

The Analysis of Surface Layers by Electron Diffraction.

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(Communicated by Sir Joseph Thomson, F.R.S.—Received May 6, 1930.)

[PLATE 11.]

The very close correspondence which has been shown to exist between the diffraction patterns formed by cathode rays passing through thin solid films,* and the crystal structure of these films, suggests the possibility of using electron diffraction to investigate surface layers of unknown composition. This possibility was indeed indicated in Davisson and Germer's original paper† and has since been further applied.‡ These experiments have all been made with slow electrons, of energies of the order of 300 volts. With such electrons the experiments do not agree well with theory even in the case of known structures, so their application to the investigation of unknown structures involves considerable uncertainty. Further, slow electrons can only be detected photographically with very long exposures, while the electric method of detection is very cumbrous if it is desired to survey the complete diffraction pattern. For these reasons I decided to use the apparatus described in the previous paper to investigate the diffraction patterns obtained by the reflection of cathode rays from the surfaces of various solids. The discharge was generally produced by an induction coil and the energy of the rays was of the order of 30,000 volts. In a few cases, an Evershed and Vignolles direct-current generator was used giving about 6,000 volts.

In the course of the investigations, it appeared that these fast rays are uninfluenced by the thin layers of gas which are normally present on surfaces in a vacuum, or, possibly, that they temporally remove the layers by bombardment. From one point of view this is an advantage, as it is therefore unnecessary to take special precautions to degas the surfaces used, or to keep a very high vacuum. On the other hand, it limits the range of the method to the investigation of solid layers.

The following paper is an account of experiments designed primarily to

* G. P. Thomson, 'Roy. Soc. Proc.,' A, vol. 117, p. 600 (1928), vol. 119, p. 651 (1928) and vol. 125, p. 352 (1929).

† Davisson and Germer, 'Phys. Rev.,' vol. 30, p. 707 (1927).

‡ Germer, 'Z. Physik,' vol. 54, p. 412 (1929); Rupp, 'Z. Electrochemie,' vol. 35, p. 586 (1929).

exhibit the possibilities of the method as a tool of research ; up to the present I have tried to avoid being drawn aside into a close investigation of any of the tempting problems which the work has suggested. Some of these are now being made the subject of special researches, but it is hoped that the samples here exhibited may be sufficiently attractive to induce others to undertake similar investigations. The technique is not difficult, and the possible applications, especially to the study of surface chemistry, seem promising.

The targets used may be divided into two classes according to whether they are single crystals, or consist of a mass of small crystals. A single crystal should, theoretically, give a pattern of spots which should only appear strongly at certain special settings, while a polycrystalline surface should give a pattern of concentric circles, or rather circular arcs, since rather more than half the field is blocked out by the shadow of the target.

Experiment confirms these predictions in a general way. There is always, in addition to the regular pattern, a background of diffuse scattering, probably mostly electrons which have lost energy by inelastic collisions. In many cases, this background is all that appears, and the method fails, because the surface layer is either really amorphous, or, if crystalline, is constructed in such a way that diffraction at small angles is impossible. It must, of course, be realized that the penetrating power of the electrons is so small, especially at the small glancing angles used, that we are only concerned with a layer a few tens of atoms thick. To this, the method owes its value for the investigation of surface layers.

Most of the experiments were made with polycrystalline targets, and these will be described first.*

Metals.—Polished metals uniformly failed to give more than the diffuse background. I tried gold, iron, lead and copper. Aluminium with the natural oxide coating, and when etched with caustic potash, also failed, as did platinum etched in aqua regia. The same holds for metals deposited by electrolysis from aqueous solutions (gold and copper tried). On the other hand, gold deposited on a quartz surface (natural or fused) gave excellent rings (fig. 1, Plate 11), identical in pattern and size with those formed by the transmission of electrons of equal speed through thin, gold films. The same was true of gold spluttered on to molybdenum. As an indication of accuracy, the value for the size of the unit cube was found on eight plates to be $4\cdot06$, $4\cdot05$, $4\cdot00$, $4\cdot23$, $4\cdot00$, $4\cdot11$, $4\cdot12$ and $4\cdot16$, with a mean value of $4\cdot09$ A° , as against $4\cdot06$ A° from X-rays. The relative sizes of the individual rings

* For theory see previous paper (Fraser and Thomson).

checked with theory to an accuracy of about 1 per cent. The chief error in the relative measurements lies in the difficulty of finding accurately the centre of the circles, *i.e.*, the place where the undeviated ray would strike the plate if the target were not in the way. Where absolute measurements are concerned, the uncertainty of the measurement of voltage by a spark gap is more important.

Platinum Black.—In view of the importance of platinum as a catalyst, I tried precipitating platinum black from solutions of chloroplatinic acid by introducing a polished metal surface. When deposited on zinc or aluminium, the platinum black surface gave rather feeble rings, measurable with some difficulty against the strong, continuous background.

The following values were found :—

Zinc.—P = 36,200 volts, radius 11·8 mm., and P = 31,600 volts, radius 12·6 mm., taking these as due to the (111) planes the unit cube is 3·86.

Aluminium.—

	Radii (mm.).			Spacing (A°).		
P = 46,600 volts		16·2	19·9		1·42	1·16
P = 43,000 volts	10·2	16·3	20·0	2·35	1·47	1·20
	Means			2·35	1·45	1·18
	Ratio			$\frac{1}{\sqrt{3\cdot04}}$	$\frac{1}{\sqrt{8\cdot00}}$	$\frac{1}{\sqrt{12\cdot00}}$

Thus the first ring* is presumably due to (111) planes, the second to (220) and the third to (222) or (311). Of the other possible planes for a face-centred cube like platinum, (200) gives a weak reflection and the others are farther out. Taking the third ring as a mean of (222) and (311), the values of the side of the unit cube as deduced from the three rings are :—

- 4·06
- 4·10
- 3·98
-
- 4·05 mean.
-

The value for platinum found by X-rays is 3·91, and the agreement is as good as can be expected in view of the poorness of the rings.

* The values of *d* for a face-centred cubic structure are $a/\sqrt{h^2 + j^2 + k^2}$, (*hjk*) being Miller indices of the plane which must be all even or all odd.

It is quite otherwise when the platinum is deposited on copper. In this case, the rings are very good, Plate 11, fig. 3, but do not correspond to the face-centred cubic structure characteristic of both copper and platinum. Rings were found with the following spacings:—

Voltage.	Spacings (Angstrom units).								
36,600	2.96	2.38	2.10	1.73	1.49	1.21	0.965	—	—
39,500	2.94	2.47	2.10	1.73	1.49	1.29	0.965	0.86	—
40,600	3.09	2.47	2.15	1.76	1.54	1.31	0.99	—	0.725
33,500	3.06	2.47	2.09	1.75	1.51	1.29	0.96	—	—
32,500	—	2.36	—	—	1.45	1.24	—	—	—
33,000	2.86	2.36	2.05	1.68	1.45	1.25	0.96	0.86	—
Mean spacing	2.98	2.42	2.10	1.73	1.49	1.26	0.97	0.86	—
Inverse ratio	$\sqrt{1.99}$	$\sqrt{3.02}$	$\sqrt{4.00}$	$\sqrt{5.90}$	$\sqrt{7.95}$	$\sqrt{11.05}$	$\sqrt{18.8}$	$\sqrt{24}$	—

The close approximation to whole numbers under the square root show that the structure is cubic, but the presence of $\sqrt{2}$ and $\sqrt{6}$, *i.e.*, (110) and (211), shows that it is not face-centred. It is presumably some alloy of platinum and copper. The side of unit cube is 4.20 Å. The appearance was the same as when the platinum was deposited on aluminium or zinc, namely, a dull black.

One experiment was made with platinum deposited on silver:—Voltage 30,100, spacings 2.60, 1.82, 1.55, 1.19. These are in the inverse ratio $\sqrt{4.00}$, $\sqrt{8.1}$, $\sqrt{11.2}$, $\sqrt{18.9}$ and presumably correspond to a face-centred cubic structure, but the side of unit cube, 5.18 Å., is far too large for platinum or silver (3.91 and 4.06).

It may be mentioned that platinum deposited on copper has been found* to have no catalytic effect, while that deposited on aluminium, and to a less extent also on zinc, is very active. The explanation is clearly that in the first case the platinum is not in a normal state.

Platinized Asbestos.—A number of experiments were made with platinized asbestos, a bundle of fibres being stretched across the holder in place of the usual solid target. This arrangement gave very good rings which curiously showed no trace of the fibrous structure to be expected from asbestos, nor did they in the least resemble those to be expected from ordinary platinum. Two samples were used, both prepared for use as commercial catalysts, one being said to be better than the other. No difference was detected in the diffraction patterns. I then tried the asbestos unplatinized, using a sample identical with the raw material of one of the first two. To my surprise, no difference

* Paul and Windisch, 'Ber. D. Chem. Ges.,' vol. 46, p. 4010 (1913).

was detectable between the patterns given by the asbestos with and without the platinum, though the latter was present to the extent of 3 per cent. or 4 per cent. and showed strongly on an X-ray photograph, besides making the asbestos dark grey in colour. The extent of the agreement is shown in the following table of spacings:—

Voltage.	Spacings in Angstrom units.						Sample.
Platinized— 41,500	2.08	1.70	1.21	—	0.74	0.64	“ D ”
31,500	2.07	1.55	1.17	0.825	0.73	0.625	“ C ”
32,200	Too black to measure		1.175	0.82	0.73	0.625	“ C ”
Mean platinized ...	2.075	1.625	1.185	0.82	0.73	0.63	
Unplatinized— 33,300	2.14	1.70	1.21	0.85	0.75	0.645	“ D ” unplatinized
33,500	—	1.67	1.175	0.82	0.73	0.625	“ D ” unplatinized
Mean unplatinized	2.14	1.685	1.19	0.835	0.74	0.635	

In addition, there were a few other lines too faint to measure accurately, but which occurred equally with and without the platinum.

This result is very hard to understand, as one would have expected the platinum to be deposited on the outside of the asbestos fibres. If that were the case, platinum alone should show in the diffraction pattern, as the electrons would not get through to the asbestos. Actually the reverse is the case, and it almost looks as if the platinum were deposited in cracks in the asbestos where the electrons could not reach it. The subject would probably repay more investigation, particularly to find if the above spacings correspond to the ordinary structure of asbestos which, I understand, is now being investigated by X-rays.

Barium Oxide.—Several attempts, all unsuccessful, were made to induce the spluttered films of gold described above to recrystallise as a single crystal. On one occasion after the film had been bombarded with electrons from a heated filament, several new rings were found, some very clear and strong. Eventually it was found that they were due to barium oxide evaporated off the filament, which was a coated one. There were four of the new rings measurable and they gave spacings of:—

3.17	1.65	1.29	1.13	(mean of two plates)
(111) 3.18	(311) 1.66	(331) 1.26	(422) 1.12	(calculated)

in the second line are given the indices and spacings of certain planes in a BaO crystal which would be expected to give strong reflection. The plane (220), which is generally strong in a structure of the type of BaO, would give a ring nearly coinciding with one of the gold rings, which were also present. If the BaO formed a continuous film, it was too thin to be visible, but it may have been present as minute specks shot off from the filament on to the target as a result of the bursting of tiny bubbles of gas.

Quartz.—After a very violent bombardment by 6,000-volt electrons from a tungsten filament, which raised the surface of the spluttered gold to near a white heat, a new set of rings appeared instead of the original gold ones. They differed from the former rings in character as well as in size, being very sharp but not very intense. The surface of the target had changed considerably in appearance; the gold appeared to have been mostly removed from the centre of the target. It seems that these new rings were due to the structure of the quartz itself, there being just enough gold left to prevent charging up, but not enough to produce appreciable diffraction. The evidence is as follows:—

Spacing corresponding to rings	2·08	1·73	1·39	1·175	0·882
Spacing of quartz planes	2·12	1·79	1·41	1·22	0·895
Indices of planes	(20 $\bar{2}$ 0)	(0003)	(30 $\bar{3}$ 0)	($\bar{2}$ 4 $\bar{2}$ 0)	(0006)

Judging from the diagram on p. 161 of Braggs's "X-rays and Crystal Structure" (1915 edition) these are the strongest lines in the region covered by the experiments, except perhaps for (20 $\bar{2}$ 1) with a spacing of 1·67, which would hardly be distinguishable from (0003). The piece of quartz used in this experiment was an old piece of fused quartz, clear and with a fairly flat surface, but not optically worked.

Oxidized Copper.—While a polished copper surface gives no rings which can be referred to the metal itself, very faint rings are observed if the specimen has been in air at atmospheric pressure for even $\frac{3}{4}$ hour. If it is left in air overnight, the rings, though still rather blurred against the continuous background, become measurable. Their intensity and clearness are greatly increased by heating the metal gently in an electric furnace till the surface shows a marked change of colour. The same occurs with a surface of copper electrolytically deposited. If the heating is afterwards continued till the surface passes through several colour changes, the clearness of the rings greatly diminishes. The sizes of the rings were found to be in the (mean) ratio of $\sqrt{2\cdot99} : \sqrt{4\cdot09} : \sqrt{11\cdot0} : \sqrt{18\cdot8}$.

The ratios suggest the familiar face-centred cubic structure for which the mean value of the side of unit cube would be 4.21 Å. The structure of Cu_2O (cuprite) is known*; the copper atoms lie on a face-centred cubic lattice, the oxygen atoms on a body-centred cubic lattice, both of side 4.26 Å. There should be a very faint $\sqrt{2}$ ring and one at $\sqrt{18}$, besides the usual face-centred cubic series ($\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$, $\sqrt{11}$, $\sqrt{12}$, $\sqrt{16}$, $\sqrt{19}$, $\sqrt{20}$). The agreement is reasonably satisfactory.

If a polished copper block is left on a red hot block of brass or copper till it turns colour, then removed and allowed to cool in air, it gives in the diffraction apparatus a totally different set of rings from the above, though the treatment is so similar. The new rings are among the finest I have obtained, and the values of the spacings calculated from them show the accuracy of the method in favourable circumstances (see Plate 11, fig. 2).

Over 20 rings were clearly visible, of which those of smallest size gave the following spacings:—

Voltage.	Spacing in Angstrom units (corrected for relativity).								
6,250	2.68	2.49	2.28	—	—	—	—	1.38	1.34
6,400	2.68	2.49	2.28	—	—	—	—	1.385	1.345
32,000	2.71	2.49	2.22	1.83	1.71	1.59	1.50	1.365†	
29,000	2.71	2.47	2.26	1.88	1.71	1.595	1.52	1.38†	
?	2.70	2.48	2.27	1.87	1.70	1.59	1.51	1.365†	
(values relative only)									
Mean	2.70	2.48	2.26	1.86	1.71	1.59	1.51	1.385	1.345

Voltage.	Spacing in Angstrom units (corrected for relativity).								
6,250	—	—	—	—	—	—	—	—	—
6,400	—	—	—	—	—	—	—	—	—
32,000	1.30	1.17	1.10	1.00	0.954	0.9315	0.890	0.858	—
29,000	1.31	1.165	1.105	1.02	0.977	0.950	0.906	0.858	—
?	1.28	1.15	1.075	1.00	0.945†		0.89	0.856	—
(values relative only)									
Mean	1.30	1.16	1.09	1.01	0.965	0.94	0.895	0.857	—

† Doublet not resolved.

It has not so far been possible to deduce the structure corresponding to these spacings, which were obtained with two specimens. It is not that of

* Greenwood, 'Phil. Mag.', vol. 48, p. 654 (1924).

tenorite (CuO) given by Niggli.* Further work is in progress with the hope of discovering what determines the crystal form taken up by heated copper, and what the chemical composition of the second form may be.

Copper Sulphide.—If a polished copper block is dipped in a dilute solution of “liver of sulphur,” the surface changes, showing the colours of thin films. Experiments were made with a surface of this kind which showed the red of the second order. The rings were fair and showed the following spacings (mean of three plates):—

	2.86 f.	2.34 f.	1.92 s.	1.64 m.	1.22 m.	1.06 m.
Inverse ratio	$\sqrt{3.6}$	$\sqrt{5.4}$	$\sqrt{8.00}$	$\sqrt{11.0}$	$\sqrt{19.8}$	$\sqrt{26.5}$

f. = faint; s. = strong; m. = medium.

Cu₂S has a structure of the CaF₂ type; the sulphur atoms lie on a face-centred cube of side $a = 5.59$, while the copper atoms are at the centres of the eight cubes of side $a/2$ into which the main cube can be divided. Taking the copper atoms only, there are spacings inversely as $\sqrt{4}$, $\sqrt{8}$, $\sqrt{12}$, ... $\sqrt{4n}$, while the sulphur atoms would give rings, probably faint, at $\sqrt{3}$, $\sqrt{11}$, $\sqrt{19}$, $\sqrt{27}$. Unless the second ring $\sqrt{5.4}$ is due to an impurity, the surface cannot therefore be Cu₂S, though the absolute side of the (assumed) unit cube agrees fairly well, namely, 5.44 against 5.59.

Copper Selenide and Telluride.—Similar experiments were made with selenium and tellurium, the copper being dipped into dilute solutions of SeO₂ in water, and of TeO₂ in dilute hydrochloric acid respectively. The mean spacings found were:—

Selenide	2.31 f.	1.95 s.	1.68 m.	1.26 f.	1.08 f.			
Inverse ratios.....	$\sqrt{5.7}$	$\sqrt{8.00}$	$\sqrt{10.8}$	$\sqrt{19.2}$	$\sqrt{26.2}$			
Telluride	4.06 f.	3.08 m.	2.38 s.	1.95 m.	1.47 f.	1.25 m.	1.15 f.	0.95 f.
Inverse ratios.....	$\sqrt{2.7}$	$\sqrt{4.8}$	$\sqrt{8.00}$	$\sqrt{11.7}$	$\sqrt{21}$	$\sqrt{29}$	$\sqrt{34}$	$\sqrt{50}$

It is fairly certain that the three are analogous compounds, and the presence in all of a ring analogous to the second of the sulphur compound makes it unlikely that the latter is due to an impurity.

These surface layers are of practical interest as finishes for copper articles. Further work on their structure is in progress at Cornell University.

Iron Oxide.—Polished iron gives no rings, but with electrons of 6,000 volts energy one photograph showed a very diffuse spot roughly in the position of specular reflection. This may possibly be evidence of a gas layer; if so, it is the only one so far obtained. If the iron be allowed to rust in water and

* Niggli quoted by Bragg, “X-rays and Crystal Structure,” p. 301.

then tested in the electron camera, a fine set of rings appears which can be easily seen on the Willemite screen. The mean spacings were:—

Observed spacing	3.15	(2.79)	2.43	2.22	(1.93)
Spacing for Fe_2O_3	3.69	2.69	2.51	2.22	2.05
Dimmed surface (see below)				(2.23)	
Observed spacing	1.84	1.64	1.455	1.31	1.14
Spacing for Fe_2O_3	1.845	{ 1.69 1.60 }	{ 1.49 1.45 }	1.31	{ 1.119 to 1.11 }
Dimmed surface (see below)	1.785		1.42	1.31	1.13

The figures in plain brackets were from one plate only. The third and fourth rings were not fully resolved, so their measurements are somewhat uncertain.

The values for Fe_2O_3 are calculated from measurements by Hedvall* of powder photographs, checked by the values of the crystal elements given by Pauling and Hendricks.† There is excellent agreement except for the first ring. This is very small, so that an error in the position of the centre would cause a large percentage change, but the difference seems to be too great for this to be the explanation, and it is more likely to be due to slight charging up of the target or to magnetic action. The error is of the order of 0.75 mm. on the plate.

Experiments were also made on a surface of iron, originally polished, then dipped in nitric acid of sufficient strength to make the iron passive, and finally washed in distilled water and dried. The surface then showed a slight dimming of its original polish. It gave good rings, both with the 6,000-volt generator and with the induction coil, only slightly less clear than those given by the iron surface covered with thick rust. The mean spacings are given in the third line of the table above. It will be seen that they agree well with the structure of Fe_2O_3 , the inner rings not being clear enough to measure. It is remarkable that a layer which was hardly visible should give such a well-defined pattern. The experiment was repeated with another surface which gave the same result. It is unlikely that these surfaces were passive when tested in the electron camera, as drying the water generally destroys the passivity. However, by treatment with suitable solutions it is possible to get a dry, passive surface, and it would be of interest to see if this gives rings.‡

Aluminium Oxide.—A piece of aluminium covered with the usual film which forms in air failed to give any definite rings. It had been cleaned with petroleum ether and alcohol.

Lead.—A piece of lead treated similarly to the aluminium above equally

* Hedvall, 'Z. Anorg. Chem.,' vol. 120, p. 327 (1922).

† 'Jour. Amer. Chem. Soc.,' vol. 47, p. 781 (1925).

‡ See note attached.

failed to give rings, nor was a specimen polished with oil on a sheet of paper any more successful. Lead freshly cut and heated to about 100° C. in air for some time also gave nothing. When, however, the lead was heated to near the melting-point for about an hour it gave measurable rings. These were not sufficiently numerous on the one specimen tested to enable the structure to be determined.

[*Note added in proof.*—I have since succeeded in keeping the iron passive throughout the whole experiment. In these circumstances the rings corresponding to Fe_2O_3 do not appear, so those in the earlier experiments must have been caused by action after the iron had ceased to be passive. Instead, a number of rather faint spots were found which agree well with the structure of ordinary iron, spots being formed instead of rings presumably because only a few crystals of iron are effective. The same pattern occurs if the iron is not passive, being the only instance so far found of a pattern from an etched metallic surface. It appears, therefore, that if the passivity of iron is due to a surface layer it must be one so thin as to elude even the sensitive test of electron diffraction. In some other experiments on iron attacked by nitric acid I have found a layer showing the structure of Fe_3O_4 .]

Discussion.

It is hoped that enough examples have been given above to show the possibilities of the method as a tool of research. Apart from particular problems, a number of questions of a general nature are suggested by the experiments we have described. One of the most important is: what are the conditions which determine whether or not a surface will give a diffraction pattern? The first requirement is clearly that the actual surface must be crystalline, for the electrons can only penetrate a very small depth, especially at a glancing angle of only 1° or 2° , without experiencing an inelastic collision which disqualifies them from forming a diffraction pattern. No doubt the reason that polished metals fail to give rings is that their surface is covered with an amorphous layer of super-cooled liquid (Beilby layer). It is less obvious why an etched metal surface should give nothing (*e.g.*, aluminium and platinum). The reason may be that such a surface consists of a succession of pits and pyramids with flat, crystal surfaces for their boundaries. If the dimensions of the pyramids are large compared with the penetrating power of the electrons, it will rarely occur that an electron can pass in at one face and out at another, after reflection from a crystal plane (not a face) inside. Thus the only chance of getting strong reflection would be for the electron to enter and leave the

same crystal surface. For this the surface must make an angle with the ray not greater than the glancing angle of selective reflection, whether the reflecting plane is the crystal surface itself or some plane in the crystal oblique to it.* Now, the angle in question is small so that a reflecting facet will present a target to the rays small compared with its true area; it is therefore very improbable that the first surface which the ray strikes will lie within the required angle. A favourable arrangement for the formation of rings is a surface covered with *small* lumps, rather like a field of cornstooks on a miniature scale. The lumps must be small enough to give an electron a chance of going right through without making an inelastic collision. In this case, if the angle for selective reflection is θ and the "tolerance" $\delta\theta$, the chance of finding the first crystalline lump in the right attitude is $p \cos \theta \delta\theta$, where p is the number of ways the crystal can be turned to give a plane of the same spacing.

In the former case, if for simplicity we suppose the surface to be formed of a number of equal pyramids disposed at random, the projected area of all surfaces with which the rays make an angle less than θ is

$$\frac{\int_0^\theta \sin \theta \cos \theta d\theta}{\int_0^{\pi/2} \sin \theta \cos \theta d\theta} = \sin^2 \theta$$

of the whole cross section of the beam. If the electron hits such a surface first, it has a chance $\cot \theta \cdot \delta\theta$ of being reflected from the surface face, and $\cos \theta \cdot \delta\theta (p - 1) q$ of reflection from some other equivalent face.† The total chance of reflection is $\cos \theta \cdot \delta\theta [\sin \theta + \sin^2 \theta \cdot (p + 1) q]$, which if θ is small is much less than $\cos \theta \cdot \delta\theta \cdot p$, the chance when the surface is covered with small lumps.

It is a general rule that a polished surface which has recently been attacked chemically gives some kind of rings. The failure of aluminium and lead covered with the ordinary protective layer of oxide to give an effect may be due to the layers having been old. In general, the clearness of the rings tends to diminish with the age of the specimen, perhaps indicating that larger crystal units are formed.

In the above argument, we have not considered the effect of refractive index.

* It is assumed that the angle between any two important reflecting planes, of which the surface will be one, is less than the angle of selective reflection.

† Here q is a numerical factor, never large compared with unity, which depends on the angles between the p equivalent faces.

As shown in an earlier paper,* the refractive index corresponding to the probable value of the inner potential of a metal would have a large effect on the deviation of an electron which was reflected from a crystal plane *parallel to a face surface*. The effect is due to the smallness of the angle of incidence, and would not occur to any appreciable extent if the surfaces through which the electron passed at entrance and exit were not closely parallel to the plane of reflection. No effect of refractive index has been observed in these experiments, and this is strong evidence for supposing that (*e.g.*) the gold deposited by spluttering is in the form of little lumps with irregular surfaces, through which the electrons pass, rather than crystals with extended flat surfaces. Or at least, that enough of the former are present to cause the observed diffraction.

If the target is not of the same material as the case of the instrument, there will be a difference of potential between a point just outside the surface of the target and one just inside the case. The field of force corresponding to this will exert forces on the beam of electrons, but for 1 volt the distance on the plate is only of the order 10^{-4} cm., which is quite negligible.

Some experiments were made with crystals of calcite and galena giving results in qualitative agreement with the work of Emslie.† Rocksalt gives well marked diffraction patterns which are being further investigated.‡

A considerable part of the work described above was done at Cornell University, U.S.A., where I was Baker Lecturer, and my sincere thanks are due to the authorities there, and especially to Prof. Dennis, for the excellent facilities provided, and also to Mr. H. R. Nelson, M.A., for his capable assistance in a number of the experiments. My thanks are also due to Mr. J. D. McKay, whose quickness and skill have been immensely valuable in all these experiments.

Summary.

(1) Using the apparatus described in the preceding paper, it was found that the surfaces of many solids give diffraction patterns with electrons. These patterns are caused by the crystalline structure of the surface and in several cases enable this to be determined.

(2) Owing to the slight penetrating power of the electrons, this method affords a means of investigating surface layers, comparable to that provided by X-rays in the case of matter in bulk.

(3) The following are some surfaces which showed measurable diffraction

* 'Phil. Mag.,' vol. 6, p. 939 (1928).

† Emslie 'Nature,' p. 977, vol. 123 (1929).

‡ See 'Nature,' July 12, 1930. [Note added in proof.]

rings corresponding to a polycrystalline structure, and the nature of this structure in so far as it could be determined from these rings :—

Surface.	Structure.
Gold spluttered on quartz	Gold.
Ditto, bombarded from a filament coated with BaO.	Gold and BaO.
Ditto after severe bombardment	Quartz.
Platinum black deposited on Zn or Al . .	Platinum.
Platinum black deposited on Cu	A cubic structure <i>not</i> Pt or Cu.
Platinized asbestos	} The same complex structure, not identified.
The same asbestos unplatinized	
Copper heated in air, 1st method	Cu ₂ O (cuprite).
Copper heated in air, 2nd method	A complicated structure <i>not</i> cuprite or tenorite (CuO).
Copper dipped in sulphide solution	Probably not Cu ₂ S.
Copper dipped in selenide solution	Not Cu ₂ Se.
Copper dipped in telluride solution	Not Cu ₂ Te.
Iron rusted	Fe ₂ O ₃ .
Polished iron, dipped in strong nitric acid, washed and dried.	Fe ₂ O ₃ (see note p. 658).

(4) Polished and etched metals gave no pattern, nor did electro-deposited gold or copper.

(5) It seems that almost any smooth surface which has recently undergone chemical change will give a diffraction pattern corresponding to its new crystal structure.

(6) Single crystals of calcite, galena and rocksalt gave diffraction patterns of spots.

