The Diffraction of Electrons by Graphite

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[Plates 6–12]

1—Introduction

The structure first attributed to graphite by Debye and Scherrer,* and by Hull† from X-ray powder patterns was confirmed by Hassell and Mark,‡ by Bernal,§ and, finally, by Mauguin‖ and Ott¶ who relied mainly on single crystal X-ray photographs. The assigned structure is such that the hexagonal unit cell has the dimensions, $a = 2{\cdot}46$ and $c = 6{\cdot}79$ A, and contains two pairs of crystallographically different carbon atoms of coordinates (0, 0, 0), (0, 0, $\frac{1}{2}$), ($\frac{1}{3}$, $\frac{2}{3}$, u), and ($\frac{2}{3}$, $\frac{1}{3}$, $u + \frac{1}{2}$), where, according to Ott, $u < 0{\cdot}004$. Hence we may picture the graphite crystal as consisting of carbon atoms situated at the points of plane, or nearly plane hexagonal network sheets parallel to, and equidistant from, each other, and so superimposed that the projections from hexagon centres in one sheet pass through atoms in the two neighbouring sheets. Thus the atoms in alternate sheets are superimposed.

Trendelenburg,** Miwa,†† and Jenkins‡‡ studied the diffraction of electrons by graphite powder and concluded that their results were in agreement with X-rays, apart from the absence or undue weakness of the 001 diffractions. This difference was satisfactorily explained by these workers as being due to the effect of the flake-like form of the crystals and the inner potential of graphite, the latter being known from measure-

* ‘ Phys. Z.,’ vol. 18, p. 291 (1917).
† ‘ Phys. Rev.,’ vol. 10, p. 661 (1917); vol. 20, p. 113 (1922).
‡ ‘ Z. Physik,’ vol. 25, p. 317 (1924).
§ ‘ Proc. Roy. Soc.,’ A, vol. 106, p. 749 (1924).
‖ ‘ Bull. Soc. Franc. Miner.,’ vol. 49, p. 32 (1926).
¶ ‘ Ann. Physik,’ vol. 85, p. 81 (1928).
** ‘ Naturwissenschaften,’ vol. 21, p. 173 (1933); ‘ Ergebn. Tech. Röntgenk.,’ vol. 4, p. 81 (1934).
†† ‘ Sci. Rep. Tôhoku Univ. *a*,’ vol. 23, p. 242 (1934).
‡‡ ‘ Phil. Mag.,’ vol. 17, p. 457 (1934).

ments by Yamaguti* and Jenkins† of electron-diffraction patterns obtained by reflexion at single-crystal cleavage faces. A similar conclusion was reached by other workers‡ who, however, have not published diffraction patterns in substantiation of their findings. Finally, Aminoff and Broome§ considered that the spot patterns and a Kikuchi line pattern obtained by them by transmission of electrons through relatively thin and thicker graphite flakes respectively were in general agreement with the accepted graphite structure, and indicated hexagonal symmetry of the structure with respect to the *c* axis or cleavage face normal.

In the course of a study of the lubricating properties of graphite, we obtained transmission patterns of graphite films formed by the drying-out of a colloidal artificial graphite (" Aquadag ") solution. Although these patterns at first sight appeared to resemble those hitherto obtained by X-ray and electron diffraction, a closer inspection revealed the existence of several rings which had previously not been observed, doubtless because of insufficient resolution, and which did not appear to fit in with the current view of the structure of the graphite lattice. It is the object of this communication to set forth these differences and to elucidate their origin.

2—Experimental

The cameras used were Nos. 2,‖ evacuated by a four-stage mercury-vapour pump, and 3,¶ fitted with an oil diffusion pump equipment. The beam accelerating potential was generally of the order of 50 kv, and the camera length, L, was approximately 28 or 50 cm, according to the type of specimen undergoing examination.

Transmission patterns were obtained from polycrystalline graphite films, formed either by drying out a suspension or colloidal solution bridging the interstices of fine-meshed nickel gauze, or by the evaporation of a drop on a thin collodion film supported on nickel gauze. Suitable specimens for single crystal reflexion and transmission were prepared

* ' Proc. Phys. Math. Soc. Japan,' vol. 16, p. 95 (1934).

† ' Phil. Mag.,' vol. 17, p. 457 (1934).

‡ Boersch and Meyer, ' Z. phys. Chem.,' B, vol. 29, p. 59 (1935).

§ ' Z. Kristallog.,' vol. 89, p. 80 (1934); vol. 91, p. 77 (1935).

‖ Finch and Quarrell, ' Proc. Phys. Soc.,' vol. 46, p. 150 (1934).

¶ No account of this camera has hitherto appeared; a somewhat similar instrument, however, but fitted with a mercury-vapour pump, has been described by Finch, Quarrel, and Wilman, ' Trans. Faraday Soc.,' vol. 31, p. 1051 (1935). Camera No. 3 was exhibited at the Society's Conversazione on May 9, 1934, by Imperial Chemical Industries, whose Winnington Research Staff was responsible for its construction to designs based on that of camera No. 2.

from relatively large natural graphite crystals by the exposure of fresh, clean, and undamaged surfaces or flakes by cleavage. Chisels ground from the finest available steel needle points and mounted in corks for convenience in handling were used for this purpose.

3—The Electron Diffraction Graphite Powder Pattern

A pattern characteristic of a colloidal graphite film deposited on a collodion substrate normal to the electron beam is shown in fig. 1, Plate 6. The great intensity of the diffraction rings indexed as *hk*0 in accordance with the X-ray graphite structure described in § 1 suggests that the graphite crystals were orientated with the cleavage planes parallel to the substrate. This was fully confirmed by the pattern, fig. 2, Plate 6 obtained with the specimen inclined to the beam, from which it will be seen that all the rings are broken up into arcs and that *hkl* diffractions appear which are absent from fig. 1. With specimens in which the graphite films were supported on the gauze without collodion and thus directly bridged the meshes, *hkl* diffractions appeared even when the film was normal to the beam, fig. 3, Plate 6, and inclination of the specimen had no visible effect upon either the continuity or relative intensity of the rings; thus in such cases the crystals were randomly disposed.

Figs. 4 and 5, Plate 6, are enlarged sections of the broad inner ring group or band in figs. 3 and 1 respectively. This band has hitherto been attributed to the combined 100 and 101 diffractions. In these enlargements, however, and more particularly in fig. 4, the group has been resolved into four distinct rings; also, in figs. 1, 2, and 3, other diffractions having no counterpart in the corresponding X-ray patterns and until now undetected, appear between this group and the 110 ring. The corresponding Bragg plane spacings, referred by double-shutter exposures to gold, $a = 4{\cdot}070$ A, and the intensities of the diffractions are set forth in Table I, columns 1 and 2, for purposes of comparison with the corresponding experimental X-ray data (columns 4, 5, and 6).

Thus the electron diffraction powder patterns contain several " extra " rings of which the corresponding spacings are not representative of any normal identity spacings of parallel sets of planes in the structure assigned to graphite by X-rays.

It seemed at this stage that the elucidation of the cause of these remarkable differences between the X-ray and electron-diffraction graphite powder patterns involved consideration of three possible alternative explanations. Thus the " extra " rings might be due to (i) impurities, (ii) lattice dimension deviations from the normal in the surface layers,

TABLE I—SPACINGS AND INTENSITIES OF GRAPHITE POWDER DIFFRACTIONS

Electron diffraction			X-ray diffraction		
Artificial graphite		Natural graphite	Natural graphite		
Spacings† in A	Intensities* (from random patterns)	Spacings† in A	Spacings‡ in A	Intensities*	Indices‡ (hexagonal)
3·42	VF	—	3·395	VS	002
2·123	MS	2·128	2·13	MS	100
2·079	MS	2·081	—	—	—
—	M	2·068	—	—	—
2·027	MS	2·032	2·03	S	{101 / 102β}
—	M	1·979	—	—	—
1·961	M	1·953	—	—	—
1·796	F	1·803	1·80	F	102
1·621	VF	1·629	—	—	—
—	—	—	1·70	S	{004 / 103β}
1·541	VF	1·544	1·55	MS	103
1·462	VF	1·456	—	—	—
—	VF	1·313	1·33	F	104
1·229	VS	1·229	1·23	MS	110
—	FM	1·226	—	—	—
—	M	1·209	—	—	
1·154	S	1·153	1·16	MS–S	{112 / 200β / 201β}
—	—	—	1·15	F	105
—	—	—	1·13	MS	006
1·061	F	1·062	{1·065 / 1·053}	F	{200 / 201}
1·055	F	1·052			
—	VF	1·040	—	—	—
—	VF	1·013	1·02	F	202
—	—	—	{1·00 / 0·997}	MS	{106 / 114}
0·991	F	0·990			

* Intensities are graded in order of increasing intensity as follows:—VVF—VF—F—FM—M—MS—S—VS.

† Referred to $a_{Au} = 4{\cdot}070$ A.

‡ These spacings and indices have been recalculated for a hexagonal structure from lattice dimensional data ($a = 2{\cdot}46$ and $c = 6{\cdot}79$ A) given by Hassel and Mark ('[Z. Physik,' vol. 25, p. 317 (1924)) and from their orthohexagonal indexing.

or to (iii) the structure hitherto assigned by X-rays to graphite being incorrect. In what follows an account is given of the results obtained on putting these alternatives to the test of experiment and of the facts and conclusions thereby reached.

TABLE II—TYPES OF GRAPHITE EXAMINED

Sample	Nature	Source of supply
"Aquadag"; batches Nos. 1 and 2	Colloidal artificial graphite prepared by the Acheson process; graphite content $> 99{\cdot}7\%$	E. G. Acheson, Ltd.
Ceylon, No. 1"	Well-developed, relatively large clean crystals with plane cleavage areas of as much as $0{\cdot}5$ cm^2; free from gangue	Natural History Museum
Ceylon, No. 2"	Distorted, coarse-grained lumps	Hopkins & Williams, Ltd.
Madagascar"	Small flakes; much micaceous gangue, not easily separable	Natural History Museum
Porto Amelia" (Portuguese East Africa)	Small flakes; some micaceous gangue, but clean flakes could be cleaved off	E. G. Acheson, Ltd.
Norwegian" (Skaland, Senja)	Coarse-grained lumps; much gangue but mostly separable	Royal School of Mines
Borrowdaile"	Microcrystalline of very close texture	Royal School of Mines
Locality Unknown, No. 1"	Large curved crystals on quartz	Royal School of Mines
Locality Unknown, No. 2"	Large curved crystals on crystalline limestone	Royal School of Mines
Locality Unknown, No. 3"	Microcrystalline; much inseparable gangue	Royal School of Mines
North American"..	Well-developed crystals, only slightly inferior to "Ceylon No. 1"	Royal School of Mines
Passau, No. 1" (Kropfmühle)	Fine powder; about 99 % C..	E. G. Acheson, Ltd.
Passau, No. 2" ..	Small flakes; 96% C	E. G. Acheson, Ltd.
Passau, No. 3" ..	Large flakes; 96% C	E. G. Acheson, Ltd.

4—THE EFFECT OF IMPURITIES

In order to examine the possible role played by impurities, electron diffraction powder patterns were obtained from a wide variety of natural graphites, together with samples of artificial graphite taken from two different batches of "Aquadag". The data regarding these graphites are collected together into Table II.

Without exception, the patterns contained all the diffractions enumerated in Table I, columns 1 and 3. In one specimen only (" Locality Unknown, No. 3 ") there appeared in addition other rings of moderate intensity, forming a pattern similar to that obtained from the powdered gangue and therefore characteristic of this impurity. Otherwise the patterns differed in effect from fig. 3 only in the spottiness of the rings (fig. 6, Plate 7); hence the main difference between these graphite samples as examined was, as regards the nature of the diffraction patterns, solely one of crystal size. Thus the " extra " rings can hardly be supposed to have arisen from an impurity inherent in the graphite. Nor can they be the result of an adventitious contamination, since some of these patterns were taken in camera No. 2 (mercury-vapour pump) and others in camera No. 3 (oil-vapour pump). The " extra " rings therefore cannot be ascribed either to mercury or to organic impurities such as grease or oil films. Furthermore the nature of the " grease " rings is such as to render them easily recognizable,* and their spacings differ from those of the graphite " extra " rings. Thus it may be concluded that the " extra " diffractions cannot be due to impurities.

5—The Effect of Dimensional Lattice Deviations

According to a theory due to Lennard-Jones,† the lattice dimensions should change slightly on approaching a surface from the interior of a crystal. Viewed in this light, we might regard the " extra " rings just outside the 100 and 101 diffractions respectively as evidence of such a change in the cleavage plane of the graphite crystal, were it not for the fact that the 110 ring, unlike the 100-101 group, is remarkably sharp and free from satellites of comparable intensity. This fact alone suffices completely to negative any explanation of the " extra " rings in terms of a dimensional lattice deviation effect.

6—Diffraction of Electrons by Thin Graphite Single Crystals

An enlargement, fig. 5, Plate 6, of the 100-101 ring complex in fig. 1, which was taken with the beam along the common direction (*c* axis) of orientation of the crystal particles, reveals the fact that the rings are continuous but differ greatly in intensity, the innermost (100) being strong, whilst the second (" extra ") is faint, the third (101) barely visible, and the fourth or outermost (" extra ") ring is virtually absent. In the original

* Mark, Motz, and Trillat, ' Naturwissenschaften,' vol. 20, p. 319 (1935).

† ' Z. Kristallog.,' vol. 75, p. 215 (1930).

negative of fig. 2 it can be seen that these four rings are of more comparable intensity and are arced in such a manner that whilst the 100 diffraction consists of two diametrically opposed arcs, the 101 and the two " extra " rings each exhibit four directions of arcing. Such breaking-up of " extra " rings into arcs on inclination of the specimen plane to the beam strongly suggests that they owe their origin to the crystal structure of the finely-divided graphite. Indeed, these facts must be accepted as evidence of the existence in the crystal flakes of sets of planes with spacings determining the corresponding " extra " ring diameters. From the dimensions and directions of arcing it is evident that the two " extra " rings are due to planes of spacings 2·08 and 1·96 A, and forming angles with the normal to the cleavage plane of approximately 12 and 24° respectively. Planes of such spacings and inclinations do not fit in with the structure assigned to graphite by X-rays.

With a view to eliminating possible anomalous crystal-edge effects, the next step was to examine by transmission single crystals consisting of transparent and almost colourless flakes cleaved from the best surfaces of " Ceylon No. 1 " which from the crystallographic point of view appeared, and, as will be seen later, actually proved to be, the most perfect of the available specimens.

TABLE III—ANALYSIS OF GRAPHITE SINGLE CRYSTAL ROTATION TRANSMISSION PATTERNS

Observed spacings* in A, referred to $a_{Au} = 4{\cdot}070$ A	Indices of diffractions fitting the X-ray assigned structure	c/a calculated from planes of appropriate indices
2·128	100	—
2·091	" extra "	—
2·081	" extra "	—
2·065	" extra "	—
2·027	101	2·70
1·980	" extra "	—
1·963	" extra "	—
1·794	102	2·72
1·541	103	2·725‡
1·462	" extra "	—
1·316	104	2·725‡

* Most of the spacings included in this column are mean values of up to as many as 9 independent determinations; the agreement was good throughout and generally of the order of 1 or 2 parts in 1000.

† Indices assigned to diffractions forbidden by structure factor.

‡ c/a values discussed in § 9.

TABLE III—(continued)

Observed spacings* in A, referred to $a_{Au} = 4{\cdot}070$ A	Indices of diffractions fitting the X-ray assigned structure	c/a calculated from planes of appropriate indices
1·229	110	—
1·228	" extra "	—
1·221	" extra "	—
1·209	111 (forbidden)†	2·73
1·174	" extra "	—
1·154	112	2·73
1·134	105	2·726‡
1·119	" extra "	—
1·105	" extra "	—
1·077	113 (forbidden)†	—
1·064	200	—
1·052	201	2·79
1·041	" extra "	—
1·014	202	2·71
0·991	114	2·724‡
0·960	203	2·71
0·898	204	2·725‡
0·826	116	2·725‡
0·805	120	—
0·799	121	2·83
0·783	122	2·76
0·771	206	2·727‡
0·758	123	2·75
0·726	124	2·730‡
0·710	300	—
0·706	301	2·89
0·694	302	2·75
0·693	118	2·730‡
0·690	125	2·729‡
0·653	304	2·72
0·615	220	—
0·605	222	2·82
0·600	306	2·74

*†‡ *See* notes, p. 351.

A typical pattern obtained with the cleavage plane normal, or nearly so, to the beam is shown in fig. 7, Plate 7. The arrangement of the spots, all of which were found to be *hk*0 diffractions, accords completely with the X-ray structure. The crystal was so thin that the zero order maximum virtually coalesces with the first Laue ring, and this corresponds to a

crystal thickness in the direction of the beam of roughly 20 A, or three X-ray unit cells.*

Rotation photographs in which a crystal was turned during exposure about an axis approximately normal to the beam were next secured. Owing to their minuteness and fragility, however, difficulty was experienced in accurately mounting such crystals, and it was soon found that rotation patterns could be more readily obtained by means of specimens consisting of transparent flakes which had been much bent during cleavage. By flooding a section of such a specimen exhibiting a wide range of curvatures, " rotation " patterns equivalent to partial rotations about several axes could be secured with the specimen stationary or with only a few degrees' rotation of the specimen carrier about its axis, thus avoiding the difficulties and uncertainties, particularly of camera-length variation, associated with a freely rotated specimen. In this manner patterns containing many " extra " diffractions not fitting the X-ray structure were obtained with flakes cleaved from the " Ceylon No. 1 " and " North American " graphites; much the best patterns of this type, however, in that a single photograph often contained as many as 11 " extra " diffractions, were furnished by the more easily distorted graphite " Locality Unknown No. 1 ". Characteristic patterns are shown in fig. 8, Plate 7 (specimen stationary), and fig. 9, Plate 7 (rotation). The spacings of these diffractions are given in the first column of Table III. All the spacings previously recorded in Table I, columns 1 and 3, are represented within the limits of experimental error; in addition many other diffractions, both normal, in that they agree with the X-ray results, and " extra ", appear with sufficient intensity for accurate measurement.

These results hardly permit of any interpretation other than that the diffractions recorded are due to the nature of the structure of the graphite specimens examined; and since it has now been shown that they are afforded by every one of the wide variety of graphites so far studied, we must conclude that this structure is common to all graphites, in spite of the fact that so many of the diffractions do not apparently fit in with the structure deduced from X-ray data.

7—Reflexion of Electrons from the Graphite Crystal Cleavage Face

Any difference between the assigned X-ray and the real structure should be revealed by the appearance of Kikuchi line systems in patterns obtained by the diffraction of electrons from a single crystal cleavage face, or by

* Finch, Quarrell, and Wilman, ' Trans. Faraday Soc.,' vol. 31, p. 1062 (1935).

transmission along suitable zone axes through flakes sufficiently thick to yield strong secondary scattering effects. Thus reflexion patterns from the cleavage plane in the $\phi = 0$, 60, 120°, etc., azimuthal settings, measured from a basal crystal axis, should be symmetrical and equivalent if the assigned X-ray structure is correct; and similar conditions should apply to the other symmetrical azimuths, *i.e.*, at $\phi = 30$, 90, and 150°. But if the " extra " diffractions are due in fact to another structure, then either this symmetry would be lost, or additional and prominent Kikuchi line systems should appear at these or intermediate azimuths.

Reflexion patterns were taken accordingly at these six symmetrical settings from different crystals of " Ceylon No. 1 " and " North American " graphite single crystal cleavage faces. Some of the thin cleavage flakes obtained in exposing undamaged faces for the reflexion experiments had previously yielded patterns containing most of the " extra " diffractions recorded in Table III. Two such characteristic single crystal reflexion patterns are reproduced in figs. 10 ($\phi = 30°$) and 11 ($\phi = 0°$), Plate 8. It will be seen that they have been successfully indexed* completely in accordance with the assigned X-ray structure and show no signs of any abnormality. In addition to these settings a wide range of intermediate azimuths were explored, and in all 22 photographs secured and searched for two Kikuchi line systems equivalent to spacings of approximately 2·08 and 1·96 A, with inclinations to the plane of incidence of about 12 and 24° respectively, *i.e.*, corresponding to the two very prominent " extra " rings near the 100 and 101 diffractions. No trace of either line pair could be found. Thus these experiments, in confirming the X-ray structure, gave results which apparently conflict with those set forth in §§ 3 and 6.

8—Transmission of Electrons Through Thick Graphite Single Crystals

In order to complete this search for planes corresponding to the " extra " diffractions, transmission patterns were taken through comparatively thick flakes from the " Ceylon No. 1 " and " Locality Unknown No. 1 " graphites. The relative weakness of the cross-grating spots and the great intensity of the secondary scattering effects (figs. 12, 13, 14, and 15) testify to the considerable thickness of the specimens. Comparison with patterns exhibiting a somewhat similar relative intensity of secondary to primary scattering from mica films whose thickness was measured by

* The indexing was carried out on the lines set forth in a paper by Finch, Quarrell, and Wilman, ' Trans. Faraday Soc.,' vol. 31, pp. 1062–1072, and p. 1080 (1935).

Darbyshire* and by Kirchner,† enables the thickness of these graphite flakes to be estimated as of the order of 10^3 A.

We have completely indexed‡ the band systems, *i.e.*, Kikuchi line pairs, recorded in altogether 8 reflexion and 20 transmission patterns, each representing a different setting, in complete agreement with the assigned X-ray structure; and in addition have partially indexed and searched through a further 14 reflexion and 16 transmission patterns without finding any evidence of abnormal planes. The planes thus indexed are enumerated in Table IV.

TABLE IV—KIKUCHI LINE DIFFRACTIONS OBTAINED FROM GRAPHITE SINGLE CRYSTAL SPECIMENS

Indices	Spacings in A calculated from $a = 2{\cdot}458$ A and $c/a = 2{\cdot}726$	Theoretical band-widths in cm at 50 kv and L = 28 cm	Observed band-widths in cm reduced to 50 kv and L = 28 cm
100	2·128	0·70	0·70
101	2·028	0·74	0·74
102	1·797	0·83	0·83
103	1·541	0·97	0·96
104	1·317	1·13	1·12
105	1·134	1·32	1·32
106	0·9891	1·51	1·51
107	0·8727	1·71	—
108	0·7746	1·93	—
109	0·7028	2·12	—
10·10	0·6389	2·33	—
200	1·064	1·41	1·41
201	1·051	1·42	1·42
202	1·014	1·47	1·47
203	0·9606	1·55	1·56
204	0·8985	1·66	1·66
205	0·8333	1·79	1·78
206	0·7705	1·94	1·92
300	0·7092	2·11	2·11
302	0·6939	2·15	2·17
304	0·6532	2·29	2·30
306	0·5990	2·49	2·49

* ' Z. Kristallog.,' vol. 86, p. 313 (1933).

† ' Ann. Physik,' vol. 11, p. 741 (1931); vol. 13, p. 38 (1932).

‡ *See* * note, p. 354.

TABLE IV—(continued)

Indices	Spacings in A calculated from $a = 2{\cdot}458$ A and $c/a = 2{\cdot}726$	Theoretical band-widths in cm at 50 kv and L = 28 cm	Observed band-widths in cm reduced to 50 kv and L = 28 cm
400	0·5319	2·80	2·80
401	0·5304	2·81	2·83
402	0·5255	2·84	2·84
403	0·5176	2·88	2·92
404	0·5070	2·94	2·93
500	0·4256	3·54	—
505	0·4056	3·70	—
600	0·3547	4·22	—
110	1·214	1·21	1·22
112	1·154	1·30	1·31
114	0·9911	1·51	1·51
116	0·8264	1·81	1·81
118	0·6920	2·16	2·13
11·10	0·5882	2·54	2·52
11·12	0·5084	2·93	—
120	0·8045	1·86	1·85
121	0·7988	1·87	1·87
122	0·7819	1·91	1·89
123	0·7570	1·97	1·98
124	0·7251	2·06	2·07
125	0·6897	2·17	2·15
220	0·6145	2·43	2·44
222	0·6040	2·47	2·49
224	0·5770	2·59	2·62
226	0·5385	2·78	2·76
228	0·4955	3·01	3·01
130	0·5902	2·53	2·52
131	0·5879	2·54	2·53
132	0·5814	2·57	2·55
133	0·5708	2·62	2·64
134	0·5567	2·68	2·66
135	0·5402	2·80	2·79
140	0·4642	3·21	3·22
142	0·4599	3·24	3·24
144	0·4474	3·33	3·33
146	0·4288	3·48	3·44

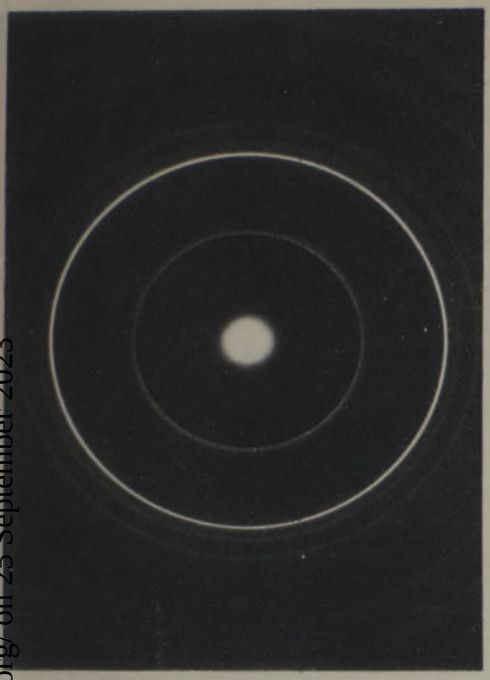

FIG. 1—Colloidal graphite on celluloid film normal to beam.

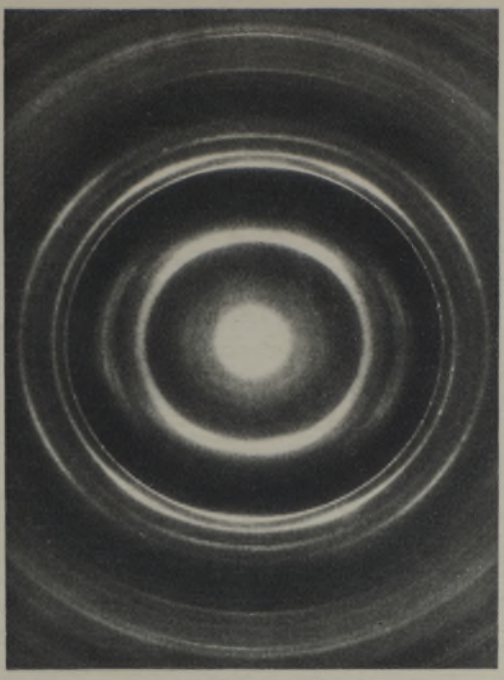

FIG. 2—As in fig. 1, but film inclined at 45° to beam.

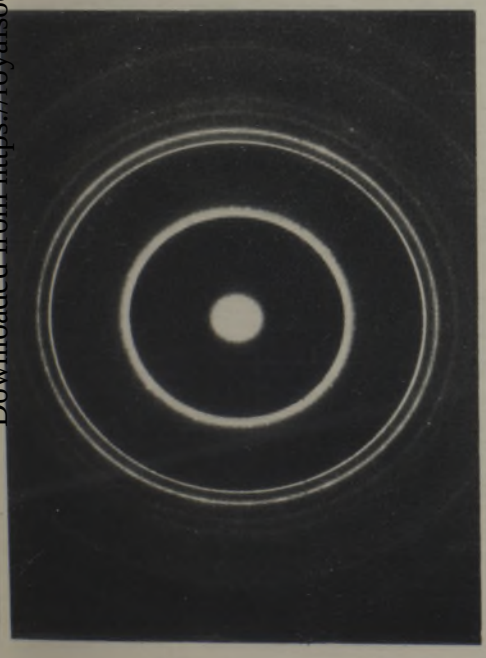

FIG. 3—Colloidal graphite crystals; random disposition.

FIG. 4—Enlargement from fig. 3.

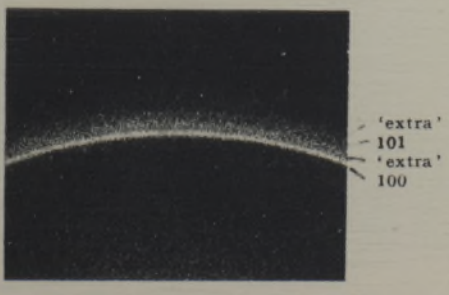

FIG. 5—Enlargement from fig. 1.

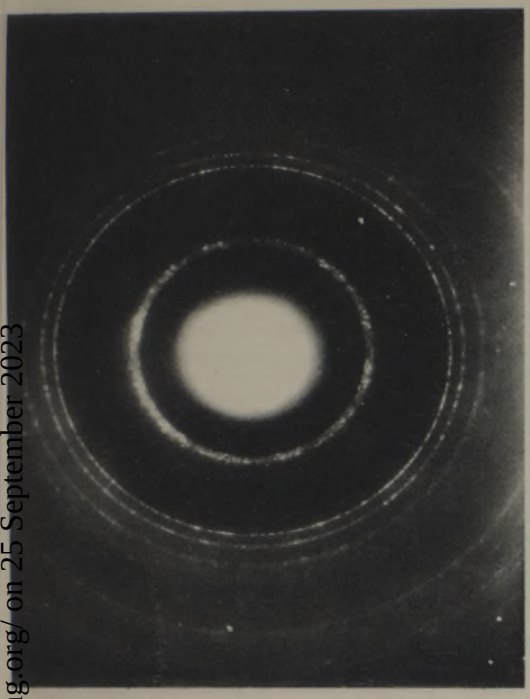

FIG. 6—Powdered Ceylon graphite.

FIG. 7—Transmission along *c* axis of a thin " Ceylon, No. 1," flake.

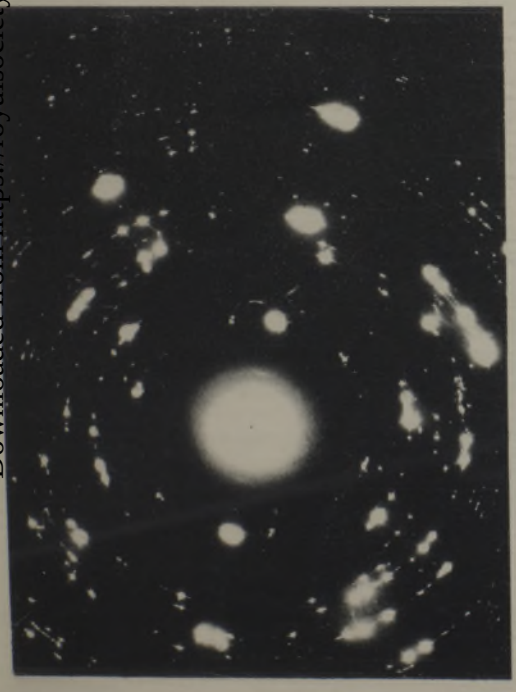

FIG. 8—Transmission through a thin curved flake of " Locality Unknown, No. 1 ".

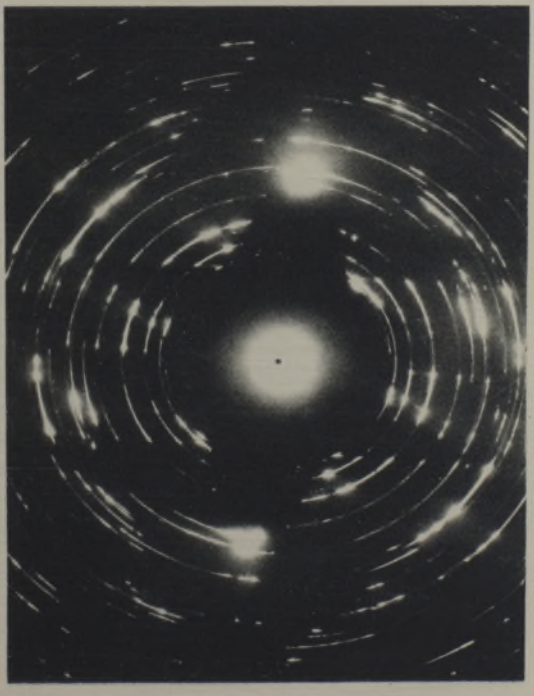

FIG. 9—Transmission with rotation about an axis normal to the beam.

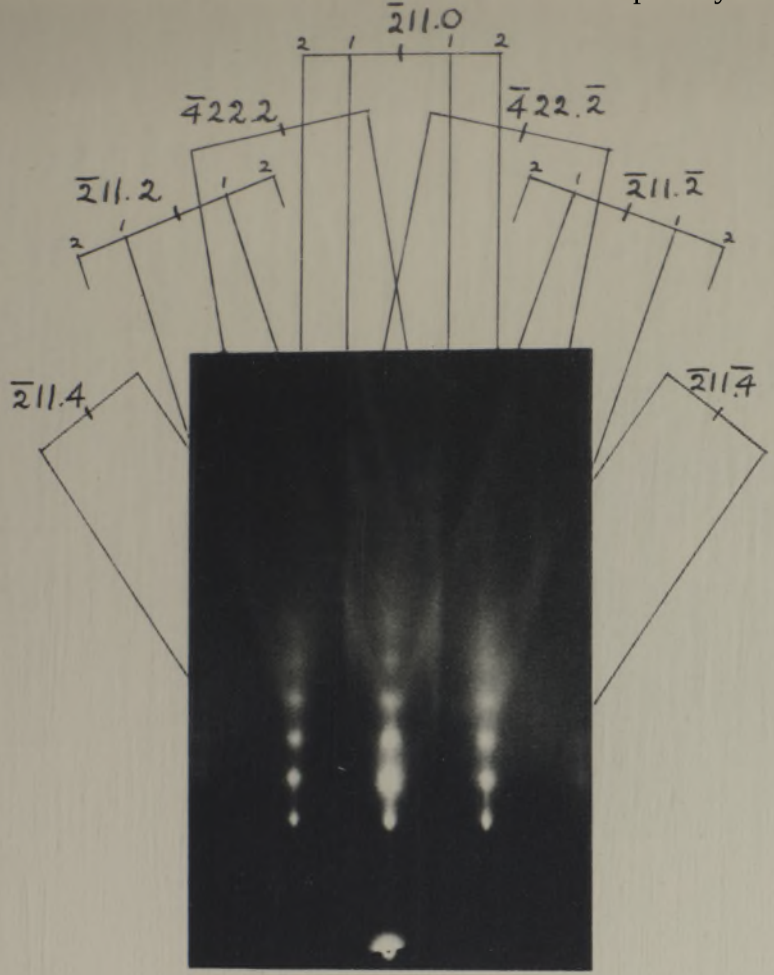

FIG. 10— $\phi = 30°$.

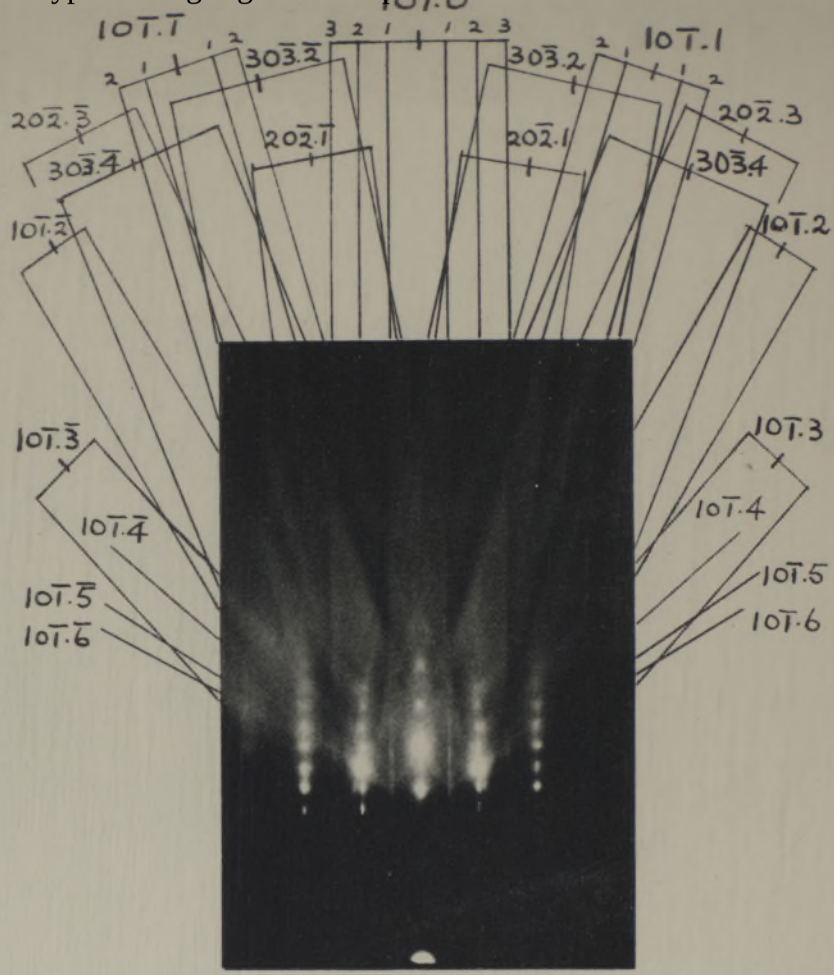

FIG. 11— $\phi = 0°$.

Reflexion patterns from a single crystal cleavage face of "Ceylon, No. 1," graphite.

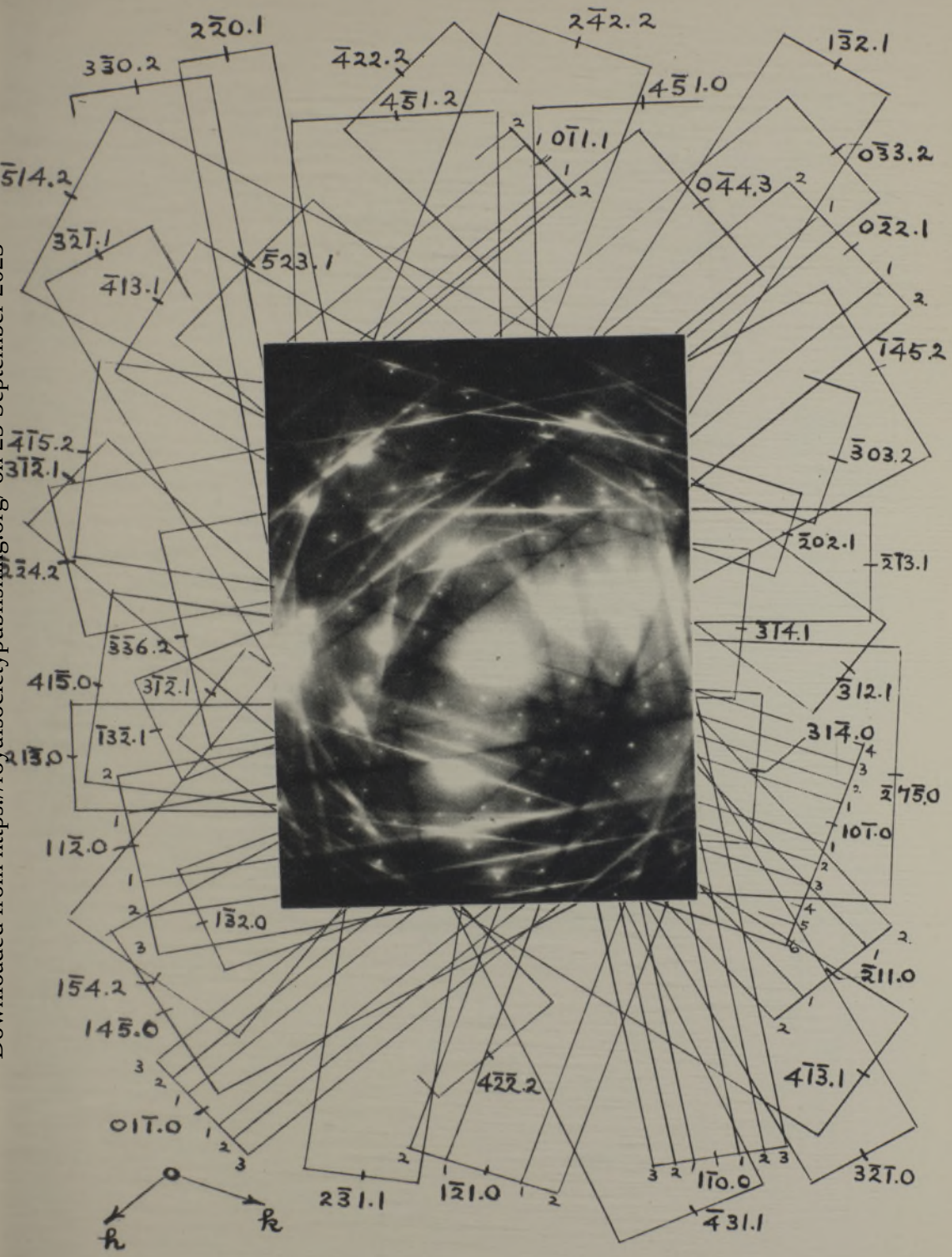

FIG. 12—Beam inclined by about 5° to *c* axis.

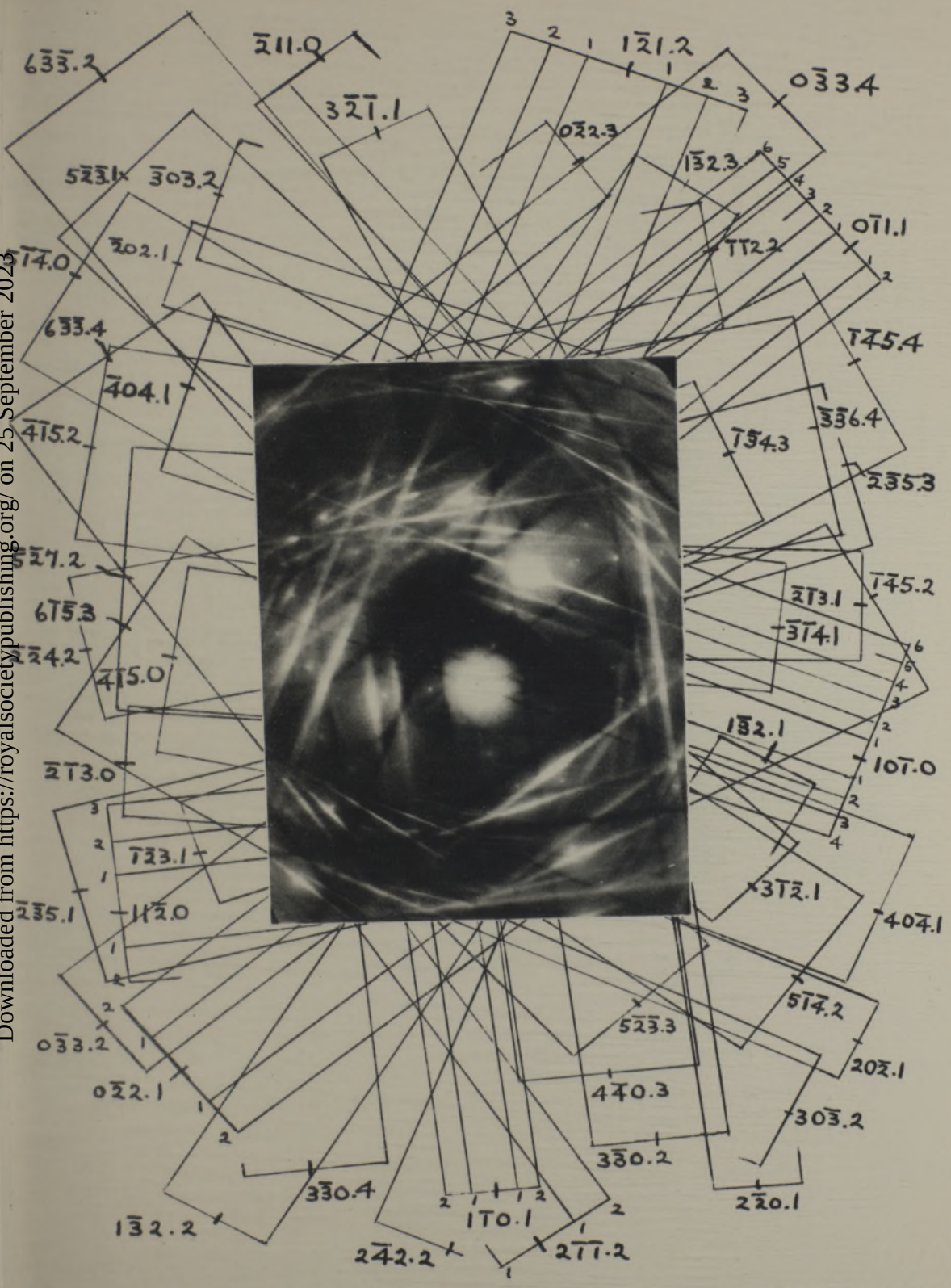

FIG. 13—Beam inclined by about 4° to the [01·1] zone axis. The medians of the 10$\bar{1}$·0 and 1$\bar{1}\bar{2}$·0 bands intersect in the *c* axis.

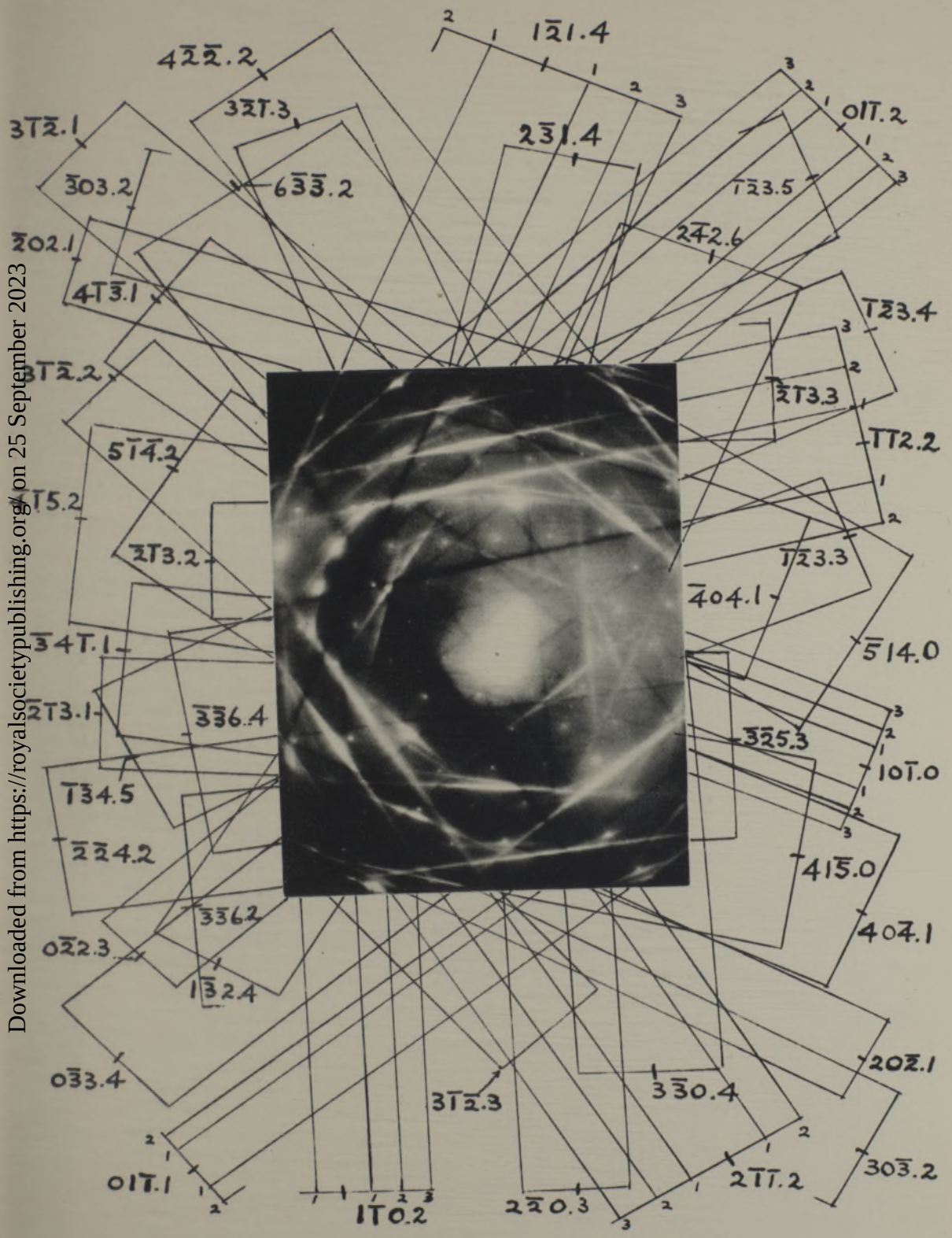

FIG. 14—Beam nearly parallel to [03·2] zone axis and inclined by about 6° to [02·1]. The medians of the $10\bar{1}\cdot0$ and $41\bar{5}\cdot0$ bands intersect in the *c* axis.

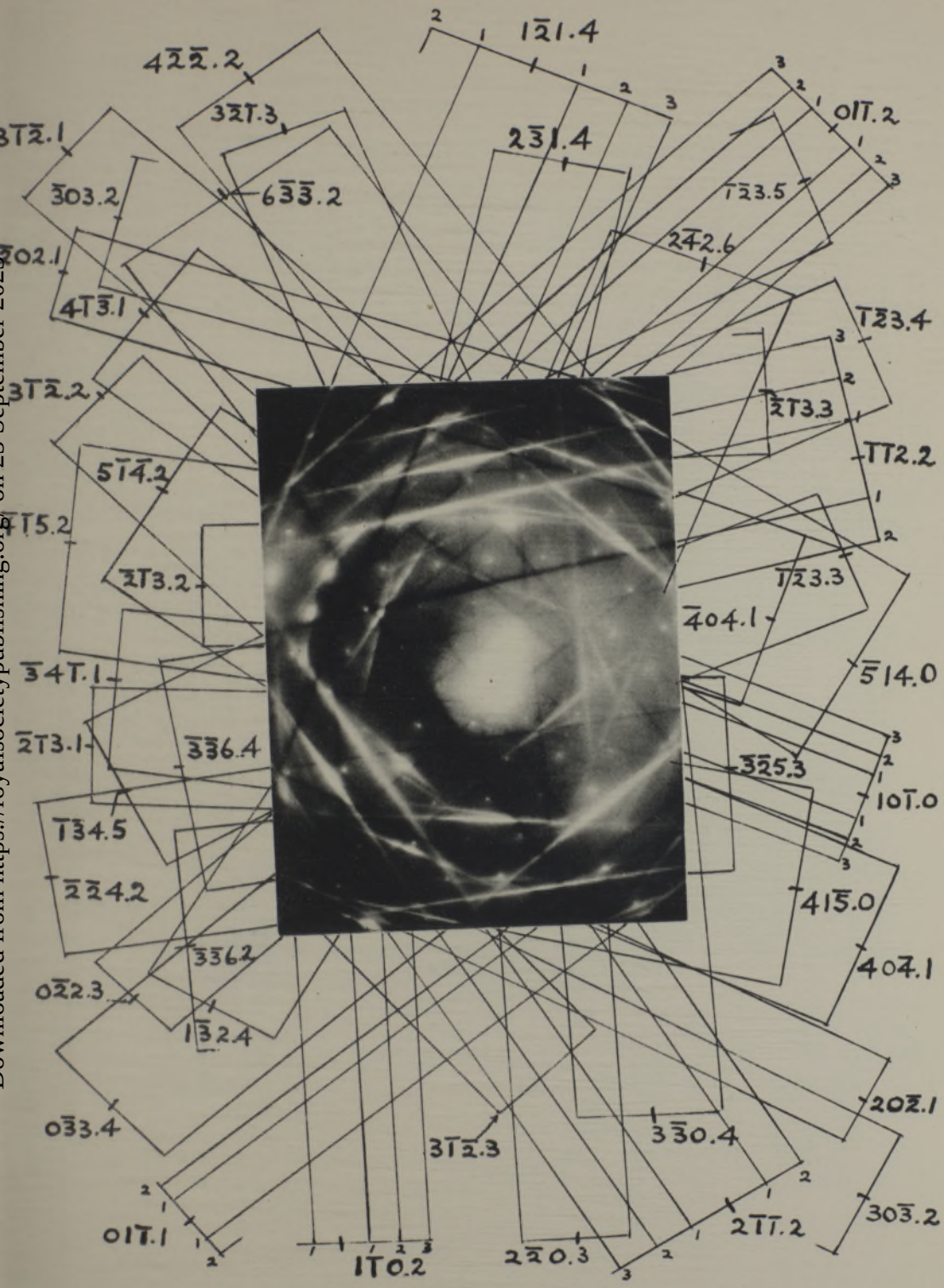

FIG. 14—Beam nearly parallel to [03·2] zone axis and inclined by about 6° to [02·1]. The medians of the 10$\bar{1}$·0 and 41$\bar{5}$·0 bands intersect in the *c* axis.

TABLE IV—(continued)

Indices	Spacings in A calculated from $a = 2{\cdot}458$ A and $c/a = 2{\cdot}726$	Theoretical band-widths in cm at 50 kv and L = 28 cm	Observed band-widths in cm reduced to 50 kv and L = 28 cm
330	0·4097	3·64	3·66
332	0·4065	3·68	3·66
334	0·3978	3·75	3·78
336	0·3847	3·89	3·91
231	0·4868	3·07	3·02
233	0·4771	3·13	3·12
235	0·4587	3·25	3·21
150	0·3823	3·90	3·85
153	0·3768	3·96	3·88
250	0·3408	4·38	4·29
252	0·3302	4·40	4·44
440	0·3073	4·86	4·88

Four indexed transmission patterns obtained from " Ceylon No. 1 " are reproduced in figs. 12, 13, 14, and 15, Plates 9 to 12, and it will be noticed that in each the direction of the beam in relation to that of the *c* axis was so chosen that planes corresponding to " extra " diffractions could hardly have failed to give rise in the pattern to well-marked band systems, had such planes indeed existed; but neither in these nor in any of the other Kikuchi line transmission or reflexion patterns have we been able to detect evidence of a plane or planes corresponding to any of the " extra " diffractions. Considering the thoroughness of this search, as testified to by the wide range of indices of the observed Kikuchi lines recorded in Table IV, and in view also of the excellent agreement between the Kikuchi line patterns and the assigned X-ray structure, we are now driven to conclude that this is in fact the true structure of graphite.

Unlike the powder and cross-grating pattern of types of spectra, the indexing of Kikuchi line patterns can, as a rule, be carried out decisively because, in addition to the band widths giving the plane spacings, the medians of such line pairs together with the position of the crystal relative to the photographic plate completely define the corresponding planes.

9—THE LATTICE CONSTANTS OF THE GRAPHITE LATTICE

Since in view of the above results, the validity of the assigned X-ray structure must now be accepted, we can calculate the axial ratio of the

graphite lattice unit cell from suitable data recorded in Table III, columns 1 and 2, but neglecting the " extra " diffractions at the moment as being in some way anomalous. Thus for this structure we have

$$\frac{1}{d_{hkl}} = \sqrt{\frac{4}{3a^2}(h^2 + k^2 + hk) + \frac{l^2}{c^2}},$$

whence

$$\frac{c}{a} = \sqrt{l^2 \Big/ \left[\frac{a^2}{d_{hkl}{}^2} - \tfrac{4}{3}(h^2 + k^2 + hk)\right]}.$$

The mean of the determinations, in all 25, recorded in column 3 gives $c/a = 2{\cdot}74$; but, in order to arrive at a properly weighted mean, only values calculated from diffractions of indices such that $l \gg h$, k, or their sum, and thus equivalent to intersections at fairly large angles with the (110) plane, should be used. Ten such suitable cases are marked with ‡ in Table III; they yield a mean value $c/a = 2{\cdot}726$, whence $c = 6{\cdot}701$ A.*

For purposes of comparison the more recent values of the graphite lattice constants obtained by X-rays and electron diffraction are grouped into Table V.

TABLE V—THE LATTICE CONSTANTS OF GRAPHITE

	Observer	a in A	c in A	c/a
X-ray diffraction	Hull, 1917 and 1922†	2·47	6·80	2·75
	Bernal, 1924‡	2·45	6·82	2·77
	Hassel and Mark, 1924§	2·46	6·76	2·75
	Mauguin, 1926‖	2·46–2·48	6·74	2·72
	Ott, 1928¶	2·48	6·78	2·73
Electron diffraction	Jenkins, 1934**	2·42	6·80	2·727
	Aminoff and Broome, 1935††	2·42	6·3	—
	Miwa, 1934‡‡	2·456	—	—
	Finch and Fordham, 1936§§	2·458*	—	—
	Finch and Wilman, 1936	2·458*	6·701*	2·726

* Referred to $a_{Au} = 4{\cdot}070$ A.

† ' Phys. Rev.,' vol. 10, p. 661 (1917); vol. 20, p. 113 (1922).

‡ ' Proc. Roy. Soc.,' A, vol. 106, p. 749 (1924).

§ ' Z. Physik,' vol. 25, p. 317 (1924).

‖ ' Bull. Soc. Franc. Min.,' vol. 49, p. 32 (1926).

¶ ' Ann. Physik,' vol. 85, p. 81 (1928).

** ' Phil. Mag.,' vol. 17, p. 457 (1934).

†† ' Z. Kristallog.,' vol. 91, p. 77 (1935).

‡‡ ' Sci. Rep. Tôhoku Univ. *a*,' vol. 23, p. 242 (1934).

§§ ' Proc. Phys. Soc.,' vol. 48, p. 85 (1936).

10—The Origin of the "Extra" Diffractions

To sum up: it has now been shown experimentally that the graphite "extra" diffractions cannot reasonably be ascribed to (i) impurities, (ii) lattice dimension deviations, or to (iii) the real graphite structure being other than that hitherto assigned to graphite on the basis of X-ray data. Our experiments have, however, established the significant fact that, whilst a relatively thick graphite crystal gives a Kikuchi line system which in its geometry accords completely with, and therefore confirms, the assigned X-ray structure, a flake cleaved from the same crystal, but sufficiently thin to afford the cross-grating type of spectrum, yields a rotation pattern in which the many "extra" diffractions afford undeniable evidence of the existence of crystal-plane spacings differing from the normal identity plane spacings of the graphite lattice. Yet it can hardly be supposed that the mere act of cleaving a thin graphite flake from a thicker crystal produces a change in structure. We are therefore faced at this stage with the apparent paradox that, although the thick and thin crystals must both have the same lattice structure, the latter contain identity spacings not exhibited by the thicker graphite. Clearly the cause of the "extra" diffractions is to be sought in some property closely connected with the thinness of the diffracting crystal.

11—The Theory of the Diffraction of Electrons by Thin Graphite Crystals

In the light of the facts set forth above, the following considerations lead to a reasonable explanation of the origin of the "extra" diffractions obtained when sufficiently thin graphite flakes are traversed by an electron beam.

In the first place it will be necessary to insist on an important point of difference between the conditions pertaining to the diffraction of X-rays and those under which the electron beam gives rise to a cross-grating type of spectrum, and which does not appear to have been previously considered. We think of a space lattice as a periodic repetition of scattering centres extending to infinity in each of three dimensions. In view of the low efficiency of scattering of X-rays and consequently the large crystal particles necessary to give intense diffraction effects, we may without appreciable error, as regards the positions of the diffractions, consider the individual crystals of a relatively coarse powder as such unbounded space lattices; and one falls, indeed, into the habit of so doing. Hence we are accustomed to accept as axiomatic that in a given space

lattice the plane spacings must decrease with the decreasing density of lattice points in the planes, although this can only be true if the lattice extends in fact sufficiently far in all directions for consecutive planes of a parallel group to contain substantially the same number of lattice points.

In the diffraction of electrons transmitted through a film so thin as to afford the well-defined diffractions characteristic of the cross-grating type of pattern we have, however, a lattice which, though virtually unbounded in directions normal to the beam, is limited in the beam direction itself. Consider, for example, the cross-grating, fig. 16, representing an (h00) cross-section in the beam direction through such a lattice; then the dots

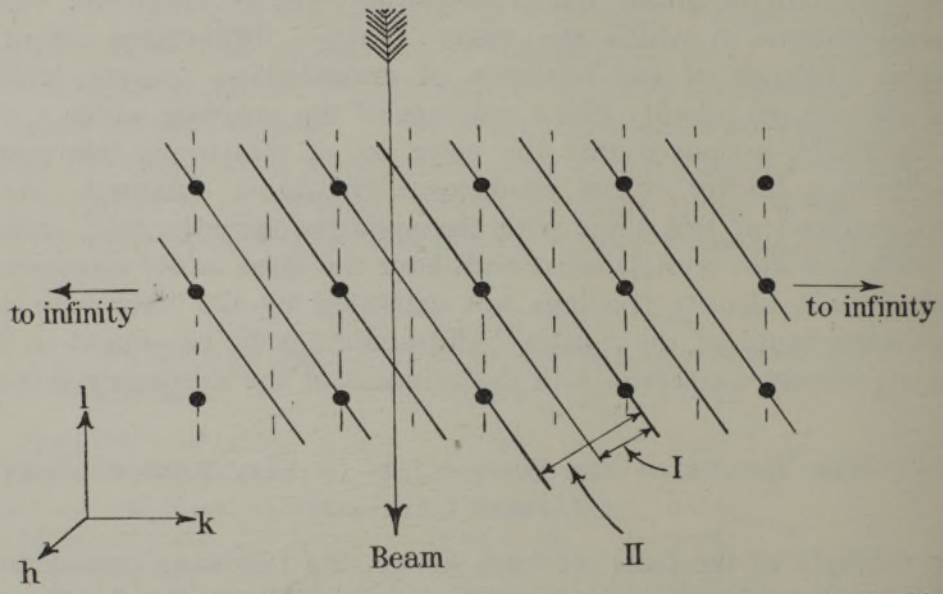

FIG. 16—I, Normal Bragg plane spacing for an infinite lattice; II, effective identity spacing.

are also projections of infinitely long atom rows. The lattice is then unbounded in the h and k directions but is strictly limited in the l direction, *i.e.*, by the thickness of the crystal, in this case taken, by way of example, as three lattice points thick.

It will immediately be evident that, although the (0k0) planes all contain equal numbers of lattice points, the successive parallel (0kl) planes (where in this example, k and l are one odd, one even, and k equals 1 or 2) in general contain different numbers of lattice rows, with the result that effective spacings occur which are integral multiples of the corresponding normal plane spacings. Thus it would seem possible under suitable conditions to obtain " extra " diffractions equivalent to simple fractional orders of the normal Laue indices. In the light of these

considerations we may now proceed to a quantitative discussion of the origin of the graphite " extra " diffractions.

For a thin graphite flake transmission specimen, the effective separations of the lattice point rows in the cleavage plane are normal, because the cleavage plane may be regarded as extending to infinity. Hence, owing to the limited thickness of the crystal, successive planes of similar population density must intersect the cleavage plane in such successive parallel rows, and the h and k (Laue, not Millerian) indices will have all possible integral values and not merely those which also give integral l values. It is a well-known experimental fact that, for thin crystals, diffractions are afforded by planes parallel to the beam and thus occur at all the reinforcement points of the cleavage plane cross-grating when the beam is passing along a given zone axis. Hence, in order to determine the positions in the screen of the more intense " extra " diffractions to which abnormal periodicities may be expected to give rise, we consider planes passing through the more densely populated atom rows in the cleavage plane and parallel to the beam, the direction of which determines their l index which may be either integral or fractional. If $[uvw]$ are the indices of the lattice row in the beam, then the Laue indices corresponding to planes parallel to $[uvw]$ are given by

$$uh + vk + wl = 0, \tag{1}$$

where u, v, w, h, and k have integral values. Thus we can construct tables of the Laue indices of diffractions possible with combinations of these integral indices. Table VI will suffice as example.

TABLE VI

Beam direction indices	Laue indices					
$[uvw]$	$1\,0\,l$	$0\,1\,l$	$1\,\bar{1}\,l$	$1\,1\,l$	$2\,\bar{1}\,l$	$\bar{1}\,2\,l$
$\bar{1}23$	$1\,0\,\frac{1}{3}$	$0\,1\,\frac{2}{3}$	$1\,\bar{1}\,\frac{\bar{1}}{3}$	$1\,1\,1$	$2\,\bar{1}\,0$	$\bar{1}\,2\,1$
$\bar{4}23$	$1\,0\,\frac{4}{3}$	$0\,1\,\frac{2}{3}$	$1\,\bar{1}\,\frac{2}{3}$	$1\,1\,2$	$2\,\bar{1}\,2$	$\bar{1}\,2\,0$
$\bar{7}23$	$1\,0\,\frac{7}{3}$	$0\,1\,\frac{2}{3}$	$1\,\bar{1}\,\frac{5}{3}$	$1\,1\,3$	$2\,\bar{1}\,4$	$\bar{1}\,2\,1$
$\bar{1}53$	$1\,0\,\frac{1}{3}$	$0\,1\,\frac{5}{3}$	$1\,\bar{1}\,\frac{\bar{4}}{3}$	$1\,1\,2$	$2\,\bar{1}\,\bar{1}$	$\bar{1}\,2\,3$
$\bar{4}53$	$1\,0\,\frac{4}{3}$	$0\,1\,\frac{5}{3}$	$1\,\bar{1}\,\frac{\bar{1}}{3}$	$1\,1\,3$	$2\,\bar{1}\,1$	$\bar{1}\,2\,2$
$\bar{7}53$	$1\,0\,\frac{7}{3}$	$0\,1\,\frac{5}{3}$	$1\,\bar{1}\,\frac{2}{3}$	$1\,1\,4$	$2\,\bar{1}\,3$	$\bar{1}\,2\,1$
$\bar{1}83$	$1\,0\,\frac{1}{3}$	$0\,1\,\frac{8}{3}$	$1\,\bar{1}\,\frac{\bar{7}}{3}$	$1\,1\,3$	$2\,\bar{1}\,2$	$\bar{1}\,2\,5$
$\bar{4}83$	$1\,0\,\frac{4}{3}$	$0\,1\,\frac{8}{3}$	$1\,\bar{1}\,\frac{\bar{4}}{3}$	$1\,1\,4$	$2\,\bar{1}\,0$	$\bar{1}\,2\,4$
$\bar{7}83$	$1\,0\,\frac{7}{3}$	$0\,1\,\frac{8}{3}$	$1\,\bar{1}\,\frac{1}{3}$	$1\,1\,5$	$2\,\bar{1}\,2$	$\bar{1}\,2\,3$

It is evident that such combinations of u, v, w, h, and k in equation (1) must lead to the Laue indices of all possible diffractions from a graphite crystal limited in the c axial direction, but otherwise unbounded. Some diffractions have fractional third indices; and some with wholly integral indices such as 111, 113, etc., are forbidden by structure factor conditions for the lattice of unlimited extent, but may be expected to occur with diffraction by the thin graphite crystal; others are the normal diffractions common to both thick and thin crystals.

As regards the intensities of the " extra " (fractional l index) and " forbidden " (for reasons of structure factor) diffractions, we may expect them in general to reflect roughly the relative intensities of the lowest corresponding multiple orders, *i.e.*, with integral hkl values, normally appearing in, for example, the Kikuchi line or X-ray pattern. Thus a forbidden diffraction, *i.e.*, one of integral hkl values, which owing to structure factor restrictions does not normally occur with a thick crystal (which is equivalent to a lattice extending practically to infinity in all directions) can appear strongly when the crystal is sufficiently thin, owing to the marked difference in scattering power of the successive planes; a difference which decreases as the structure factor restrictions approach to the normal with increasing crystal thickness. The indices of the more important possible " extra " and " forbidden " diffractions compiled on the lines indicated in Table VI, together with the corresponding calculated spacings and estimated intensities are grouped into Table VII which contains also similar data regarding the actually observed " extra " diffractions.

The observed " extra " and forbidden ring spacings and intensities agree so well with the calculated spacings and intensities of the corresponding assigned fractional orders and forbidden diffractions as to afford strong support to the theory outlined above, particularly in view of the fact that the hk indices are either 10, 11, or 20, *i.e.*, the corresponding planes pass through densely populated atom rows in the cleavage plane. Furthermore, the more conspicuous " extra " diffractions have l values such that the planes also contain densely populated atom rows in the beam direction.

12—Further Experimental Confirmation of the Theory of Diffraction by the Limited Space Lattice

In addition to the excellent quantitative agreement between fact and theory shown in Table VII, we have in the experimental material already to hand further facts which are in harmony with the new view of the

diffraction of electrons by the limited space lattice as exemplified by a thin graphite crystal.

It was pointed out in § 6 that, for the two prominent " extra " rings appearing in the 100–101 group of diffractions, the directions of arcing correspond to planes forming angles with the normal to the cleavage plane of approximately 12 and 24°. The indices assigned by the theory to these diffractions are $10\frac{2}{3}$ and $10\frac{4}{3}$ (Table VII). The corresponding planes, (302) and (304), enclose angles with the cleavage plane normal of

TABLE VII—THEORETICAL AND OBSERVED " EXTRA " AND FORBIDDEN DIFFRACTIONS FROM THIN GRAPHITE CRYSTALS

Indices	Estimated order of intensities	Calculated spacings in A	Observed spacings in A	Observed order of intensities
$10\frac{3}{5}$	F	2·091	2·091	F
$10\frac{3}{4}$	S	2·082	2·081	S
$10\frac{4}{5}$	F	2·069	2·067	M
$10\frac{3}{4}$	F	2·070		
$10\frac{5}{4}$	F	1·978	1·980	M
$10\frac{4}{3}$	S	1·960	1·958	S
$10\frac{8}{3}$	M	1·624	1·625	M
$10\frac{10}{5}$	M	1·461	1·460	M
$11\frac{1}{4}$	F or M	1·228	1·226	M
$11\frac{1}{5}$		1·227		
$11\frac{1}{9}$	F	1·223	1·221	F
$11\frac{2}{8}$		1·220		
111	S	1·208	1·209	S
$11\frac{4}{3}$	F	1·175	1·174	F
$11\frac{7}{4}$	F	1·121	1·119	F
$11\frac{6}{8}$	F	1·104	1·105	F
113	M	1·077	1·077	M
$20\frac{4}{3}$	M	1·041	1·041	M

11° 57′ and 22° 57′ respectively. In view of the good agreement already noted in the spacings of these two rings, such close correspondence between the observed and theoretical orientations of the originating planes is indeed most convincing. In the original negative of fig. 2 the directions of arcing of the $10\frac{8}{3}$ and $10\frac{10}{3}$ diffractions can be seen to be such as to confirm this indexing in a similar manner.

In the graphite powder patterns, and more particularly in figs. 3, 4, and 6, the 100, $10\frac{2}{3}$, 101, and $10\frac{4}{3}$ rings appear as if superimposed upon a band extending from the inner (100) to the outermost ($10\frac{4}{3}$) ring. The microphotometric record, fig. 17, of this region of a graphite powder

pattern clearly shows that this is indeed so. This band can immediately be accounted for in terms of the theory as being due to fractional orders of higher denominations and of relatively slight intensities compared with those listed in Table VII. Over 30 such diffractions with l values between $\frac{1}{9}$ and $\frac{11}{9}$ and of denominators between 2 and 9 lie within the region of this band, and thus satisfactorily account for its existence in the powder patterns.

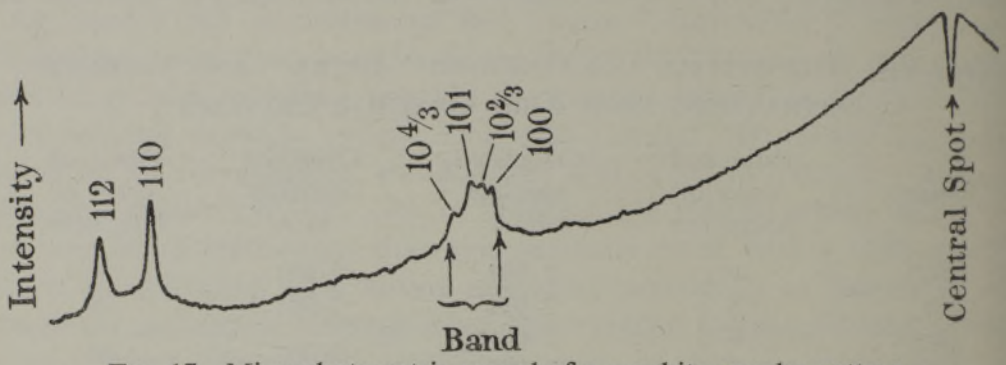

FIG. 17—Microphotometric record of a graphite powder pattern.

The thin graphite single crystal " rotation " patterns all exhibit remarkable streaks joining up and passing through diffraction spots, both normal and " extra ". Several such streaks are visible in the pattern, fig. 8, Plate 7, for instance, at approximately 5 and 11 o'clock positions and $2\frac{1}{2}$ cm from the undeflected beam. They are much more easily seen in the original plates, where they are indeed very conspicuous. These streaks always appear in pairs symmetrically disposed about the central spot; hence they are undoubtedly due to a two-dimensional diffraction effect produced by the progressive inclination to the beam of the cross-grating formed by the graphite cleavage plane. When, during such inclination, a zone axis comes into line with the beam, strong reinforcement occurs and bright cross-grating spots appear. Thus this streak phenomenon not only justifies the premises made in building up the theory, but also affords a striking demonstration of the relaxation of structure factor restrictions due to the limitation of the lattice dimensions in a given direction.

We wish to thank the Government Grant Committee of the Society, the Department of Scientific and Industrial Research, Messrs. E. G. Acheson, Ltd., Ferranti, Ltd., Imperial Chemical Industries, Ltd., and Messrs. C. C. Wakefield, Ltd., for financial assistance and apparatus. We are also indebted to Dr. W. R. Jones of the Royal School of Mines and to Dr. Bannister of the Natural History Museum for supplying specimens,

and to Dr. Martin and Mr. Gull who, by the courtesy of Sir Robert Robertson, F.R.S., obtained the microphotometric record, fig. 17, from one of our graphite powder patterns.

12—Summary

The diffraction of electrons by graphite has been studied. It has been found that both artificial and natural graphite powders give diffractions, many of which do not appear to fit in with the structure hitherto assigned to graphite by X-ray workers. It has been shown experimentally that these " extra " diffractions are due neither to impurities nor to two-dimensional lattice deviations at the crystal surfaces. It has been found further that thin single crystals of graphite, like the powder, also yield the " extra " diffractions; on the other hand, thick crystals give Kikuchi line patterns which accord completely with the X-ray results.

It is concluded that the " extra " diffractions obtained with thin crystals are due to the fact that the graphite lattice, though virtually unbounded in the cleavage plane directions, is limited in the remaining dimensions by the thinness of the crystal; with the consequence that diffractions of fractional l index, *i.e.*, equivalent to fractional orders of the normal Laue indices, and also diffractions normally forbidden by structure factor considerations can occur.

This theory is supported by the occurrence of diffraction lines joining up groups of diffractions and by the agreement found between the calculated and observed spacings corresponding to, and the directions of arcing of, the " extra " diffractions afforded by graphite.

The lattice constants of graphite have been determined in terms of that of gold.