Spacing $a=5.53\text{\AA}.$	Intensity.
111	3.27 $\text{\AA}^\circ$	3.20 $\text{\AA}^\circ$	m
200	2.78	2.77	s
211	2.32	2.26	ff
220	1.96	1.95	ss
311	1.65	1.67	m
222	1.58	1.59	m
400	1.38	1.38	f
331) 420)	1.23	1.25	ss
422	1.11	1.13	s
511) 333)	--	1.06	-
440	--	.98	-
531	--	.94	-
442) 600)	.92	.92	ff

s Strong, ss Very Strong, m Medium.

f Faint ff Very Faint.

It is very probable that this oxide is another form of partially organised crystal related to $\gamma\text{Al}_2\text{O}_3$

Many of the crystals in the film were orientated with a cube face parallel to the plane of the specimen, this being indicated by sharp spots on the rings produced by the spacing between the cube faces, (i.e. the (200), (400), (600) rings).

In the case of films of similar thickness to those referred to above, prepared under poorer vacuum conditions, the specimens became clouded with a white bloom when heated to 250°C . Electron diffraction examination of this surface film showed it to be composed of a mixture of the two oxides which have already been described.

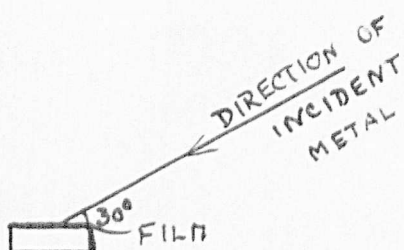
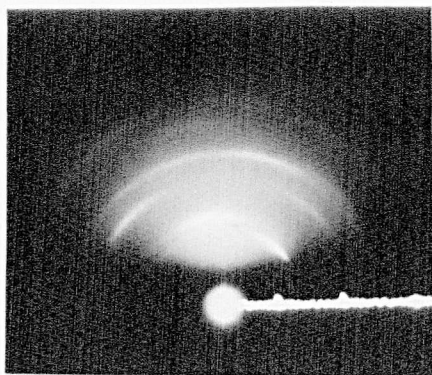
The oxide crystals were much bigger than in the case of films prepared under better vacuum conditions. This was indicated by the presence of marked spots in many parts of the rings. The crystals of the oxide of type 1 showed a tendency to orientate on a (111) face, while those of type 2 tended to orientate with a cube face parallel to the glass surface. The crystals were of the order of 10^{-3} cms. square, (estimated from the size of the spots on the rings) and were therefore of sufficient size to affect the reflecting power by virtue of their roughness alone.

The thick films, which were pure aluminium on the surface, showed no change when heated to 250°C . It is

probable that, both before and after heating, they were covered with an exceedingly thin protective film of oxide, which might not show up under electron diffraction examination owing to the relative weakness of the pattern arising from such a thin layer, compared with the pattern from the aluminium itself. Aluminium forms a very good protective layer and we should expect this layer to be very thin, of the order of a few molecules thick, since it would kill its own growth.

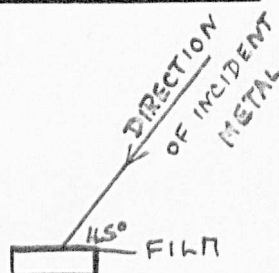
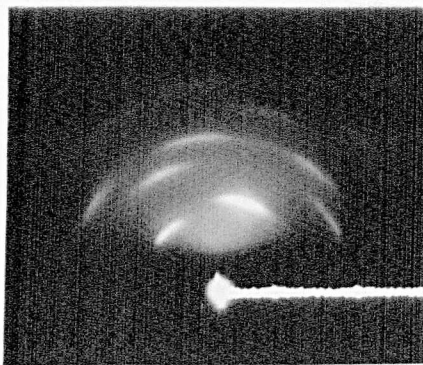
ORIENTATION OF THE ALUMINIUM CRYSTALS.

As has been mentioned earlier, the aluminium crystals in the thick films showed a tendency to orientate with a cube face parallel to the surface. This tendency was, however, disturbed by the direction in which the aluminium was fired on. Although this effect had no direct bearing upon the main problem to be investigated and could not therefore be studied in detail, it was thought worth while to examine the general nature of the phenomenon. Further work on this effect might provide a very valuable check on any proposed dynamic theory of crystal growth. As has already been explained, aluminium was evaporated on to one face and one edge of the glass strips, by firing the metal obliquely on to the face to be examined, at an angle from 20° - 40° with the surface, from a filament parallel to the strip, but to



Specimen as viewed
along electron beam.

Fig. 5.



Specimen as viewed
along electron beam.

Fig. 6.

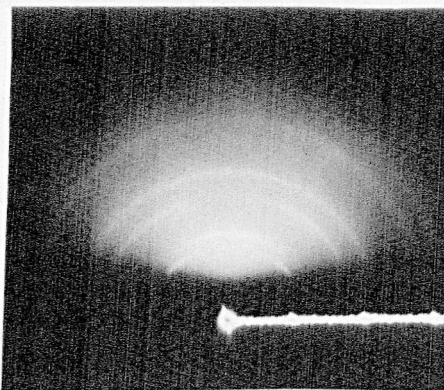


Fig. 7.

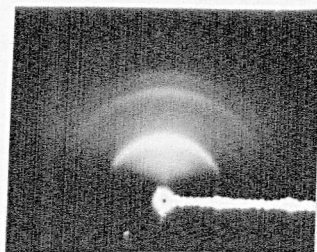


Fig. 8.

one side of it. When a small specimen, cut from the strip, was examined in the diffraction camera with the beam crossing the surface in a direction perpendicular to the length of the strip, the pattern was arced symmetrically about the centre line in such a way as to indicate that all the crystals tended to orientate on a cube face. When the electron beam was fired across the specimen face in a direction parallel to the length of the strip, the pattern was arced symmetrically about a line making an angle of about 10° with the centre line of the pattern, on the side remote from the line of fire of the incident metal. The type of pattern is shown in Fig. 5. This means that the aluminium crystals were orientated with a cube face parallel to a plane whose normal lay in the plane of incidence of the evaporated metal, and was inclined at an angle of about 10° to the normal to the specimen surface. When the angle between the direction of incidence of the evaporated metal and the specimen surface was increased to 45° , the electron diffraction pattern showed the crystals to be orientated with a cube face ^{roughly} parallel to a plane whose normal lay in the plane of incidence of the metal, and which made an angle of about 15° with the normal to the specimen surface, on the side of it nearer the heating filament. The type of pattern is shown in Fig. 6.

Specimens were also prepared with the metal fired normally on to the glass surface. In this case, the crystals were found to be orientated with a cube face parallel to the specimen surface, (Fig.7). It is difficult to come to a very definite conclusion with so little detailed information, but it seems quite likely that the orientation observed might be due to the conflict of tendencies on the part of the crystal to grow with a cube face parallel to the surface, and also with a cube face perpendicular to the direction of incidence of the metal.

CHROMIUM FILMS.

In the case of chromium, films of varying thickness were examined. Exceedingly thin, almost invisible films gave a pattern consisting of a few rings due to oxide, and a few diffuse rings probably due to chromium. When heated, such films gave an oxide pattern with a ring arrangement identical with that from heated aluminium films.

Thicker films of chromium gave a diffuse ring pattern due to small crystals of the pure metal. Even films thick enough to be opaque showed this pattern, there being no increase in crystal size with increased film thickness. corresponding to that observed with aluminium. On heating, these films became coated with a purplish bloom, and electron diffraction examination showed this to be the same form of oxide as that formed on thin films, the cube side being

$a = 5.46\text{\AA}$, which was slightly smaller than the corresponding aluminium oxide spacing. The mean spacings from a number of plates are shown in Table 3, while the actual pattern is shown in Fig. 3.

In the case of one specimen of medium thickness, the oxide layer formed on heating was a mixture of the oxide mentioned above, and an oxide similar in structure to the Type 1 aluminium oxide referred to earlier. The pattern is shown in Fig. 4.

TABLE 3.

Plane.	Observed Spacing.	Calc. Spacing $a=5.46\text{\AA}$	Intensity.
111	3.27 $\text{\AA}$	3.16 $\text{\AA}$	m
200	2.74	2.72	s
211	2.22	2.23	ff
220	1.94	1.93	ss
311)	1.60	1.64	m
222)		1.57	
400	1.35	1.36	f
331)	1.22	1.25	s
420)		1.22	
422	1.10	1.11	m
333)	-	1.05	-
511)			
440	-	.96	-
531	-	.92	-
442)	.90	.91	ff
600)			

ALUMINIUM ON CHROMIUM FILMS.

Thick films of aluminium were evaporated on to chromium films on glass. Orientated aluminium patterns, similar to those from thick aluminium films on glass, were obtained. Heating the films to 250° C made no difference to the surface.

COPPER FILMS, ON GLASSAND ON ALUMINIUM ON GLASS.

Films of copper of varying thickness were examined, and in no case was a pattern of pure copper obtained. With some of the thicker specimens, copper rings were observed in addition to the predominating pattern due to cuprite, Cu_2O . One set of copper specimens, ranging from a film which was barely visible to one which was almost opaque, gave a peculiar pattern which is shown in Fig.8. The very strong ring and the sharper rings are probably due to Cu_2O , while the innermost ring and the third ring, which are diffuse, have not yet been accounted for. The very strong ring corresponds to the (110) ring from cuprite, but is far stronger than this ring should be. A similar set of specimens of copper, on aluminium on glass, gave a ring pattern with spacings corresponding to those of cuprite, but with different intensities, the (110) ring again being abnormally strong.

Although the actual crystal structure and nature

of the compounds formed has not been determined in all cases, it is most probable that oxygen is either trapped in or combined with the copper in all these films.

When the films are heated to 250°C , they tarnish very readily. This film of tarnish, which is thick enough to show interference colours, was shown by electron diffraction examination to consist of cuprite. The readiness with which the tarnishing occurs is probably due to the presence of oxygen trapped in the film.

MECHANICAL PROPERTIES OF THE FILMS.

In the case of aluminium, the thinner films were found to adhere best. They were unaffected by the sticking on and pulling off of a piece of adhesive tape, while some of the thicker films would not stand this test. All the aluminium films could be scratched easily with the point of a knife, but were able to withstand fairly well vigorous rubbing with dry cotton wool. They could be washed with wet cotton wool without suffering any harm. The films were able to withstand the attack of both concentrated hydrochloric and nitric acids for some time, (i.e. about 30 seconds in the case of HCl , and much longer in the case of HNO_3).

The chromium films were very hard, it being impossible to scratch them with the point of a knife. Aluminium on chromium films also appeared to withstand the test.

this test, but this may have been only apparent. The aluminium may have been scratched off, although the scratch was not visible on account of the opaque chromium backing.

SUMMARY AND DISCUSSION.

It has been shown that thin evaporated films of aluminium, chromium and copper consist mainly of the respective oxides of the metals although these oxides have not their usual crystal forms. The actual structures of these oxides have not been fully determined, but it seems probable that in the case of aluminium the oxide is related to $\gamma\text{Al}_2\text{O}_3$. The structure of the oxide present in a thin film of chromium is similar to that present in a thin film of aluminium.

The oxides formed on both metals after heating to 250°C have the same structure, and almost the same spacing. It is just possible that the form of oxide observed on heated aluminium films is the same as that observed by Steinheil*, on an aluminium foil which had been subjected to atmospheric oxidation. There is a difference in the cube side and in the relative intensities of the rings. The latter difference might easily be due to orientation, since Steinheil's pattern was obtained by transmission.

* A.Steinheil, Ann.Physik. (5) 19, (1934).

The spacing found by Steinheil was $5.35\text{\AA}$, which differs from the value found in this work by about 4 per cent, which is rather greater than would be expected after allowing for experimental errors.

In view of the non-tarnishing properties common to aluminium and chromium, it is of interest to notice that they both form other oxides of the same structure, in addition to the common rhombohedral forms.

Thick films of aluminium and chromium were apparently pure metal on the surface. It is suggested that the protective oxide layer, which must have been present, was so thin as not to be observed.

Under normal evaporating conditions, the initial pressure in the chamber was such that the mean free path for the metal atoms was greater than the distance from heater to mirror. It seems unlikely, therefore, that the oxygen in the films was picked up by the metal atoms in crossing between the filament and the mirror. It is possible that some gas was liberated from the filament itself, but as aluminium oxide is stable at high temperatures, it seems probable that most of the oxygen would have remained trapped in this form in the case of aluminium. The most likely explanation of the presence of an oxide film on the glass would seem to be that the gas liberated from the glass itself, under the action of the bombardment by metal atoms.

This is supported by the fact that the orientation of the oxide crystals is unaffected by the direction of incidence of the metal, which suggests that the combination with the oxygen probably occurs after the metal atoms have struck the glass.

The manner in which the orientation of the metal atoms in thick films is governed by the position of the filament with respect to the glass surface shows that there is a predominating direction of arrival of the metal atoms at the surface. This must not be taken, however, as an indication that the atoms travel straight from the filament to the glass. That this is not so may be shown by attempting to form a shadow (i.e. a patch free of metal) on a glass plate, by interposing a stop between the plate and the filament. If the distance from heater to plate is about 10 cm. and the distance from stop to plate is 2 cm. only a very ill-defined shadow is obtained. The reason for this is that there is a high concentration of metal atoms in the neighbourhood of the filament, (the number of atoms liberated is about $10^{20}/\text{sec.}$), and this cloud acts as a source of atoms. Near the filament, many collisions occur, and the further out the atoms travel, the fewer collisions there will be. Thus, although the majority of the atoms arriving at the specimen surface have a direction approximately parallel

to the line joining filament and specimen, they do not arrive without first having made collisions with other metal atoms.

The readiness with which oxide layers form on the metal films when they are heated to 250°C , suggests that there is a good deal of oxygen trapped in the films themselves. Certainly far thicker oxide layers form than would be the case with the metal in its ordinary state. This is especially so in the case of chromium films, and of aluminium films prepared under poor vacuum conditions.

The Imperial College of Science,
South Kensington,

Abstract.

Part A. The Quantitative Examination of Some Electron Diffraction Patterns.

Intensity measurements have been made on the electron diffraction patterns from a (111) natural face of diamond. The relative intensities of the reflected spots have been determined and the tolerances in Bragg angle have been measured and compared with the widths of the corresponding Kikuchi lines and with the values predicted by Bethe's theory. The inner potential of diamond has been measured and various qualitative observations have been made, a case where a spot has been partially suppressed by Kikuchi lines has been recorded.

The discrepancies between the observed results and existing theory are pointed out and discussed.

Part B. An Examination of the Structure of Some Evaporated Metal Films by Electron Diffraction

Films of aluminium, chromium and copper evaporated on to glass were examined, both as freshly prepared and after heating to 250°C in air. Several new crystal forms of the oxides of the various metals were found. An interesting type of orientation, apparently dependent upon the direction of incidence of the metal, was observed in the case of some of the aluminium films. The results are discussed.

*Some Quantitative and Qualitative Observations on the
Electron Diffraction Pattern from the Natural (111) Face
of Diamond. By R. BEECHING*.*

[Plate VIII.]

Introduction.

ELECTRON diffraction by reflexion from a single crystal cleavage face differs considerably from the analogous X-ray case, in so far as several diffracted spots may appear at once and the spots persist over quite a wide range of angle of incidence. Attention was first drawn to the latter phenomenon by Prof. G. P. Thomson, and it has been attributed to lack of penetration of the electron beam. The great objection to this explanation of the persistence of the spots is that the Kikuchi lines, from crystals showing considerable spread of the spots, are quite sharp. Since there is no reason for supposing that the diffuse radiation which gives rise to the lines will penetrate more than the main electron beam, it is difficult to account for the sharpness of these lines. We should expect their angular breadth to be of the same order as the range of angle of incidence over which the spots are found to persist.

The purpose of this work was to measure the angles over which the spots persist and also the breadth of the corresponding Kikuchi lines. The diamond was used because it very closely approaches a perfect crystal. This was confirmed by the fact that all the specimens used gave very sharp Kikuchi lines, and sharp lines are an indication of interior crystal perfection. Also, the diamond shows the persistence of the spots in a very marked manner. If an electron beam is diffracted by reflexion from a natural face of diamond which is parallel to the (111) planes a faint spot, in the position for specular reflexion, is visible at all angles of incidence. At the Bragg angle the spot becomes much more intense and then, as the angle is increased, it fades until it reaches a minimum at an angle about two-thirds of the way between one order and the next. As the angle is further increased the intensity again rises to a maximum value for the next Bragg reflexion.

* Communicated by Prof. G. P. Thomson, M.A., F.R.S.

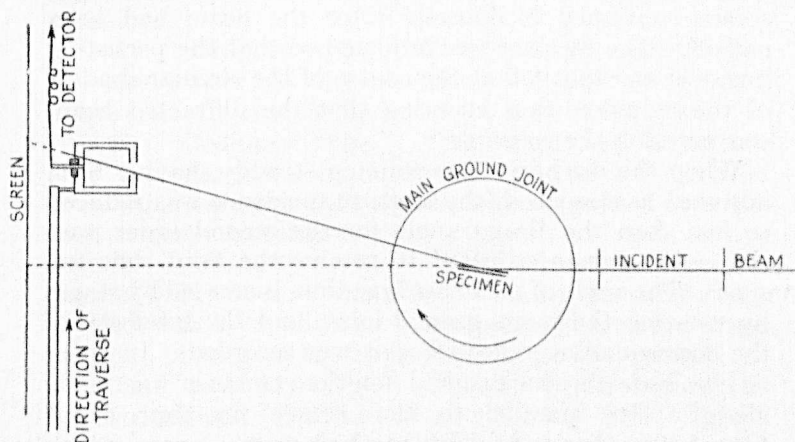
In this work also the intensity of the second order reflexion has been compared with that of the third order (the first order does not appear on account of the high inner potential of diamond). The second order should not appear according to the simple theory either in the case of X-ray or electron diffraction, since it is forbidden by the structure factor. A faint second order appears with X-rays, but in the case of electrons the second and third orders have comparable intensities, as Prof. G. P. Thomson has shown.

Apparatus and Experimental Procedure.

The electron diffraction apparatus used was a modification of that designed by Prof. G. P. Thomson. A small Faraday cylinder was arranged to traverse across the inside of the camera at right angles to the beam and just in front of the fluorescent screen. The cylinder was moved by means of a rack and pinion, worked through a ground-joint. The hole in the earthed casing of the cylinder was between 3 and 4 mm. in diameter, and that in the inside chamber was of the same size. The inner casing was insulated from the outer by an amber bush, and the lead from it was connected to a terminal passing through an insulating bush in the outer wall of the camera. The connexion between this terminal and the detecting system was made by a thick copper wire enclosed in a glass tube, and supported in an earthed brass tube by amber bushes. The current reaching the cylinder was allowed to leak away through a high resistance of the sputtered chromium type, of the order of 2×10^{11} ohm. The potential drop across this resistance was measured by a Lindemann electrometer, the circuit arrangement being that usually used with such instruments. The whole detecting system was included in an earthed, perforated zinc box, which provided satisfactory shielding in spite of the presence of the high tension supply in the room. Slow changes of the intensity of the primary beam and of the leakage resistance caused variation in the readings obtained from day to day, but since absolute measurements of intensity were not required this slow changing of conditions was of no importance. A more serious difficulty was the maintaining of the beam at a constant voltage during the course of a set of readings

which might require up to half an hour to obtain. The high tension supply circuit was the one usually employed in conjunction with the Thomson-Fraser type of apparatus, except that the capacity of the smoothing condenser was increased to $\cdot 014$ microfarads. The discharge was run for about half an hour before readings were commenced, and the spark-gap was adjusted so that a spark passed once or twice per minute. A fall of about 1 kv. in the voltage across the tube, due to pressure change, was accompanied by an increase of current which was easily detectable by means of a millimeter connected in the earth lead from the camera. An increase in voltage

Fig. 1.



Arrangement of apparatus.

caused a spark to pass, and with this arrangement a fairly steady potential drop was maintained across the tube. However, the greater part of the uncertainty in this work was due to variations in the voltage.

In order to ensure that the whole of the electron beam struck the crystal face, even at the smallest angles of incidence employed, the distance between the holes defining the beam was increased from the usual 6.5 to 11.5 cm. This brought the top hole, which, like the bottom hole, was 0.15 mm. in diameter, within 1.5 cm. of the specimen. This not only had the effect of reducing the divergence of the beam but also ensured that the beam was only about 0.15 mm. wide where it struck the specimen. The

specimen was approximately 1 cm. long, so that even at a glancing angle as small as $\cdot 02$ radians the whole beam struck the face.

The changes in angle of incidence of the beam were measured by means of a galvanometer lamp and scale, the spot being reflected from a small mirror on the main ground-joint of the camera, to which the specimen was attached.

The adjustment of the Faraday cylinder was made in the following way. The cylinder was pivoted eccentrically at the end of the traversing arm, so that by rotating it about this point it was possible to adjust it in a direction perpendicular to the line of traverse and to the beam. When the camera was in use the screen continued to fluoresce after the beam had been cut off. The receiver was adjusted so that the persisting image of the spot fell at the centre of the circular shadow of the cylinder, thus ensuring that the diffracted beam was entering the collector.

When the discharge was running steadily, having been adjusted as described, the angle of incidence was reduced to less than the Bragg angle for the second order, and the collector was adjusted to receive the faint reflected spot. The angle of incidence was then increased by stages by rotating the main ground joint, and the intensity of the corresponding reflected spot was recorded. In order to eliminate the background another traverse was made along a line parallel to the centre line but about 3 to 4 mm. from it. This method gave a curve which was certainly a good approximation to the background distribution of intensity.

When calculating the spread of a spot by his dynamical theory, Bethe ⁽¹⁾ assumed that there was only one strong diffracted beam. In order to satisfy this condition as far as possible the azimuth setting of the crystal was always arranged so that any spots appearing during the traverse other than those in the plane of incidence were always far out from the central spot, since then the interaction is less important.

The Diamonds.

The diamonds used were kindly lent by Sir Robert Robertson, F.R.S.⁽²⁾, and the numbers by which they are referred to here are those which he has given them.

Details about some of the stones will be found in his paper on the two types of diamond.

D. 2. "Extraordinary type." Most of the work was done with this stone, which had a highly polished (111) natural face showing only a few cleavage lines. The face was approximately an equilateral triangle of 1 cm. side.

D. 1. "Ordinary type." This stone had previously been examined by Prof. G. P. Thomson by electron diffraction, and had given a good pattern. When examined for the purpose of this work it was found to give only a few blurred spots and much background. This could probably be attributed to the fact that gold had been sputtered on to it since it was previously examined.

D. 10. "Ordinary type." This stone was smaller than the others used, having a natural (111) face which was approximately circular and about 4 mm. in diameter.

D 26. "Ordinary type." This stone had a natural (111) face which was an equilateral triangle of 1 cm. side. It charged up very badly, even when mounted in a cell with mercury backing.

D. 27. "Ordinary type." This diamond had two natural (111) faces. Examination under the microscope showed small equilateral triangular plates on these surfaces, presenting the appearance of parallel growth.

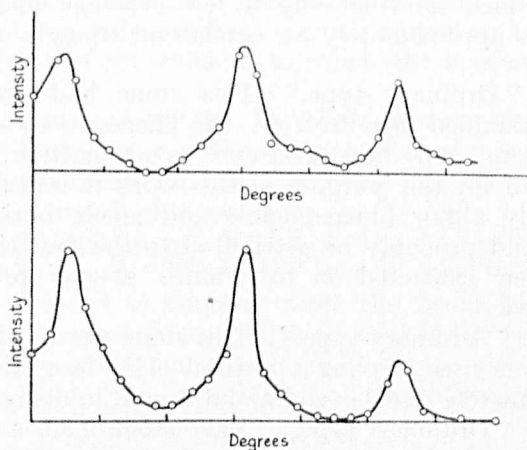
D. 28. "Ordinary type." This specimen had a triangular natural (111) face of about 1 cm. side. Microscopic examination showed it to be dotted with small pyramid growths. The stone did not give a very good pattern.

Results of Intensity Measurements.

From the sets of readings obtained curves were plotted showing intensity in arbitrary units against change in angle. The curve for the background intensity was plotted on the same graph, and from these pairs of curves, curves showing the difference in intensity between the spots and the background were plotted. Two typical curves of this sort are shown in fig. 2, while the relative intensities and half intensity spreads of the various orders obtained from five curves are shown in Table I. The values of the spread shown in the table are the sum

of the deviations on either side of the Bragg position, which reduce the intensity to half the maximum.

Fig. 2.



Curves from D. 2.

TABLE I.

D. 2.

No.	Wave-length.	Half-intensity spread in minutes of arc.			Relative intensities.	
		2nd order.	3rd order.	4th order.	3rd order 2nd order	3rd order 4th order
1.....	·067 Å.	33'	23'	18'	.77	2·6
2.....	·072	43	29	19·5	1·12	1·39
3.....	·060	38	36·5	25	1·26	1·32
4.....	·069	23	29·5	23	1·46	3·95
5.....	·072	38	21	23	1·02	2·58
Mean ..	—	35±3	28±3	22±1	1·1±·1	2·4±·5

The mean spreads are shown, although all the curves were not taken at the same voltage. This has been done since the change of spread over the range of wave-length used is likely to be less than the experimental error.

A number of preliminary curves were obtained with the apparatus before the anode was lengthened and with

only $\cdot 002$ microfarads smoothing in the high tension supply circuit. The values for the relative intensities of the orders agreed very well with those obtained under the final conditions, but the spreads were 20–30 per cent. larger. This was probably due to slight inhomogeneity of the beam. A few curves were taken under the original conditions with D. 10. The curves were of the same general shape as those with D. 2 except that the second order was about 20 per cent. less intense and its spread uncertain, due to charging up.

Examination of the Kikuchi Lines.

In the first case an attempt was made to measure the intensity distribution across the Kikuchi lines by means of a Faraday cylinder with a fine slit in it parallel to the line. It was found possible to detect the lines in this way, but owing to the fact that they were only about 5 per cent. more intense than the background it was impossible to measure the distribution of intensity. This method was given up in favour of a photometric method.

For this purpose the plate attachment, which had been removed for the first part of the work, was replaced. The part of the plate to be exposed at any one time was limited, by means of a mask of sheet brass, to a strip 3 mm. wide perpendicular to the shadow edge (*i. e.*, to the line in which the plane of the crystal met the screen) and slightly to one side of the centre line of the pattern. The specimen was adjusted so that several orders of the lines parallel to the shadow edge were seen crossing the strip. A number of exposures were then made on one plate, the time of the first exposure being one second and those of the succeeding exposures increasing by intervals of one second. From seven to eleven exposures were made on each plate, the strips being parallel side by side.

In order to obtain intensity curves from the photographic records the plates were microphotometered by means of a Cambridge recording microphotometer. A traverse was made along the one-second exposure strip and a second traverse was made at right angles to the strips. From the second record, which presented the appearance of a series of flat-topped humps, a curve

was plotted showing the instrument reading against the corresponding value of It , where I is the electron intensity, which was the same at corresponding points on all the strips, and t the time of exposure. It has been shown that the blackening of the plate by electrons depends only on the product It , and it was therefore possible by means of this curve to convert the photometer record for the traverse along the strip into a curve showing intensities against distance along the strip.

Three curves were obtained in this way for D. 2 and two for D. 27.

Results of Kikuchi Line Measurements.

Two typical intensity curves are shown in fig. 3. The intensity in arbitrary units is shown plotted against

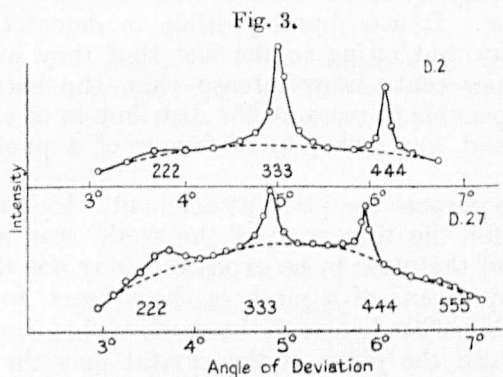


TABLE II.

Curve.	Wave-length.	Angle of half-intensity spread in minutes.		
		2nd order.	3rd order.	4th order.
D. 2. Curve 1.....	·071 Å.	15'	9'	5·5'
2.....	·071	—	11	7·5
3.....	·072	20	10	6·5
D. 27. Curve 1.....	·061	16·5	10·5	5·5
2.....	·067	—	8	7·5
Mean	—	17·2	9·7	6·1

the angle between the main and the scattered rays. The half-intensity spreads of the lines are shown plotted in

Table II. The relative intensities of the lines depend upon the distribution of intensity in the diffuse radiation producing them, and hence upon their proximity to a diffracted spot. For this reason values of the relative intensities of the Kikuchi lines have little meaning until more is known about the diffuse radiation.

These results should all be reduced by about 1.5' to allow for the finite width of the beam.

Determination of the Inner Potential.

A number of determinations of the inner potential were made for D. 2 and D. 26 by the rotation method as first used by Yamaguti ⁽³⁾. The necessary measurements were made on the fluorescent screen. The inner potential was also determined in the case of D. 2 and D. 27 from measurements on the Kikuchi lines parallel to the shadow edge, the method being due to Shinohara ⁽⁴⁾. The measurements for this purpose were obtained from photographs.

Results of Inner Potential Measurements.

The values of the inner potential for the various specimens examined are shown tabulated below.

TABLE III.

" Ordinary type."		" Extraordinary type."	
Rotation method.	Kikuchi lines.	Rotation method.	Kikuchi lines.
volts.	volts.	volts.	volts.
D. 26. 24.3	D. 27. 20.1	D. 2. 23.4	D. 2. 20.7
20.4	17.9	19.4	17.5
24.0	20.7	21.4	21.0
	20.7	19.4	20.6
Mean 6. . 21.1 $\pm$.8 volts.		Mean . . . 20.4 $\pm$.6 volts.	

The mean value for all specimens is 20.8 $\pm$.7 volts.

Qualitative Examination of the Diamond Pattern.

A number of ordinary electron diffraction photographs were taken from D. 2, D. 27, and D. 28; also rotation

photographs were taken with D. 2 and D. 27. The latter specimen charged up slightly at small angles of incidence, but the plates showed the persistence of the spots over a considerable range of angle of incidence and also the asymmetry of spread mentioned in the Introduction.

In the case of D. 2 it was found that for all settings of the azimuth a faint fine line, similar to a Kikuchi line, always appeared, passing through the spot in the plane of incidence and perpendicular to the shadow edge. In symmetrical or nearly symmetrical settings of the crystal as many as five similar vertical lines appeared, passing through the various side spots. In such settings, the lines were much more intense (figs. 5 & 6, Pl. VIII.). The broad bands which are normally found with other crystals under such circumstances were not observed.

It has not been decided to what these lines are due. With many crystals elongation of the spots in a direction perpendicular to the shadow edge is observed, and may usually be attributed to one of two causes :

(1) Part of the crystal surface being broken into small blocks, tilted slightly with respect to one another.

(2) Part of the crystal surface being composed of very small blocks which have maintained their alignment but which are separated by fine cracks.

The effect of crystal imperfection of the first type would be to produce a rotation pattern superimposed upon the ordinary spot pattern. The lines should therefore show minima at certain places, but they do not. The elongated spots produced should be rather broad, since the normals to the small crystal facets will not necessarily lie in the main plane of incidence. Actually the lines are very sharp ; also this theory would not account for the greatly increased intensity of the lines in all symmetrical settings of the azimuth.

The objections to an explanation based upon a supposed imperfection of the second type are very similar. The way in which elongated spots are produced by such imperfection is by relaxation of one of the diffraction conditions described by Kirchner ⁽⁵⁾, as a result of the small extent of the crystal blocks in the direction of the beam. The pattern produced will resemble a rotation picture superimposed on the ordinary pattern. As has already been

pointed out the lines from diamond did not show the features to be expected in a rotation pattern.

For the reasons given it seems that the observed lines cannot be attributed to the causes mentioned. Many crystals, when set in symmetrical or nearly symmetrical positions with respect to the electron beam, give rise to a pattern of dark bands, an effect first mentioned by Shinohara ⁽⁶⁾. No such bands were observed in the case of diamond, and it is possible that the vertical lines are a modified form of band. In some cases a vertical white line also appeared; one such is just visible inside the bright line on the left of fig. 6 (Pl. VIII.).

With all the specimens which gave good patterns it was possible to find a symmetrical setting, such that the fourth order reflected spot was flanked on either side by an intersection of several Kikuchi lines. Under these circumstances the spot was noticeably diminished in intensity by the proximity of the lines. This effect is shown in figs. 7 and 8 (Pl. VIII.); fig. 7 shows the general appearance of the pattern, while fig. 8 shows the spot when normal and when partially suppressed. The two exposures were made on the same plate for the same time.

This suppression of the spot would seem to indicate interference between the spots and the Kikuchi lines. If this is so it must mean that the lines are produced, partly at least, by electrons which have only been scattered elastically.

Discussion and Comparison with Theory.

This work has shown no definite differences between the electron diffraction patterns obtained from the two types of diamond. It is felt that no importance can be attached to the fact that the second order reflexion appeared to be slightly less intense in the case of the ordinary type, since the specimen used charged up badly. All the specimens of the ordinary type showed this charging up, while D. 2 only charged at very small angles of incidence indeed. Since D. 2 was the only stone of the ordinary type examined it is impossible to decide whether this difference is a feature of the two types or not. D. 2 showed the vertical lines in a much more

marked manner than the other specimens, although D. 27 showed the effect slightly. With none of the specimens were any bands observed.

The quantitative results are not in agreement with any existing theory. Bethe's ⁽¹⁾ dynamical theory predicts that over a small range of angle the reflexion will be *total*, while outside this range the intensity will fall off very rapidly. In the case of electrons of the velocities used the range of total reflexion predicted is of the order of 2' for the (333) reflexion, and less for higher orders. Actually the diffracted spots are found to have an intensity of only about 1 per cent. of that of the primary beam, and the third order has a half-intensity spread of about 30'.

Recently Kikuchi ⁽⁷⁾ has arrived at a result similar to that of Bethe by a somewhat different method. He has also measured the spread of the spots for zinc blende by photometric measurements on a rotation photograph, and he finds that the actual spreads are about twenty times those predicted by theory. This is in good agreement with the results obtained from diamond. Kikuchi suggests that the discrepancy between the theoretical and practical results is due to the fact that absorption has not been taken into account in the theory, while in practice it limits the depth of penetration of the electron beam. As has been pointed out in the Introduction this is the view that has been advanced many times before to explain the spread of the spots, but it does not account for the sharpness of the Kikuchi lines.

From the thickness of polycrystalline metal film which an electron beam will penetrate before falling to half intensity (*i. e.*, about 500 Å.) it is possible to deduce that at the small glancing angles employed in reflexion work the effective depth of penetration of the beam will be of the order of five or six planes. This is sometimes advanced as an argument in favour of the theory that the spread is due to lack of penetration, and since the observed form of curve would be produced if only about four planes were effective the agreement seems to be good. It is questionable, however, whether the value of penetration, determined on the basis of transmission through polycrystalline films, may be applied to the case of reflexion from a single crystal at glancing incidence.

In the case of reflexion from some types of crystal a so-called "surface pattern" occurs, consisting of two or more semicircles of spots which occur simultaneously and persist over a wide range of angle of incidence. Such patterns satisfy the condition for diffraction by a plane cross-grating (as formed by the top net plane) at grazing incidence. The appearance of such patterns is usually explained in terms of lack of penetration. This type of pattern might, however, be equally well explained by supposing that the top few planes differ from the bulk of the crystal in some respect.

J. W. Harding has suggested that the observed effects may be due to an expansion or contraction of the spacing between the surface planes. He is at present working further upon this idea, and until the theory has been fully considered it is impossible to say whether it will explain the experimental results, but it promises to do so.

The appearance of the (222) reflexion is forbidden on the simple theory, but Bethe's dynamical theory predicts such a beam as a result of interaction between the (111) and (333) beams in the crystal. Bethe⁽¹⁾ has suggested that the weak (222) beam found with X-rays may be due to a similar effect made possible by the high perfection of the diamond. It has been shown that the relative intensity of the (222) reflexion is less the harder the X-rays and the less perfect the diamond, which suggests that it is dependent upon the magnitude of the interaction between the waves and the crystal. In the case of electron waves, which are easily scattered, we should expect the relative intensity of the forbidden order to be far greater than in the case of X-rays.

A commonly accepted explanation of the appearance of a (222) order from diamond with X-rays is that the carbon atoms are distorted by their neighbours and can therefore no longer be regarded as spherically symmetrical as they are in the simple theory. Since in the case of electron waves the greater part of the scattering is due to the nucleus, we should expect the effect of such distortion to be less than for X-rays, since it is likely to affect only the outer shells of the atom. It has already been pointed out that the (222) order is relatively far more intense in the case of electrons than for X-rays, so that it seems highly improbable that the appearance of the forbidden orders can be attributed to distortion in the

electron case. The second order cannot be due to a purely surface effect, since a fairly sharp (222) Kikuchi line appears. It would seem probable therefore that the forbidden maximum is produced in the manner suggested by Bethe.

Attention has been drawn in the Introduction to the fact that the intensity of the reflected spots does not fall off symmetrically on either side of the Bragg angle. The intensity falls off more slowly on the side of large angle, which is in the opposite sense to the asymmetry observed by Yamaguti ⁽⁸⁾ in the case of a natural face of pyrite.

Kikuchi has offered an explanation of the effect observed by Yamaguti ⁽⁸⁾. He attributes the asymmetry to the effect of intermediate crystal planes. He considers first of all a simple crystal with equally spaced planes parallel to the surface, and by assuming that each plane scatters the same amount of the incident wave he arrives at the solution

$$|S_0|^2 = \frac{\sin^2\left(\frac{2\pi}{\lambda} nd \sin \theta\right)}{\sin^2\left(\frac{2\pi}{\lambda} d \sin \theta\right)},$$

where $|S_0|^2$ is the intensity of the scattered beam, n the number of planes, and d the plane spacing.

In the case where there are intermediate planes distance x from the original planes this expression becomes

$$|S|^2 = 4S_0^2 \cos^2\left(\frac{2\pi}{\lambda} x \sin \theta\right),$$

where $|S|^2$ is the new intensity of the scattered beam and S_0 has the same meaning as before. Since $|S_0^2|$ represents a symmetrical distribution in the spots the asymmetry is introduced by the $\cos^2\left(\frac{2\pi}{\lambda} x \sin \theta\right)$ term.

In the case of diamond x is $d/4$, so that this term becomes

$$\cos^2\left(\frac{n\pi}{4}\right).$$

On this theory the second order is missing, the third order falls off more slowly on the side of large angle, the fourth order is symmetrical, while the fifth order falls off more slowly on the side of small angle. Actually all the orders fall more slowly on the side of large angle, so that this theory certainly does not hold in the case of diamond.

Summary.

Intensity measurements have been made on the electron diffraction pattern obtained from a (111) face of diamond. The relative intensities of the main spots have been determined and the tolerances in the Bragg angles have been compared with the widths of the corresponding Kikuchi lines. The inner potential has been measured and various qualitative observations have been made. A case where a spot has been partially suppressed by Kikuchi lines is recorded.

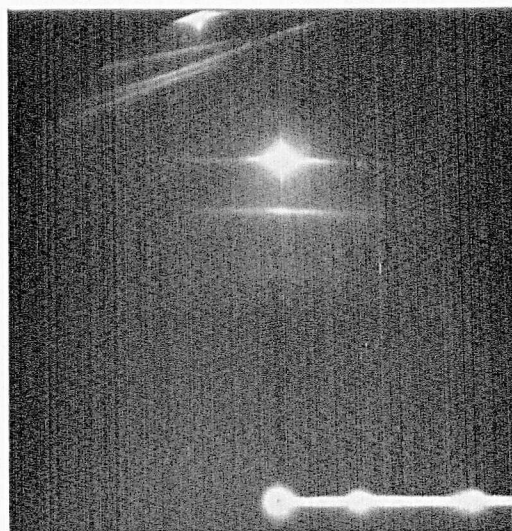
In conclusion, I should like to thank Prof. G. P. Thomson for suggesting the main problem and for his helpful advice and kind interest during the work; I should like also to thank Sir Robert Robertson for the loan of the diamonds which has made this work possible.

References.

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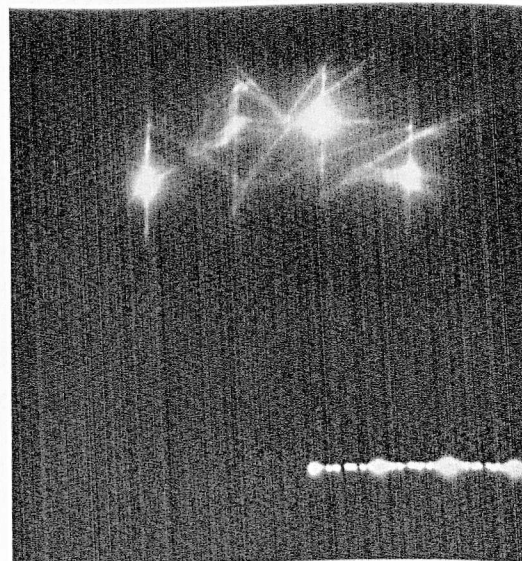
Imperial College of Science, S. Kensington.
21st June, 1935.

FIG. 4.



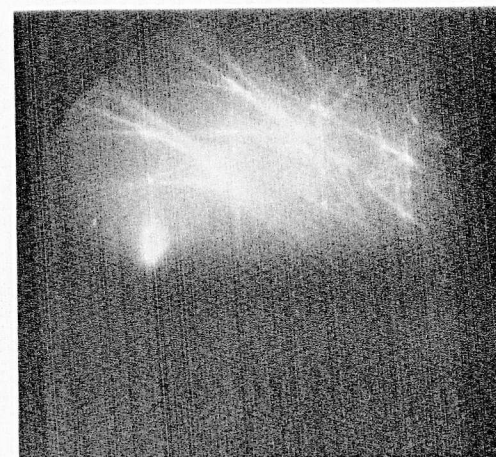
D. 27.

FIG. 5.



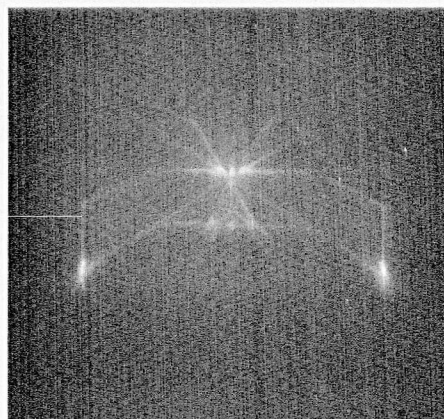
D. 2.

FIG. 6.



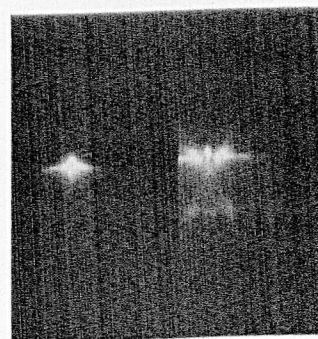
D. 2.

FIG. 7.



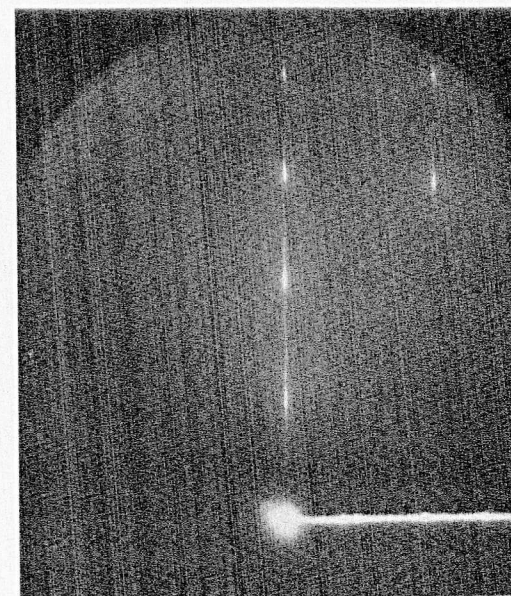
D. 2.

FIG. 8.



D. 2.

FIG. 9.



D. 2. Rotation.

THE STRUCTURE OF ALUMINIUM, CHROMIUM,
AND COPPER FILMS EVAPORATED ON
GLASS.

*The Structure of Aluminium, Chromium, and Copper
Films Evaporated on Glass. By R. BEECHING,
A.R.C.S., B.Sc. **

[Plates VIII. & IX.]

Introduction.

DURING the course of research, conducted with a view to establishing the best method of preparing evaporated metal films for mirrors, specimens of aluminium, chromium, and copper films on glass were examined by electron diffraction. Several interesting features in their structure were observed, although, owing to the necessity for keeping the immediate practical

* Communicated by Prof. A. O. Rankine, D.Sc., F.R.S.

object in view, it was not possible to examine some of the effects in detail.

Preparation of Specimens.

The evaporation, which was not performed by the author, was carried out in a metal chamber, the initial pressure in which was of the order of 10^{-4} mm. of mercury. When the evaporation was begun there was a momentary drop in pressure, followed by a rise to two or three times the initial value. After the evaporation was over the pressure was lower than at the beginning, which suggests that the evaporating process has a "gettering" effect.

In order that specimens of suitable dimensions for electron diffraction examination might be prepared with minimum handling, the metal was evaporated on to glass strips about 1 cm. wide and about 5 cm. long. These were divided into six parts by diamond scratches on the face upon which the metal was to be evaporated. A sharp tap with a file on the back face was sufficient to break the strips into pieces. The metal was evaporated from a filament placed slightly to one side of the glass strip, so that one edge of the strip was coated as well as the face to be examined. This was done in order to enable contact to be made with the metal film, to prevent charging up when the electron beam was incident upon the specimen surface.

A standard method of cleaning the glass was adopted. The strips were washed in aqua regia, then in distilled water, rubbed hard with clean cotton-wool soaked in hydrogen peroxide solution, and finally dried on dry cotton-wool. In order to prevent contamination from handling, rubber gloves washed with ammonia were worn. This method of cleaning is that recommended by Mr. E. W. Foster of the Imperial College of Science for the preparation of sputtered silver films, where conditions of cleanliness are of extreme importance. The cleaning procedure was probably more stringent than was necessary, but was adopted to eliminate uncertainty in the results as far as possible.

Aluminium Films: Scheme of Examination.

It was decided first of all to vary the thickness of the films, then the path from heater to mirror, also the

speed of evaporation, and finally the vacuum conditions. Under each set of evaporating conditions three strips of specimens were prepared. One of these was examined without further treatment, one was heated to 250° C. in an air-oven, and one was washed with methylated spirits before examination. One strip was washed with methylated spirits because it has been suggested that this treatment hardens the film. It is difficult to imagine a possible mechanism for such hardening, and, in fact, no such effect was observed. Electron diffraction examination showed no change in structure, and the washed specimens were found to scratch as easily as the unwashed ones.

Change of Thickness of the Film.

The structure of the evaporated films was found to vary in a very marked manner with increasing thickness. Very thin films, about 100–200 Å. thick (*i. e.*, films which were barely visible by transmitted light, but which appeared to reflect quite well and had a metallic lustre by reflected light), gave electron diffraction patterns which showed no trace of aluminium metal. A considerable number of plates of this pattern were taken, and the mean crystal spacings calculated from them are shown in Table I. The intensities of the rings are not given, as these were found to vary from specimen to specimen. A typical pattern is shown in fig. 1 (Pl. VIII.).

The compound producing these rings is almost certainly some form of aluminium oxide (Al_2O_3). There are several reasons for supposing this. Firstly, the residual gas in the apparatus was air, and since no known form of aluminium nitride exists the oxide seems the obvious choice. Added to this the diffraction pattern shows the compound to have a crystal structure with a face-centred cubic lattice of cube side $a=7.82$ Å. In this respect the structure is similar to that of $\gamma\text{Al}_2\text{O}_3$, which has a face-centred cubic lattice the cube side of which has been given as 7.77 Å. and 7.90 Å. by different workers. The ring intensities in the pattern from thin films were, however, quite different from those in the $\gamma\text{Al}_2\text{O}_3$ pattern. According to Verwey* the structure of $\gamma\text{Al}_2\text{O}_3$ is a face-centred cubic lattice of oxygen with aluminium atoms

* Verwey, *Zeit. f. Krist.* xci. p. 65 (1935).

distributed at random, in certain proportions, over a limited number of possible positions in the cell. In the case of another form of the oxide, γ' - Al_2O_3 , Verwey* suggests a similar structure with even less constraints upon the positions of the aluminium atoms. It would seem quite probable, therefore, that the compound giving rise to the patterns obtained from very thin films of aluminium is some form of Al_2O_3 related to the γ form. The supposition that the compound is Al_2O_3 is strengthened by the fact that films of evaporated chromium

TABLE I.

Plane.	Observed spacing.	Spacing of $\gamma\text{-Al}_2\text{O}_3$.
111	4.56 Å.	4.49 Å.
200	3.87	3.88
211	3.20	3.17
220	2.73	2.74
311	2.33	2.34
222	—	2.24
400	1.98	1.94
331	—	1.78
420	—	1.74
422	1.65, very faint.	1.58
511 }	—	1.49
333 }	—	1.37
440	1.39	1.37
531	—	1.31
442 }	—	1.29
600 }	—	1.29
620	1.22	1.23
533	—	1.18
622	—	1.17
444	1.12	1.12

Cube side $a = 7.82$ Å. $a = 7.77$ Å. Steinheil.

give a similar pattern when heated. The only oxide of chromium which would be expected to have a crystal structure similar to that of an aluminium oxide is Cr_2O_3 .

Thicker films of aluminium, about 500–1000 Å. thick (*i. e.*, films which are quite blue by transmitted light, but which are too thick to allow print to be read through them), give patterns showing both oxide rings and the ordinary aluminium pattern. Usually only one or two

* Verwey, 'Laboratoria.' N. V. Phillips, Gloeilampenfabrieken, Eindhoven, Holland (1935).

oxide rings appear, and, as a rule, the aluminium rings tend to be rather diffuse, indicating small crystal size. In some cases the pattern consists of very diffuse aluminium rings with no oxide rings. A probable explanation of these patterns is that in some cases the upper surface of the film consists of aluminium and oxide mixed, while in others the oxygen prevents the formation of large crystals without actually going into combination. (Large crystals, as referred to here, mean crystals of over 100 Å. side, while crystals so small as to give really diffuse rings have dimensions of about 20 Å.)

Still thicker films of aluminium (*i. e.*, films which are almost or quite opaque) give sharp ring patterns due to crystals of aluminium more than about 100 Å. square. In nearly all cases these patterns show a tendency for the aluminium crystals to orientate with a cube face parallel to the glass surface. A further account of the orientation of these films will be included later.

Variation of the Distance from Heater to Mirror.

Variation of the distance from heating filament to the specimen surface appears not to affect the film, provided the thickness of the film is about the same in each case, except that films prepared at about 8 cm. from the heater, which was the shortest path used, tended to contain oxide rather more than the others.

The Speed of Evaporation.

The speed at which a certain thickness of film may be reached depends upon the distance from the heater to the specimen and upon the rate of evaporation. In the case of fast evaporation it took from 5–10 secs. to prepare a film, while a film prepared very slowly might take a minute or more to deposit. The slower the evaporation the poorer the electron diffraction pattern produced in so far as the intensity of the rings, compared with the diffusely scattered background, becomes less and the rings themselves tend to be diffuse. When the rate of evaporation is very slow even an opaque film, such as would normally give a sharp ring-pattern, gives only two diffuse rings. There are two possible explanations of this effect. Either the crystals in the surface are very small or the surface is so flat that there are no fine

projections through which the electron beam can penetrate. Since it seems unlikely that a very flat surface will result in this particular case only, the first explanation is the more probable. One would normally expect larger crystal size to result from the slower crystal growth consequent upon slower evaporation. This effect is probably offset by the fact that more gas is trapped in the metal during a slow evaporation.

Effect of Poorer Vacuum Conditions.

A number of specimens prepared under poorer vacuum conditions, the initial pressure being of the order of 10^{-3} mm., were examined. The effect of the increased pressure appeared to be similar to that due to the slowing down of the evaporation. The diffraction rings were diffuse, and in one or two cases oxide rings were observed in the patterns from quite thick films. These films became cloudy when heated to 250°C ., and this will be discussed further under the next heading.

The Effect of Heating the Films to 250°C .

The effect of heating all the types of specimen so far discussed was investigated. In the case of the very thin films, which already showed an oxide film, there was no change either in the appearance or the structure of the film when it was heated to 250°C . Those thicker films, which were partly oxide and partly aluminium, gave a pattern which showed no aluminium rings at all after heating. The pattern obtained was such as would be produced by a face-centred cubic lattice of side $a=5.53\text{ \AA}$. As this spacing is equal to half the face diagonal of the $\gamma\text{Al}_2\text{O}_3$ cube, the ring spacings are common to the two patterns. This is shown in Table II., while the actual pattern is shown in fig. 2 (Pl. VIII.).

It is very probable that this oxide is another form of partially organized crystal related to $\gamma\text{Al}_2\text{O}_3$.

Many of the crystals in the film were orientated with a cube face parallel to the plane of the specimen, this being indicated by sharp spots on the rings produced by the spacing between the cube faces (*i. e.*, the (200), (400), (600) rings).

In the case of films of similar thickness to those referred to above prepared under poorer vacuum conditions

the specimens became clouded with a white bloom when heated to 250° C. Electron diffraction examination of this surface film showed it to be composed of a mixture of the two oxides which have already been described. The oxide crystals were much bigger than in the case of films prepared under better vacuum conditions. This was indicated by the presence of marked spots in many parts of the rings. The crystals of the oxide of type I. showed a tendency to orientate on a (111) face, while those of type II. tended to orientate with a cube face parallel to the glass surface. The crystals were of the

TABLE II.

Plane.	Observed spacing.	Calc. spacing, $a=5.53 \text{ \AA.}$	Intensity.
111	3.27 $\text{\AA.}$	3.20	m
200	2.78	2.77	s
211	2.32	2.26	ff
220	1.96	1.95	ss
311	1.65	1.67	m
222	1.58	1.59	m
400	1.38	1.38	f
331 }	1.23	1.25	ss
420 }			
422	1.11	1.13	s
511 }	—	1.06	—
333 }			
440	—	.98	—
531	—	.94	—
442 }	.92	.92	ff
600 }			

ss, very strong ; s, strong ; m, medium ; f, faint ; ff, very faint.

order of 10^{-3} cm. square (estimated from the size of the spots on the rings), and were therefore of sufficient size to affect the reflecting power by virtue of their roughness alone.

The thick films, which were pure aluminium on the surface, showed no change when heated to 250° C. It is probable that, both before and after heating, they were covered with an exceedingly thin protective film of oxide, which might not show up under electron diffraction examination owing to the relative weakness of the pattern arising from such a thin layer, compared with the pattern from the aluminium itself. Aluminium forms a very good

protective layer, and we should expect this layer to be very thin, of the order of a few molecules thick, since it would kill its own growth.

Orientation of the Aluminium Crystals.

As has been mentioned earlier the aluminium crystals in the thick films showed a tendency to orientate with a cube face parallel to the surface. This tendency was, however, disturbed by the direction in which the aluminium was fired on. Although this effect had no direct bearing upon the main problem to be investigated, and could not therefore be studied in detail, it was thought worth while to examine the general nature of the phenomenon. Further work on this effect might provide a very valuable check on any proposed dynamic theory of crystal growth. As has already been explained aluminium was evaporated on to one face and one edge of the glass strips by firing the metal obliquely on to the face to be examined (at an angle from $20-40^\circ$ with the surface) from a filament parallel to the strip, but to one side of it. When a small specimen, cut from the strip, was examined in the diffraction camera with the beam crossing the surface in a direction perpendicular to the length of the strip, the pattern was arced symmetrically about the centre line in such a way as to indicate that all the crystals tended to orientate on a cube face. When the electron beam was fired across the specimen face in a direction parallel to the length of the strip the pattern was arced symmetrically about a line making an angle of about 10° with the centre line of the pattern, on the side remote from the line of fire of the incident metal. The type of pattern is shown in fig. 5 (Pl. IX.). This means that the aluminium crystals were orientated with a cube face parallel to a plane whose normal lay in the plane of incidence of the evaporated metal, and was inclined at an angle of about 10° to the normal to the specimen surface. When the angle between the direction of incidence of the evaporated metal and the specimen surface was increased to 45° the electron diffraction pattern showed the crystals to be orientated with a cube face roughly parallel to a plane whose normal lay in the plane of incidence of the metal, and which made an angle of about 15° with the normal to the specimen

surface, on the side of it nearer the heating filament. The type of pattern is shown in fig. 6 (Pl. IX.).

Specimens were also prepared with the metal fired normally on to the glass surface. In this case the crystals were found to be orientated with a cube face parallel to the specimen surface (fig. 7, Pl. IX.). It is difficult to come to a very definite conclusion with so little detailed information, but it seems quite likely that the orientation observed might be due to the conflict of tendencies on the part of the crystal to grow with a cube face parallel to the surface and also with a cube face perpendicular to the direction of incidence of the metal.

Chromium Films.

In the case of chromium, films of varying thickness were examined. Exceedingly thin, almost invisible films gave a pattern consisting of a few rings due to oxide and a few diffuse rings probably due to chromium. When heated such films gave an oxide pattern with a ring arrangement identical with that from heated aluminium films.

Thicker films of chromium gave a diffuse ring pattern due to small crystals of the pure metal. Even films thick enough to be opaque showed this pattern, there being no increase in crystal size with increasing film thickness corresponding to that observed with aluminium. On heating, these films became coated with a purplish bloom and electron diffraction examination showed this to be the same form of oxide as that formed on thin films, the cube side being $a=5.46 \text{ \AA.}$, which was slightly smaller than the corresponding aluminium oxide spacing. The mean spacings from a number of plates are shown in Table III., while the actual pattern is shown in fig. 3 (Pl. VIII.).

In the case of one specimen of medium thickness the oxide layer formed on heating was a mixture of the oxide mentioned above and an oxide similar in structure to the type I. aluminium oxide referred to earlier. The pattern is shown in fig. 4 (Pl. VIII.).

Aluminium on Chromium Films.

Thick films of aluminium were evaporated on to chromium films on glass. Orientated aluminium patterns,

similar to those from thick aluminium films on glass, were obtained. Heating the films to 250° C. made no difference to the surface.

Copper Films, on Glass and on Aluminium on Glass.

Films of copper of varying thickness were examined, and in no case was a pattern of pure copper obtained. With some of the thicker specimens copper rings were observed in addition to the predominating pattern due to cuprite, Cu_2O . One set of copper specimens, ranging

TABLE III.

Plane.	Observed spacing.	Calc. spacing, $a=5.46 \text{ \AA}$.	Intensity.
111	3.27	3.16	m
200	2.74	2.72	s
211	2.22	2.23	ff
220	1.94	1.93	ss
311 }	1.60	{ 1.64 }	m
222 }		{ 1.57 }	
400	1.35	1.36	f
331 }	1.22	{ 1.25 }	s
420 }		{ 1.22 }	
422	1.10	1.11	m
333 }	—	1.05	—
511 }	—		—
440	—	.96	—
531	—	.92	—
442 }	.90	.91	ff
600 }			

from a film which was barely visible to one which was almost opaque, gave a peculiar pattern, which is shown in fig. 8 (Pl. IX.). The very strong ring and the sharper rings are probably due to Cu_2O , while the innermost ring and the third ring, which are diffuse, have not yet been accounted for. The very strong ring corresponds to the (110) ring from cuprite, but is far stronger than this ring should be. A similar set of specimens of copper, on aluminium on glass, gave a ring pattern with spacings corresponding to those of cuprite, but with different intensities, the (110) ring again being abnormally strong.

Although the actual crystal structure and nature of the compounds formed has not been determined in all

cases, it is most probable that oxygen is either trapped in or combined with the copper in all these films.

When the films are heated to 250°C . they tarnish very readily. This film of tarnish, which is thick enough to show interference colours, was shown by electron diffraction examination to consist of cuprite. The readiness with which the tarnishing occurs is probably due to the presence of oxygen trapped in the film.

Mechanical Properties of the Films.

In the case of aluminium the thinner films were found to adhere best. They were unaffected by the sticking on and pulling off of a piece of adhesive tape, while some of the thicker films would not stand this test. All the aluminium films could be scratched easily with the point of a knife, but were able to withstand fairly well vigorous rubbing with dry cotton-wool. They could be washed with wet cotton-wool without suffering any harm. The films were able to withstand the attack of both concentrated hydrochloric and nitric acids for some time (*i. e.*, about 30 sec. in the case of HCl and much longer in the case of HNO_3).

The chromium films were very hard, it being impossible to scratch them with the point of a knife. Aluminium on chromium films also appeared to withstand this test, but this may have been only apparent. The aluminium may have been scratched off, although the scratch was not visible on account of the opaque chromium backing.

Summary and Discussion.

It has been shown that thin evaporated films of aluminium, chromium, and copper consist mainly of the respective oxides of the metals, although these oxides have not their usual crystal forms. The actual structures of these oxides have not been fully determined, but it seems probable that in the case of aluminium the oxide is related to $\gamma\text{Al}_2\text{O}_3$. The structure of the oxide present in a thin film of chromium is similar to that present in a thin film of aluminium.

The oxides formed on both metals after heating to 250°C . have the same structure and almost the same spacing. It is just possible that the form of oxide observed on heated aluminium films is the same as that

observed by Steinheil * on an aluminium foil which had been subjected to atmospheric oxidation. There is a difference in the cube side and in the relative intensities of the rings. The latter difference might easily be due to orientation, since Steinheil's pattern was obtained by transmission. The spacing found by Steinheil was $5.35 \text{ \AA}$., which differs from the value found in this work by about 4 per cent., which is rather greater than would be expected after allowing for experimental errors.

In view of the non-tarnishing properties common to aluminium and chromium it is of interest to notice that they both form oxides of the same structure in addition to the common rhombohedral forms.

Thick films of aluminium and chromium were apparently pure metal on the surface. It is suggested that the protective oxide layer, which must have been present, was so thin as not to be observed.

Under normal evaporating conditions the initial pressure in the chamber was such that the mean free path for the metal atoms was greater than the distance from heater to mirror. It seems unlikely, therefore, that the oxygen in the films was picked up by the metal atoms in crossing between the filament and the mirror. It is possible that some gas was liberated from the filament itself, but as aluminium oxide is stable at high temperatures it seems probable that most of the oxygen would have remained trapped in this form in the case of aluminium. The most likely explanation of the presence of an oxide film on the glass would seem to be that the gas is liberated from the glass itself under the action of the bombardment by metal atoms. This is supported by the fact that the orientation of the oxide crystals is unaffected by the direction of incidence of the metal, which suggests that the combination with the oxygen probably occurs after the metal atoms have struck the glass.

The manner in which the orientation of the metal atoms in thick films is governed by the position of the filament with respect to the glass surface shows that there is a predominating direction of arrival of the metal atoms at the surface. This must not be taken, however, as an indication that the atoms travel straight from the filament to the glass. That this is not so may be shown by

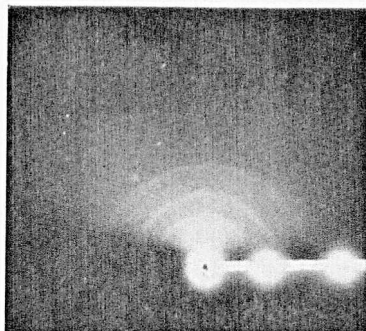
* A. Steinheil, *Ann. Physik*, (5) p. 19 (1934).

attempting to form a shadow (*i. e.*, a patch free of metal) on a glass plate by interposing a stop between the plate and the filament. If the distance from heater to plate is about 10 cm., and the distance from stop to plate is 2 cm., only a very ill-defined shadow is obtained. The reason for this is that there is a high concentration of metal atoms in the neighbourhood of the filament (the number of atoms liberated is about 10^{20} /sec.), and this cloud acts as a source of atoms. Near the filament many collisions occur, and the farther out the atoms travel the fewer collisions there will be. Thus, although the majority of the atoms arriving at the specimen surface have a direction approximately parallel to the line joining filament and specimen, they do not arrive without first having made collisions with other metal atoms.

The readiness with which oxide layers form on the metal films when they are heated to 250°C . suggests that there is a good deal of oxygen trapped in the films themselves. Certainly far thicker oxide layers form than would be the case with the metal in its ordinary state. This is especially so in the case of chromium films and of aluminium films prepared under poor vacuum conditions.

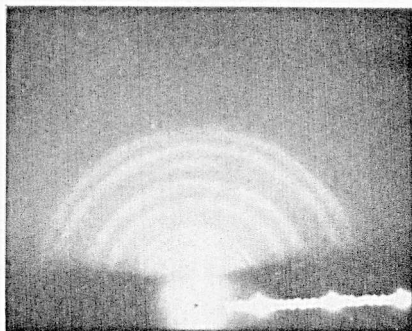
The Imperial College of Science,
S. Kensington.
9th June, 1936.

FIG. 1.



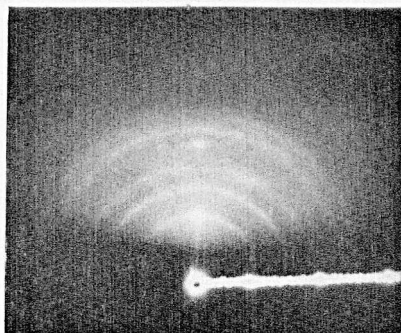
Aluminium oxide, type 1.

FIG. 2.



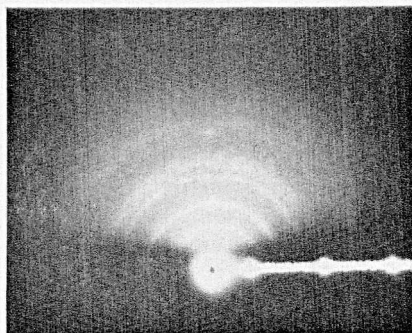
Aluminium oxide, type 2.

FIG. 3.



Chromium oxide,

FIG. 4.



Chromium oxide,

FIG. 5.

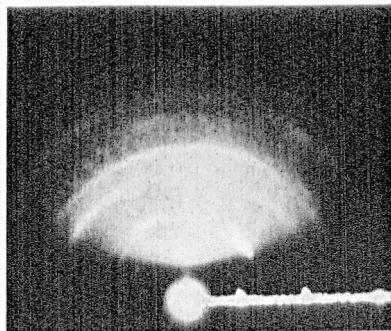
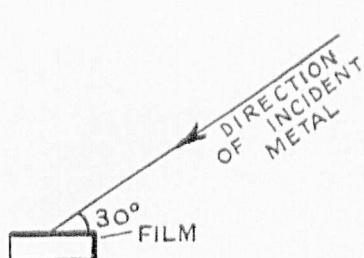
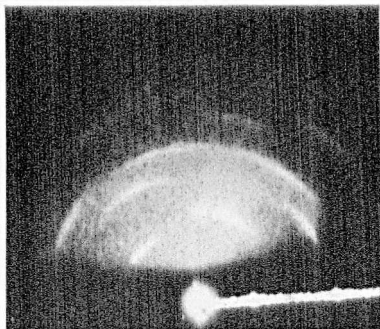
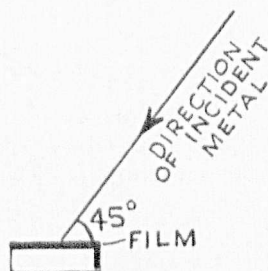


FIG. 6.

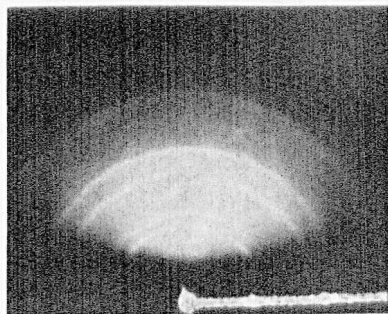


Specimen as viewed approximately along electron beam.



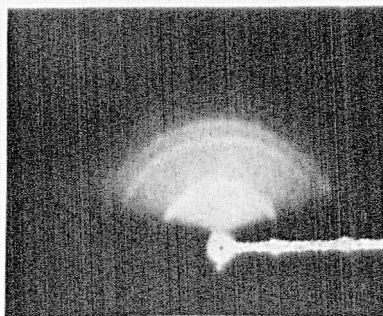
Specimen as viewed approximately along electron beam.

FIG. 7.



Aluminium normal incidence,

FIG. 8.



Copper film.