XIII. *Two Types of Diamond.*

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INTRODUCTION.

GENERAL ACCOUNT OF RECOGNITION OF TWO TYPES OF DIAMOND.

Among a number of diamonds supplied to us by Professor W. T. GORDON, of King's College, London, one, by a fortunate chance, was found to differ from the rest in its infra-red spectrum. Having confirmed by various methods that a large absorption band at 8 μ present in the spectrum of all the other diamonds, was absent in this particular one, we explored photographically the ultra-violet spectrum of all the diamonds then available, and found that the stone which was transparent at 8 μ in the infra-red was also transparent from about λ 3000 to λ 2250 in the ultra-violet, the other diamonds being opaque beyond λ 3000.

At this stage, between two and three hundred diamonds were examined visually by means of a simple ultra-violet spectroscope with fluorescent eye-piece without another diamond transparent beyond λ 3000 being found.

Among other physical and optical properties examined in comparison, little difference was found between diamonds of the usual and the transparent type: their water-whiteness, density, refractive index, dielectric constant, Raman frequency and the earlier X-ray patterns appeared the same. A difference in the crystalline condition was, however, noted, for the transparent diamond was made up of a large number of parallel laminæ, and it was also more nearly isotropic when examined by polarized light than the others.

With this lead a further search was made, resulting in five diamonds in all (and some small ones) being found, which exhibited a laminar condition, and that transparency in the regions of the infra-red at 8 μ and ultra-violet spectrum already mentioned.

We have further been able to show that these transparent diamonds possess another feature, a marked photo-electric or photo-conductive effect, very feeble in diamonds of the usual type; and a more recent exploration of the X-ray patterns also indicates a difference.

PREVIOUS RECOGNITION OF DIFFERENCES IN SPECIAL FEATURES OF DIAMOND.

References are to be found in the literature to some features which can now be recognized as pertaining to the transparent or laminar type, but no correlation between the characteristics of each of the two types has been recorded.

Thus, ROBERT BOYLE[*] speaks of a diamond which he caused to be set in a ring as " consisting of several plates having their edges distinguishable like those of a book a little opened."

This feature of fine lamination is illustrated by the striking photographs reproduced by WILLIAMS,[†] who also mentions, as does SUTTON,[‡] the silky effect due to striations, especially in dodecahedral diamonds.

BOYLE also exhibited to this Society on October 28, 1663, a diamond which glowed on being rubbed. We find, however, that this property is common to both types of diamond.

CROOKES,[§] among his interesting observations and speculations on diamond, mentions that there are " few exceptions " to the rule that diamonds are under strain as shown by the polarizing microscope.

In one of the earliest papers on the " Transparency of various Bodies," MILLER,[||] who used a rocksalt spectrometer and a quartz lens for his camera, gives values for the extension of the spectrum in the ultra-violet for three diamonds, of which two have the relative lengths of 59 and 62, the third being only 19 ; from the fiduciary lines of the solar spectrum quoted, and the relative extensions for quartz (74) and window-glass (16), it is clear that the two former diamonds were of the transparent, and the last of the opaque type.

REINKOBER,[¶] who investigated the infra-red absorption spectrum of diamond, had without doubt a diamond of the transparent type, for he calls attention to transparency at 8 μ where ÅNGSTRÖM,[**] in 1892, and JULIUS,[††] in 1893, found strong absorption.

Again, PETER[‡‡] when choosing stones for his work on the refractive index of diamond in the far ultra-violet found that out of 30, only 2 were transparent beyond λ 3000, and remarks that diamonds of this kind are evidently rare.

GUDDEN and POHL,[§§] in 1920, in experimenting on the photo-conductivity of diamond,

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[*] 'Works,' p. 577 (1772).

[†] " Genesis of the Diamond," vol. 2, p. 460 (1932).

[‡] " Diamond," pp. 28, 81 (1928).

[§] 'Proc. Roy. Inst.,' vol. 15, p. 488 (1897).

[||] 'Phil. Trans.,' vol. 152, p. 861 (1862).

[¶] 'Ann. Physik,' vol. 34, 243 (1911).

[**] 'Phys. Rev.,' vol. 1, p. 597 (1892).

[††] 'Verh. Akad. Wet.,' Amst., p. 1 (1893).

[‡‡] 'Z. Physik,' vol. 15, 358 (1923).

[§§] 'Z. Physik,' vol. 3, p. 123 (1920) ; see also " Lichtelektrische Erscheinungen," p. 155, by B. GUDDEN (Berlin, 1928).

found that diamonds which absorbed light of wave-length less than λ 3000, on the application of a high voltage were very much less photo-conductive than one which was transparent as far as λ 2250.

In a research on photo-conductivity, Miss LEVI* gives photographs of ultra-violet spectra which clearly show that she had examples of the two types.

There are thus scattered through the literature references to diamonds that have been examined for various specific unrelated properties, and among them we now recognize a type which is transparent in certain regions of the infra-red and ultra-violet, markedly photo-conductive, and possesses fine laminar structure, isotropy, and some difference from normal in the X-ray intensity. This more transparent type is rare, although we have found it in diamonds from the Cape and from Brazil.

It may be mentioned that all the diamonds described in this paper are of the " water-white " class, and mostly non-fluorescent when subjected to ultra-violet light passed through a Wood's filter.

Table I contains data on most of the diamonds examined. They are numbered consecutively as they were received, but in the Table the diamonds of the usual type (" Type 1 "), that is, opaque at 8 μ in the infra-red and also below λ 3000 in the ultra-violet, are placed first, followed by the more transparent specimens (" Type 2 ").

APPEARANCE AND MORPHOLOGY.

(With Professor W. T. GORDON.)

This section has been inserted here to present at an early stage a description of the appearance and form of the crystals examined, although appreciation of the bearing of their differences came later.

In colour, nearly all the diamonds were water-white, only a few of Type 1 having a slight yellow colour : those of Type 2 were all free from colour. For work on absorption in the infra-red region, the best thickness for resolution of the bands was found to be from 1 to 2 mm.

Table I contains short descriptive notes on their thickness, weight and crystalline condition.

With the exception of the fine specimens D 17, D 18, D 25, few of the crystals are perfect octahedra ; D 1, D 3, D 4, D 6 are octahedral twins of plate form; but most are deformed octahedra, or cleavages showing an octahedral (111) face, or are cleavage fragments of various kinds.

A short description of diamonds of Type 2 and of several interesting examples of Type 1 will next be given, as their crystallographic peculiarities appear to have relation to other features optical and electrical to be discussed later.

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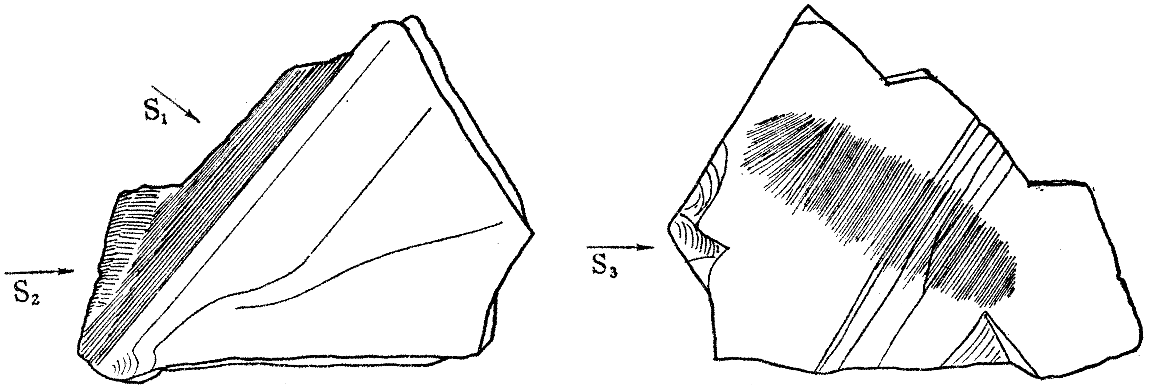
* 'Trans. Roy. Soc. Can.,' vol. 16, 3rd series, p. 243 (1922).

TABLE I.—Properties of Diamonds.

No. of Diamond	Form or Appearance.	Weight, gm.	Thickness, mm.	Sp. gr. at 15° C./15° C.	Infra-red Absorption Bands. At 3 μ, 4·1 μ, 4·8 μ, 8 μ.	Infra-red Absorption Bands. At 3 μ, 4·1 μ, 4·8 μ. —	Ultra-violet Absorption. Below 3000 λ.	Raman Difference, 1332 cm.$^{-1}$	Optical Isotropy	Photo-electric Conductivity.
Type 1										
—	ÅNGSTRÖM'S; not completely smooth; 1892	—	—	—	Present	—	—	—	—	—
—	JULIUS'S; "plate"; 1893	—	4·25	—	Present	—	—	—	—	—
D 1	Spinel twin—natural faces	0·6530	3·11	3·514	Present	—	Opaque	R	Partial	Slight.
D 3	Small spinel twin; natural faces	—	1·61	—	Present	—	—	—	—	—
D 4	Do. do.	0·4504	1·52	—	Present	—	—	—	Partial	—
D 5	Large irregular crystal with vicinal faces	—	3·63	3·512	Present	—	—	—	Partial	—
D 6	Octahedron—interpenetrating twin	—	3·0 (abt.)	—	Present	—	—	—	Partial	—
D 7	Flake; parallel cleaved faces	—	1·07	—	Present	—	—	—	Partial	—
D 8	Do. do.	—	1·61	—	Present	—	—	—	Partial	—
D 9	Flat octahedron; natural faces	—	0·75	—	Present	—	—	—	Partial	—
D 10	Do. do.	0·0560	1·08	3·50	Present	—	Opaque	—	Partial	Slight.
D 11	Do. do.	0·382	2·61	—	Present	—	—	—	—	—
D 12	Half of an octahedron; parallel to 111 face; including the three apices	0·434	—	—	Present	—	—	—	—	—
D 13	Lozenge-shaped plate formed by one slice parallel to the 111 face, fused to similar plate along one edge of an octahedral face	0·757	2·62	—	Present	—	—	—	—	—
D 14	Like D 11	0·361	2·56	—	Present	—	—	—	—	—
D 15	Like D 11	0·405	3·16	—	Present	—	—	—	—	—
D 17	Large, nearly perfect octahedron	0·9164	7·0	3·517	Present along 4 trigonal axes	—	Opaque	—	—	—
D 18	Do. do.	0·5137	6·0	3·514	Like 17	—	Opaque	—	—	—
D 20	Columnar	0·5257	3·00	3·510	Present	—	Opaque	R	Partial	Slight.
D 21	Irregular stepping	0·2310	1·89	3·511	Present	—	Opaque	R	Partial	Slight.
D 23	Intersecting planes	0·1650	1·71	3·511	Present	—	Opaque	R	Partial	Marked.
D 25	Nearly perfect octahedron	0·2827	—	3·508	—	—	Opaque	—	Partial	Slight.
Type 2										
—	REINKOBER'S; "plate"; 1911	—	1·26	—	—	Present	—	—	—	—
D 2	Triangular flake; external face natural; cleavage face (111) striated; finely stepped on edge	0·4504	2·09	3·513	—	Present	Transparent	R	Large	Strong.
D 16	Block of three laminated crystals	0·6149	2·9	3·523	—	Present	Transparent	R	Large	Slight.
D 19	Plate-laminated	0·2727	2·27	3·519	—	Present	Transparent	R	Large	Strong.
D 22	Triangular flake; laminated	0·2141	1·86	3·516	—	Present	Transparent	R	Large	Very strong.
D 24	Laminar	0·1086	1·69	3·502	—	Present	Transparent	R	Large	Marked.

Colour: all were water-white except D 5 and D 6, which were slightly coloured. Refractive index: for D 1 and D 2, ca. 2·41 for λ 5461.
Dielectric constant: D 1, 5·01; D 2, 4·88.
X-ray pattern is the same for both types of diamond, with differences in intensity.

D 2. Fig. 1 (*a*) and (*b*).—The top face is a cleavage with edge zone stepping of parallel steps (fig. 1 (*a*), S_1). It is important to note that this stepping is a natural feature of growth and represents the building up of a pyramid on an octahedral face. The top face is not smooth, and has low cleavage steps (fig. 1 (*a*), S_2). The other face is a cleavage with strongly-marked cleavage steps, parallel for the most part, but breaking away towards the edge in a conchoidal fashion (fig. 1 (*b*), S_3). The edges are fractures.



(*a*) FIG. 1. (*b*)

The general condition of this diamond shows an apparent growth by thin layers parallel to the octahedral face.

This diamond is mainly isotropic, showing a cross-hatching due to reflections from the several steppings.

D 16. Fig. 24, Plate 11.—This is a fragment of what was probably three crystals in nearly perfect alignment. There is in consequence a certain amount of cross-graining.

D 19. Fig. 2.—D 19 has no natural face. It is highly laminated with a partial cleavage showing interference colours where cleavage planes have been opened and air has penetrated. On one face there is a finely marked cleavage stepping. This face has fine striations parallel to these steps. There are also ripples broader than the striations and at 60° to the striations on both large faces and on the edges. They are

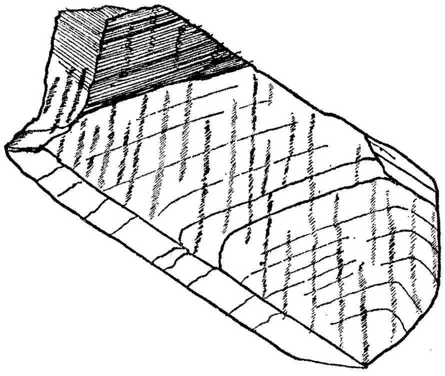


FIG. 2.

like equatorial planes through the crystal. On the other side the markings are not so regular. One of the fractured edges suggests that this diamond also consists of layers similar to D 2.

This diamond is nearly isotropic with some fine anisotropic lines, but no obvious cross-hatching.

D 22. Fig. 3.—There are three natural surfaces. The two main ones show low hexakisoctahedron forms, the set on one side being hollow, that on the other domed. An important feature (see *d*—arrow) is the penetration of an octahedral formation into the hexakisoctahedral. The striations on the latter are much finer than those on the octahedron.

In polarized light there is general isotropy with no sign of cross hatching.

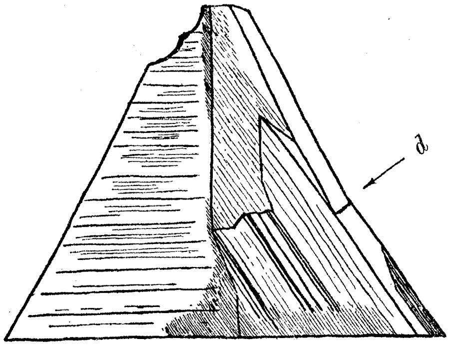


Fig. 3.

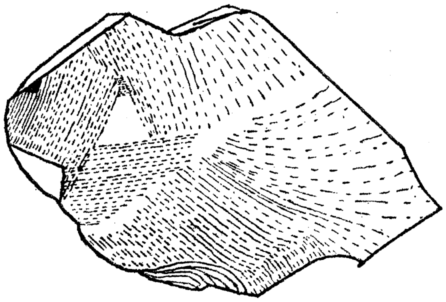


Fig. 4.

D 24. Fig. 25, Plate 11.—This specimen is flat, triangular and bounded entirely by cleavages. The upper flat face is a cleavage showing very fine, nearly parallel cleavage steppings; the lower face has one very deep cleavage step and on the two treads of the step a finer cleavage stepping appears, this being similar to that on the top face. The edges also show similar cleavage steppings.

The above five diamonds are of Type 2.

D 20. Fig. 26, Plate 11.—This is a natural crystal flattened on two parallel octahedral faces. The surface is remarkable in having a parallel fibroid appearance. The "fibres" are parallel to the other emerging octahedral planes.

In polarized light, dark with brilliant anisotropy on the emerging quasi-fibres.

D 21. Fig. 27, Plate 11.—One natural octahedron face, deeply indented, with irregular hexakisoctahedron faces. This face shows etching figures on the octahedron steps. The other face is a cleavage with stepping resulting from imperfect cleavage fracture. It has no regular parallel striation. There is no dominant lamination parallel to one octahedral face as is shown by the saw-like edges of the main cleavage steps.

In polarized light, anisotropic, with broad isotropic patches.

D 23. Fig. 4.—On one natural octahedral face there are granulations oriented parallel to the other three octahedral directions. The other face is also natural, built up of coarsely stepped domes irregularly placed (these are oscillations between octahedron and hexakisoctahedron). The structure indicates that no particular octahedral plane is dominant.

In polarized light, honeycombed appearance with much anisotropy in centres of granules.

Conclusions from the crystallographic peculiarities of diamonds of Types 1 and 2 :—

Diamonds of Type 1 are crystals with nearly perfect faces (octahedra or flattened octahedra or twinned octahedra—spinel twins) or faces with coarse oscillation steps, *i.e.*, oscillation forms between the octahedron and the triakisoctahedron or hexakisoctahedron.

In these no obvious stratification or layering is seen except in the last type, where there are oscillation flutings (*e.g.*, D 20) ; but such flutings are coarse.

The diamonds of Type 2 show a finer fluting parallel to the octahedron faces.

The selection of specimens was made first to secure flat faces of the octahedron, but very few showed anything but opacity in infra-red and ultra-violet and low photoconductivity. When the basis of selection was altered to secure crystals with *fine* oscillation flutings or *fine* striæ on cleavage faces the proportion of diamonds of Type 2 at once rose.

It therefore appears important to secure crystals with a definite fine structure parallel to the octahedral face. That direction in cubic minerals is a common direction of cleavage, parting, twinning and glide planes, *cf.*, diamond, fluor-spar, magnetite, spinel, etc., and it is not incompatible with macroscopic crystallographic features that there might be some want of alignment (superposition) of twin or glide laminæ or laminæ of parting. Evidently such coarse laminæ do not produce the effects of Type 2 but there is no *a priori* reason against the occurrence of a lamellar structure finer than either of these, though not so fine as would be included between two molecular or cleavage planes. Indeed, the results seem to point to some such " staggering " of thin lamellar growths.

This appears to be perfectly in line with the conclusions arrived at by WILLIAMS, who says (*op. cit.*, vol. 2, page 462) that " A very careful study has been made of diamonds showing this phenomenon (glide planes) and all evidence definitely points to the fact that the striæ have been produced by stress only," and he points to one of his photomicrographs (Plate 166) where the growth projections on the face of the octahedron have been actually shifted on a plane parallel to the octahedral face.

Spacing of Laminæ.

Attempts have been made in two ways to evaluate the distance of the laminæ from one another.

Thus, by focussing neighbouring planes of the laminæ emerging as steps on the " staircase " of D 2 (see fig. 1) with a microscope fitted with a fine micrometer screw.

varying thicknesses were found of about 10 μ, but there was evidence that the spacing between many of the laminæ was about 1 μ.

Again, the striations which represent steppings were photographed along with a fiduciary scale divided into fractions of a millimeter for comparison. In this way it is possible that the finer laminations were not detected. The results varied from 16 to 17 μ for D 19; from 18 to 25 μ for D 22; and from 25 to 40 μ for D 24. The columnar fibres of D 20 were about 50 μ in thickness.

OPTICAL ISOTROPY.

Brewster, in 1815, recognized birefringence in diamond and recently Friedel* has examined over 200 diamonds of diverse origin and has found a feeble birefringence in all, irrespective of source. Birefringence is also mentioned by Crookes (*loc. cit.*) as a feature he has commonly met with in diamonds.

When diamonds are examined between crossed nicols, Friedel states that the observed black isotropic bands which are displaced when the nicol is turned, sweep over part of the surface, pivoting themselves round certain points and that they are not linked up with the cubic symmetry of the crystal. Experimenting with heated plates of rocksalt and of glass, he obtained effects in the polarizing microscope similar to those which he saw in diamond. From this he concluded that diamond, originally cubic and isotropic, on setting from a plastic state acquired a permanent deformation inducing a small birefringence. In a paper with Ribaut† the effects of heating crystals to high temperature are described. Up to a temperature of 1,885° C. the birefringence is unaltered, but thereafter undergoes a profound change in its distribution. At this temperature transformation into graphite becomes very rapid.

It is to be noted that the kind of irregular birefringence described by Friedel is that which Crookes observed (*loc. cit.*) and which we have found in all our diamonds of Type 1; diamonds of Type 2 we find much more nearly isotropic, some being quite dark when examined between crossed nicols.

In the section dealing with the morphology of the diamond and in Table 1 the effects observed between crossed nicols are noted for the various specimens.

The main distinction is optical anisotropy of the kind observed by Friedel for diamonds of Type 1, while those of Type 2 are mainly isotropic.

A peculiar feature is exhibited in some of the diamonds of Type 2 and notably in D 2, and this is exemplified in fig. 28, Plate 11. In this the general darkness between the crossed nicols is traversed by fine bright lines intersecting at about 60° to the octahedral edge, producing a cross-hatched pattern. It has been brought to our notice by Dr. H. H. Thomas, F.R.S., that leucite behaves similarly, and that the appearance is consistent with the crystal being made up of agglomerates of sphenoids in juxtaposition

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* 'Bull. Soc. Fran. Mineral,' vol. 47, p. 60 (1924); and 'Z. Kristallog.,' vol. 83, p. 42 (1932).

† 'Bull. Soc. Fran. Mineral,' vol. 47, p. 94 (1924).

so arranged that packing is perfect. This would be in accordance with the impression of the mosaic character of this crystal which even visual inspection of this diamond indicates.

The subject of the mosaic character of crystals has recently assumed importance in various directions. SMEKAL[*] has divided the properties of crystals into "structure-sensitive" and "structure-insensitive," and in this paper says that "the alterability of structure-sensitive properties is linked with the possibility that the number and quality of a small proportion of loose building elements alter without at the same time markedly influencing the majority of the lattice elements." SMEKAL considers ions on the internal "surface" of a crystal or edge of discontinuity in its structure to be more loosely held and much freer to move in the crystal than the "lattice" ion type by which is meant an ion in a part of the crystal where it is surrounded by a perfect lattice. These surface ions are similar to the "edge" ions of BLÜH and JOST.[†] This idea was followed by ZWICKY,[‡] who considers that superimposed on the primary structure of crystals as deduced from X-ray analysis there is a secondary structure, leading to the conception of a mosaic condition, and he gives instances of phenomena attributable to such a condition. Examples of phenomena explainable by the hypothesis of this mosaic structure are now frequent. Thus, TOY and HENDERSON[§] find these ideas in agreement with their experiments on the photo-conductivity of silver halides, and MILES[||] gives as an explanation of the spontaneous detonation of crystalline explosives, distortions of the crystal structure, since at such places the energy of the structure will be higher than normal and thus require there a smaller increment of external energy to bring about detonation. For the quieter phase of gas evolution of mercury fulminate, GARNER and HAILES[¶] have evolved the explanation that thermal decomposition begins in the Smekal cracks of the crystal and then spreads to crystallites isolated by the destruction of the cementing material.

If these general conceptions of SMEKAL and ZWICKY are applied to diamonds of Type 2, it is to be noted that all of these that have so far come our way are formed of parallel plates. In some, *e.g.*, D 2, D 19, the development of a mosaic by planes parallel to the 111 face is noticeable even to the eye. It is thus considered that in diamonds of this type we have the conditions of "structure-sensitivity," such as contiguous portions of one layer lacking lattice conformity with its neighbour, either through want of register or by very minute gaps. As the layers are probably not more than 1 μ in thickness there is sufficient substance to give a normal X-ray diagram, although even here, as ZWICKY predicted (*loc. cit.*, p. 820), with soft X-rays there is an indication of a difference from the monolithic character of Type 1 (see next section).

[*] 'Z. Physik,' vol. 55, p. 289 (1929).

[†] 'Z. phys. Chem.,' B, vol. 1, p. 270 (1928).

[‡] 'Proc. Nat. Acad. Sci. Wash.,' vol. 15, p. 816 (1929).

[§] 'Proc. Roy. Soc.,' A, vol. 127, p. 614 (1930).

[||] 'J. Chem. Soc.,' p. 2539 (1931).

[¶] 'Proc. Roy. Soc.,' A, vol. 139, p. 576 (1933).

X-RAY EXAMINATION OF DIAMOND.

By Mr. Bernard Robinson, *Davy-Faraday Laboratory.*

Through the kindness of Sir William Bragg, O.M., F.R.S., Director of the Davy-Faraday Laboratory of the Royal Institution, an X-ray examination of a number of our diamonds has been made.

The results are as follows :—

Table II.—X-ray results.

Diamond.		Ratio $\frac{111}{222}$ (intensity).
Type 1.	Type 2.	
(This is the more opaque type.)	(Transparent type, *i.e.*, no I.R. band at 8 μ and transparent in U.V. to λ 2250, whereas Type 1 goes out only to λ 3000.)	
D 1		13·5
D 9		34
D 10		12
D 21		46
D 23		87 (bright side) — (dull)
D 25		10·5
	D 2	41
	D 16	301
	D 19	100–500
	D 22	120
	D 24	78

Owing to the irregular surfaces of the specimens and the method of examination used, large variations in the ratio $\frac{111}{222}$ might be expected to occur over the surface ; only a complete survey in a much more detailed manner would give a truly representative value.

Generally, it can be said that the X-ray pattern is the same for both types, but a difference was observed in the ratio of the intensity given by reflection from the 111 plane to that from the 222 plane, those of Type 2 being generally higher—a greater indication of mosaic structure.

ELECTRON DIFFRACTION.

By Professor G. P. Thomson, *F.R.S.*

Two diamonds, D 1 and D 2, were examined by electron diffraction, using reflection from an octahedral face, the apparatus and method being the same as previously used for rocksalt.* Brilliant spots and lines (" Kikuchi " lines, *loc. cit.*) appeared on the fluorescent screen. Measurements made on the spots formed by reflection from the exposed face, showed that reflections of the 2nd, 3rd, 4th and 5th orders were present. The first order could not be observed, owing to a real or effective inner potential of the crystal of the order of 20 volts. Of the orders visible, the " forbidden " second order was not markedly weaker than the others. No striking difference in this respect was observed between the two diamonds, but it should be mentioned that no quantitative measurements were made, and that the diamonds were observed on different days, so that the comparison is very rough.

It was noticeable that each spot was visible over a wide range as the angle of the crystal was altered. Indeed, under the best conditions the spot never vanished but merely passed through maxima of intensity at the positions corresponding to the various orders. This implies a surprisingly small penetration of the electrons, which must be caused by a process analogous to the " extinction " of X-rays. Here also there was no marked difference between the two specimens, but it is hoped to investigate the point further. Photographs showed a fine array of Kikuchi lines.

REFRACTIVE INDEX.

In his paper on the refractive index of diamond, PETER (*loc. cit.*) describes his choice of the more rarely occurring type of diamond transparent beyond λ 3000, which for his experiments he worked into a prism. With this diamond prism he obtained values for refractive index as far into the ultra-violet as λ 2265. He tabulates his results as well as those of previous workers who had crystals for which, however, they reported values in no case beyond λ 3130. A comparison shows that the values of other workers, who evidently had diamonds of the opaque type, and his with a transparent crystal are identical in the region ($\lambda > 3130$) which they have in common.

This similarity in refractive index for the two types of diamond we have confirmed for D 1 and D 2 (see Table I).

DIELECTRIC CONSTANT.

Of those physical properties of diamonds which might disclose further differences between the two types of diamond the dielectric constant seemed to be a promising field of inquiry. The results on record are widely divergent. SCHMIDT gives 5·5,† COEHN and RAYDT 5·18 to 8·0,‡ and PIRANI 16·5.§ The value of SCHMIDT would correspond to a refractive index about 2·35 for λ_∞, and is not far from the value calculated by PETER for n^2 ($n = 2\cdot38$), namely, 5·67.

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* THOMSON, ' Proc. Roy. Soc.,' A, vol. 133, p. 1 (1931).

† ' Ann. Physik,' vol. 11, p. 114 (1903).

‡ ' Ann. Physik,' vol. 30, p. 777 (1909).

§ " Ueber Dielektricitätsconstanten fester Körper," Berlin (1903).

As it is not known which type of diamond was used in the foregoing determinations, and the results are far too variable, fresh determinations were carried out by a method specially devised to deal with small quantities of solids. This consists of measuring the small change in capacity (about 1 μμ F) at radio frequencies of a small air condenser when the diamond is placed in the condenser. Variations in the capacity of the small condenser are compensated by means of a large standard variable condenser placed in series with a small condenser, the condenser containing the diamond being in parallel with these two. By this method, and on applying a correction for the irregular shape of the diamond, results may be obtained on single diamonds which are accurate to a few per cent. of the value of the dielectric constant.

The result for diamond No. 1 was 5·01 and for No. 2 4·88, and the difference in these values is within the experimental errors inherent in the method, which had to be used because of the small size of the specimens available. It was ascertained that the ratio of the capacity of the condenser containing diamond to that containing accurately cut glass models made from the same piece of optical quality glass was 0·789 for diamond No. 1 and 0·813 for diamond No. 2, clearly showing that the dielectric constant is the same. We have not, therefore, found any difference in the dielectric constant of the two types of diamond.

FLUORESCENCE AND TRIBOLUMINESCENCE.

While it is a common property of diamonds, especially of those which contain obvious impurities, to fluoresce in ultra-violet light, few of those examined in this paper gave this effect. One exception is D 22, which fluoresced and phosphoresced under light of λ 2300, but not with longer wave-lengths. Another is D 20, which has a bright blue fluorescence, followed by a yellow phosphorescence.

Some experiments were made on the production of light by rubbing. The diamonds were held against a rag-mop polisher rotating fairly fast, and with all a bluish glow was obtained during the friction, but it ceased on withdrawing the stone.

There was no discrimination between diamonds of the two types.

SPECIFIC GRAVITY AT 15°/15° C.

Apparatus and procedure.—For this determination the diamonds were weighed in air and then in water, a small silica tray being used for holding each diamond while it was being weighed in water. The silica tray was suspended from one arm of a balance by means of a fine thread of fused silica, about 0·1 mm. thick.

From the data thus obtained and the known expansion of water, the specific gravity at 15°/15° C. was calculated.

Results.—These are recorded in Table I and lie for the most part between 3·51 and 3·52: no distinction is traceable between diamonds of Types 1 and 2. The values given in the literature for clear diamonds vary to a greater extent than this. Thus

Mellor* gives a range of values from 3·336 to 3·5585, quoting a mean of values of **Baumhauer** and **Wülfing** as 3·520 ± 0·02 at 4° C. which is equivalent to 3·523 ± 0·02 at 15°/15° C.

INFRA-RED SPECTROSCOPY OF DIAMOND.

Introductory.

By calculation from constants of diamond other than those deduced from the result of actual imposition of radiation, it has been shown that its constituent atoms are vibrating : thus a natural frequency of about 13 μ was deduced by **Einstein** from its compressibility ; of 9·2 μ by **Lindemann** from melting point ; of 7·5 μ by **Nernst** and **Lindemann** from specific heat ; 7·7 μ as an upper limit by **Debye**, from specific heat ; and a like figure by **Schroedinger**, following **Debye** and **Grüneisen**. Diamond might therefore be expected to exhibit one frequency in the neighbourhood of 7 to 8 μ.

Direct observations on the absorption spectrum of diamond in the infra-red region were made as early as 1892 by **Ångström** (*loc. cit.*) and by **Julius** (*loc. cit.*) in 1893, and these pointed to the presence of a band system which now would be associated with movement of the electric moment in the substance. **Julius** using a rather thick stone (4·25 mm.) obtained bands at about 3, 5·15, and 8 μ, but missed a band at 4·1 μ. **Ångström's** bands were similar to those of **Julius**, but through an optical imperfection appeared as if shifted somewhat towards the visible region.

The next investigation was made in 1911 by **Reinkober** (*loc. cit.*), who obtained absorption bands at 3, 4·1 and 4·8 μ, but was puzzled as he failed to get the band at 8 μ indicated but left incomplete by **Julius**. He reported an absorption band of small intensity at 14·1 μ.

Reinkober also investigated the reflection of diamond in the infra-red, using a large worked stone with a face of 18·5 mm. long, but reports no break in the curve of reflection from 1 μ up to 18 μ. In this we agree with **Reinkober**.

As the literature contained no other references to the behaviour of diamond in the infra-red than the somewhat conflicting data just quoted, it was thought to be of interest to investigate its absorption and reflection spectra in this region of the spectrum, with the object of throwing more light on the band structure, and if possible getting some interpretation of it.

This investigation led us further afield as it became clear that correlation with work in other regions of the spectrum and the determination of other optical and physical properties were necessary, and such a quest was imposed on us when we encountered diamonds whose spectrum in the infra-red differed by presence or absence of a band at 8 μ. Having confirmed (see p. 484) that the absence of this band in certain diamonds was real, we next found that in the same diamonds absorption in the infra-red at this frequency was associated with absorption in the ultra-violet (see next section), and

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* Op. cit., vol. 5, p. 760.

similarly the type more transparent in the infra-red transmitted much farther into the ultra-violet than did the more opaque type. REINKOBER's difficulty in accepting the 8 μ absorption band of JULIUS is thus explained : he had a diamond of the more transparent type, while those of JULIUS and ÅNGSTRÖM clearly belonged to the other and more usual variety.

ARRANGEMENT OF INFRA-RED APPARATUS.

Generally the apparatus was similar to that described to this Society,* at least so far as the spectrometer, source of radiation and general arrangements are concerned. Some alterations have been made, however, and will be briefly noticed as being possibly of general application. These refer to a change in the galvanometric system, an improved method of changing slit-width and a rocking mount devised for holding solids at ordinary temperature and down to that of liquid oxygen.

Galvanometer System.

The system of detecting the energy received on the thermopile by deflection of a galvanometer of the Paschen type used in our previous work had to be abandoned on account of magnetic disturbances over which we had no control. We therefore resorted to a primary galvanometer of the moving coil type adequately shielded from such influences, and magnified the indications of this instrument by a relay, followed by another galvanometer. The beam reflected from the mirror of the primary galvanometer was concentrated on the relay of MOLL and BURGER,† and the same sensitiveness as we had hitherto obtained with the Paschen galvanometer (about 7×10^{-11} amp. per mm. of scale at $1\frac{1}{2}$ metres) was secured by the train : thermopile → Moll moving coil galvanometer → Moll relay → Tinsley galvanometer (10^{-8} amp. per mm. at 1 metre). This procedure had the advantage of steadiness of reading so that even during daytime the spot on the scale oscillated only a few tenths of a millimetre.

Alternatively, we have employed satisfactorily the system Zernicke galvanometer (type Zc., sensitivity 10^{-9} amp./mm.) → differential cuprous oxide cell → Cambridge galvanometer (A.M. standard pattern). A beam of light from an automobile lamp (6 v. and 4 amp.), run from large capacity accumulators, was reflected from the mirror of the Zernicke galvanometer and caused to form an enlarged image of the filament on the cuprous oxide cell of the type described by HILL.‡ When the image equally illuminated the two halves of the cell no e.m.f. was produced and the galvanometer of low sensitivity connected to the cuprous oxide cell registered no deflection ; but if the mirror of the primary galvanometer moved, the image moved likewise across the cell and a current passed through the second galvanometer. It was demonstrated that, under

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* ROBERTSON and FOX, 'Proc. Roy. Soc.,' A, vol. 120, p. 128 (1928).

† 'Phil. Mag.,' vol. 50, pp. 618, 624 and 626 (1925).

‡ 'J. Sci. Instr.,' vol. 8, p. 262 (1931).

our conditions of working, the deflection of the second galvanometer was proportional to the primary current. A sensitivity of 5×10^{-11} amp./mm. was easily maintained.

Slit changing.

In order to protect the thermopile in its air-tight box from draughts, a wooden casing was placed round it (*loc. cit.* page 144), enclosing also the back-slit of the instrument, the casing being stuffed with coarse black worsted. This had the disadvantage that the casing had to be opened when it was desired to alter the setting of the symmetrical slit, thus causing a delay of perhaps half an hour while the thermopile came into equilibrium with its environment. By fitting a toothed wheel over the milled ring which operated the slit, and causing a smaller toothed wheel to engage with that attached to the ring, it was possible to rotate the ring by means of a spindle passing through the box and attached to the centre of the smaller toothed wheel and so to open or close the slit. This spindle passed outside the casing, where it was furnished with an ebonite recording drum calibrated to accord with the markings indicating aperture of slits on the ring. Slits could thus be opened or closed without interrupting a run of readings, with a considerable gain in time and convenience.

Rocking device.

As it was preferred to make observations in which the reading on the galvanometer indicating the energy passing through the diamond was followed at once by a blank reading with no diamond in the train, a rocking holder was devised and is shown in fig. 5. This was arranged so as to bring into optical alignment alternately the apertures in the disk A, the one being for the diamond and the other being adjusted, as to its size, so that the quantity of energy transmitted was comparable with that passed by the diamond in a region where the diamond was found to be transparent. A rocksalt lens was used to focus the radiation from the Nernst filament through one or other of the apertures of the rocker on to the slit of the spectrometer.

The spindle B carrying the disk was mounted in ball races in the brass tube C. An ebonite collar D was screwed on to the spindle and carried the brass rod E, fitted with a small terminal and insulated from the rest of the mount. The disk A was arranged so that it could oscillate between two positions fixed by the stop and two adjustable brass plates F, screwed to the brass tube C. This was done by means of the strings attached to the

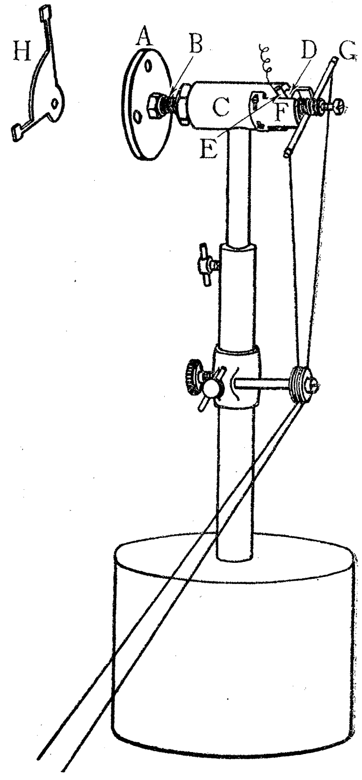

Fig. 5.—Rocking device.

lever-arm G. When either of the plates F was touched by the stop E an electrical circuit was made which caused the wave-length drum of the spectrometer to be illuminated, thus indicating to the operator moving the drum (*loc. cit.* page 142) that the disk was in one of its two correct positions.

Disk A was replaced by H, upon which diamonds were mounted, for measurements of reflection.

Dewar vessel and rocking device for use at low temperatures.

For the examination of absorption spectra at the temperature of liquid oxygen, the modified Dewar vessel of fig. 6 was constructed. To the inner tube of soda glass was

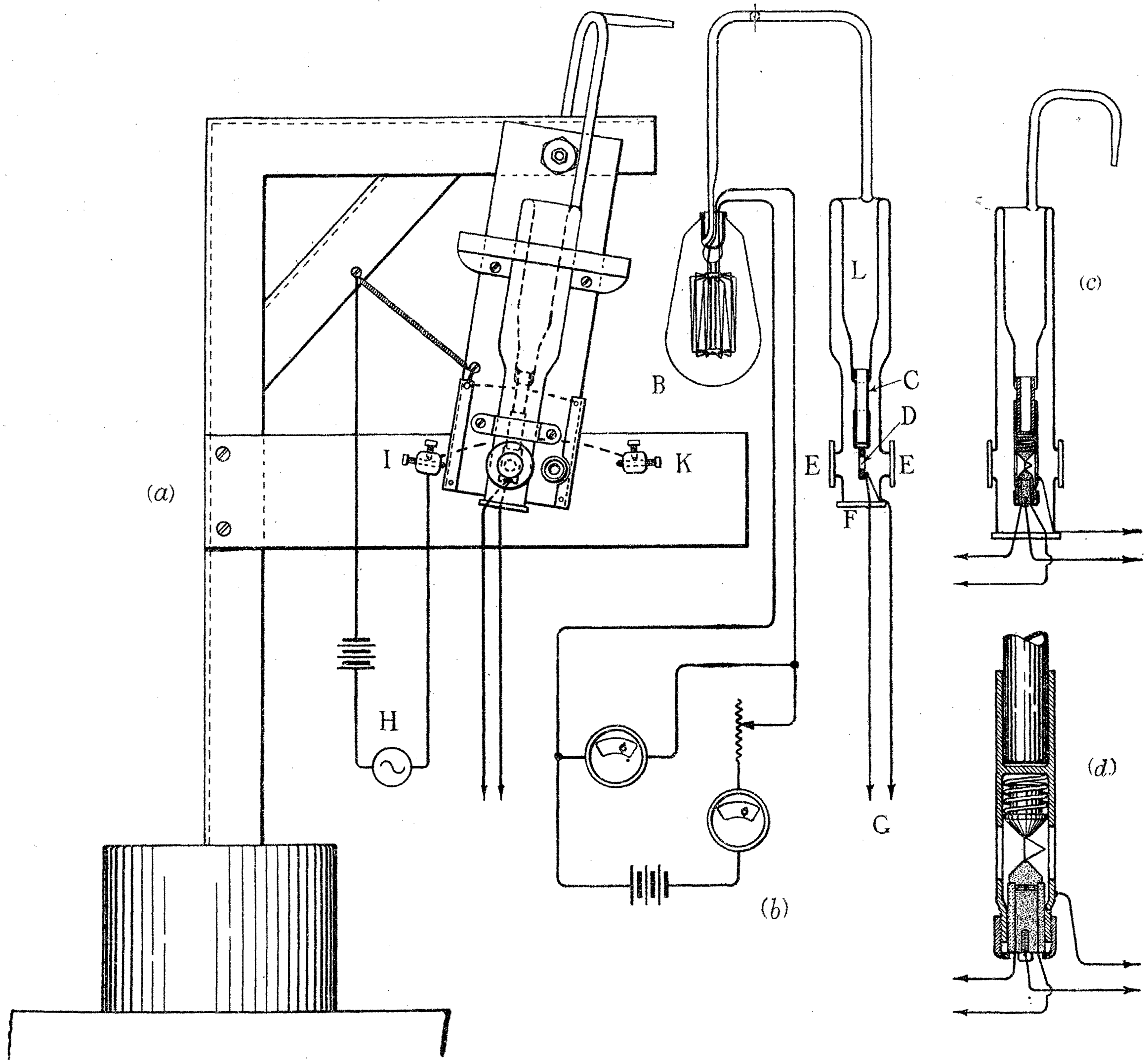

Fig. 6.—Rocking device and Dewar vessel for use at low temperatures. (*a*) Rocking frame for Dewar vessel containing diamond. (*b*) Detail of Dewar vessel containing copper sheath and diamond with thermo-couple attached, Pirani gauge and meters for measuring pressure.

(*c*) Dewar vessel for determining photo-conductivity of diamond at low temperatures, with leads for measurement of temperature and also current produced on illumination. (*d*) Detail of (*c*) showing method of cooling, arrangement of electrodes and leads. (*c* and *d*, see p. 500.)

sealed a copper tube C closed at its lower end. Two short glass side tubes had their ends ground flat and parallel for the attachment of plates of rocksalt or quartz E through which the radiation from the source passed. The diamond D could be inserted through the aperture at the bottom of the vessel, so that it fell into the optical train. In order to cool the diamond liquid oxygen was contained in the inner glass tube L and copper tube of the Dewar vessel, while the periphery of the diamond was coated with Wood's metal, leaving the centre free for radiation to pass through. The Wood's metal was soldered to a small copper sheath that was slipped over the copper tube C. A calibrated thermo-junction was attached to the Wood's metal and its leads G carried through the cement by which the plate F closing the aperture was attached, and brought to a millivoltmeter.

In all experiments the Dewar vessel was exhausted by a mercury diffusion pump, backed by a " Hyvac." For work in the infra-red where rocksalt windows were used, a Pirani gauge B was left sealed in the circuit to indicate the condition of the vacuum. So long as the vacuum held, no trouble was found from deposition of moisture on the rocksalt.

For determining the infra-red absorption spectra, this Dewar vessel was mounted in the rocking frame shown in fig. 6 (*a*), so that the diamond could be swung in and out of the optical path with accurate return to its true position. An electrical circuit H was fitted to cause a glow-lamp to light when the rocker made contact with the stops I and K. The view of the Dewar vessel in fig. 6 (*b*), is at right angles to that in (*a*).

When it was unnecessary to use the rocker, as for ultra-violet absorption, the Dewar vessel was continuously evacuated.

PROCEDURE.

Alternate readings of the galvanometer were taken and from the difference in the scale readings with and without the diamond in position, the percentage absorption was calculated. This was plotted as ordinate with wave-numbers (cm.$^{-1}$) as abscissæ, the latter being corrected for calibration of the wave-length drum and for temperature of the prism in the spectrometer (*loc. cit.* page 149); no correction was made for loss of radiation by reflection.

RESULTS AND GENERAL CHARACTER OF THE ABSORPTION BANDS.

In fig. 7 the band system of diamond as we have determined it is mapped so as to show percentage absorption against wave-numbers in one cm. In addition wave-lengths in μ ($1\ \mu = 0 \cdot 001$ mm.) are indicated along the top of the figure.

It will be seen that there are three distinct regions of absorption in diamonds of Type 1 and two in diamonds of Type 2. These regions have been distinguished by the letters A, B and C starting from the region nearest to visible, and the finer structure of each region by small Greek numerals.

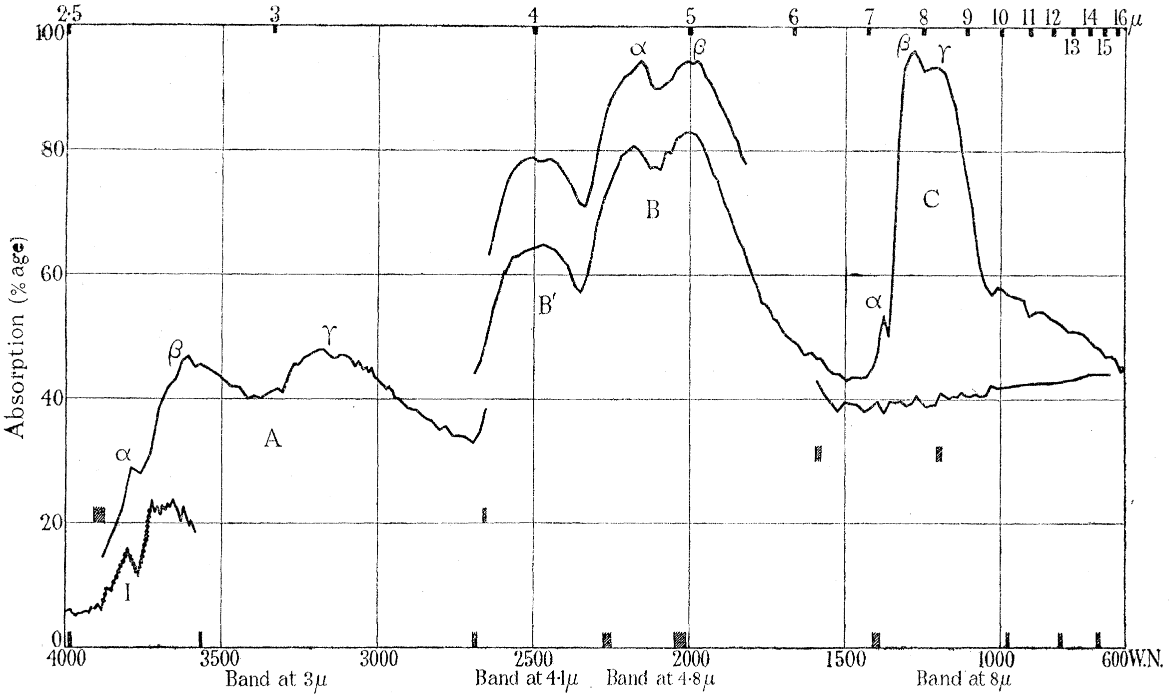

FIG. 7.—Infra-red spectrum of diamond.

Throughout the spectrum no difference was detected in the structure of the bands given by the two types of diamonds with the exception of the lack of a band in diamonds of Type 2 at 8 μ. A direct comparison was made with diamonds No. 10 (of Type 1) and No. 2 (of Type 2) over the summit of the band at 4·8 μ, using small progressions of wave-length. It will be seen from the figure that when allowance is made for the somewhat greater thickness of No. 2, the bands are identical in contour and in position in the spectrum.

An attempt was made to photograph absorption in the near infra-red by the aid of ammonia sensitized neocyanine and dicyanine plates, also Ilford infra-red sensitive and Ilford hypersensitive panchromatic plates, and also by the use of a sector photometer, but no evidence of absorption bands was obtained. Nor was any band observed by the prism spectrometer before 2·5 μ.

Positions of the absorption bands.

TABLE III.—Values of wave-lengths (and wave numbers). Positions of Infra-red Bands of Diamond.

Band.			cm^{-1}.	μ.	Extreme values.
3 μ	Aα	Both types	3790	2·64	—
	Aβ	,, ,,	3600	2·77	—
	(dip)	,, ,,	3400	2·94	—
	Aγ	,, ,,	3160	3·16	—

TABLE III—*continued.*

Band.			cm^{-1}.	μ.	Extreme values.
4·1 μ (B^1)		mean of 8	2481	4·03	2462–2491
	Type 1	. . . . .	2481	4·03	2462–2487
	„ 2	. . . . .	2482	4·03	2474–2491
4·8 μ (Bα)		mean of 6	2176	4·59	2167–2187
	Type 1	. . . . .	2175	4·60	2167–2187
	„ 2	. . . . .	2179	4·59	—
	(dip)	mean of 6	2095	4·77	2080–2104
	Type 1	. . . . .	2092	4·78	2080–2106
	„ 2	. . . . .	2104	4·75	—
	(Bβ)	mean of 6	2007	4·98	1992–2015
	Type 1	. . . . .	2005	4·99	1992–2015
	„ 2	. . . . .	2010	4·97	—
8 μ	Cα	mean of 7	1372	7·29	1365–1387
	Cβ	mean of 8	1289	7·76	1283–1297
	C dip	mean of 9	1247	8·02	1239–1252
	Cγ	mean of 5	1208	8·30	1196–1216
8 μ	Type 2	Wanting	—	—	—

Bands about 3 μ.

Great difficulties have been experienced in obtaining the correct contour of this band or group of bands. Rocksalt has a poor dispersion in this region, which also contains the sharp absorption band of quartz at 2·95 μ. The fluorite prism gave the best results and the small branch A α at 2·64 μ, indicated with the fluorite prism, was clearly defined when the quartz prism was used (see lower curve I in fig. 7).

The band covers the somewhat large range of about 1000 $cm.^{-1}$, and considered as one band has a distinct dip at 3400 $cm.^{-1}$, with peaks at 3790, 3600 and 3160 $cm.^{-1}$.

The intensity of this band is less than that of the others, being about 40–50%, while they approach 90% absorption.

Bands from 4 *to* 4·8 μ.

If this be one band it is somewhat large, extending over about 800 $cm.^{-1}$ The branch on the side nearer the visible B^1 is most likely a separate band partially fused with the main band; its breadth, comparable with the top of the double peak B α to B β, and its distance from the nearest apex of that peak (305 $cm.^{-1}$) seem to remove it from being considered the R-like branch of the band as a whole, especially as the distance between the doublet peaks B α and B β, is only 169 $cm.^{-1}$

Region 6 *to* 7·5 μ.

In diamonds of Type 1, no band is revealed until there appears that definite but small one C α at 7·29 (1372 $cm.^{-1}$), which will be considered in relation to the larger band Cβ — Cγ.

In diamonds of Type 2, no definite bands, even of small intensity, were discovered from 6 μ out as far as 17 μ.

Absence of absorption band at 8 μ *in some diamonds.*

Before describing the characteristics of the band at 8 μ found in diamonds of Type 1, an account may be given of the experiments performed to satisfy ourselves both that this band was really lacking in diamonds of Type 2, and that diamonds of Type 1 did not, under varying conditions of radiation, lose their property of absorption in this region. When the band is present it is one of considerable intensity, absorptions of about 90% being obtained with more than 20 diamonds.

Various modifications in technique were introduced to eliminate the chance that the transparency might be due to some effect, instrumental or other. These experiments were performed on diamonds Nos. 2 and 16 of Type 2, but mostly on the former, and were as follows :—

With a rocksalt prism in the spectrometer, direct radiation from the Nernst filament passed through the diamond—

(1) entering normal to the top face ;
(2) as above, but diamond swung through 90° in the same plane ;
(3) entering normal to the bottom face ;
(4) as above, diamond rotated as in (2) ;
(5) entering bottom face tilted to normal incidence ;
(6) as above, but tilted at right angles to setting of (5) ;
(7) entering normally a face flooded with ultra-violet light from mercury arc ;
(8) entering normally, the diamond being at a temperature of — 170° C.

Radiation from Nernst polarized by reflection—

(9) plane of polarization bisecting triangular top face of diamond ;
(10) plane of polarization parallel to a triangular face.

Monochromatic radiation, obtained from prism spectrometer—

(11) passed normally through the faces.

A fluorite prism substituted for the rocksalt prism used in the spectrometer in the above experiments led to no change in the result.

With none of these variants did an absorption band at 8 μ appear.

On the other hand, the 8 μ band was found in the majority of diamonds, and it persisted under conditions such as those that follow :—

When radiation was passed down each of the four trigonal axes, in turn, of the large perfect octahedra, D 17 and D 18 ;

When in D 17 and D 18 the radiation was passed along any arbitrary path ;

In the thin octahedra or slices, radiation being normal or oblique ;

When a transparent diamond such as D 2 was interposed between the source of radiation and an opaque diamond (D 1);

Flooding the diamond with ultra-violet light from a mercury arc had no effect on the band;

Cooling to — 170° C. had no effect on the band, nor on any of its branches.

We were therefore satisfied that the absence of a band at 8 μ in certain diamonds was real and not due to some instrumental condition or method of setting in the path of the radiation. It was not related to the absence of polarization nor to mixed frequencies in the incident light. Further, various physical conditions led to no disappearance or production of a band.

As it was not found possible to pass sufficient radiation through the edges of transparent diamonds parallel to their faces, to be registered in the infra-red apparatus, transparency was confirmed by the length of the spectrum in the ultra-violet region and in the experiments on the Raman effect (see p. 492).

Several more diamonds transparent at 8 μ were discovered, and when these were found to be also transparent in the ultra-violet far beyond the rest (see p. 491), the reality of the two types was established.

Region about 8 μ.

The band at 8 μ found in diamonds of Type 1 is a well-marked band reaching an intensity of absorption of 85 to 90%. It has three peaks, varying considerably in intensity ($C\alpha$, $C\beta$ and $C\gamma$). Of these the first is small, but can be found in diamonds of varying thicknesses, while the intensity of the last decreases relatively to the central branch as thinner specimens of diamond are examined. An indefinite region of general absorption is frequently found beyond $C\gamma$.

This band has the appearance of being distorted, but has branches which for a gas would be designated P, Q and R branches, the R branch ($C\alpha$) being definite but small; the wave-number difference between the peaks is constant. Thus:

$$C\alpha - C\beta = 1372 - 1289 = 83 \text{ cm.}^{-1}; \text{ and } C\beta - C\gamma = 1289 - 1208 = 81 \text{ cm.}^{-1}$$

In the same region no absorption band is found with diamonds of Type 2, but an indefinite region of general absorption may occur, especially in the thicker specimens. No bands around 8 μ, even of a feeble character were found, although searched for, and it is considered that the small perturbations of 3% of absorption or less shown on the curve of REINKOBER (*loc. cit.*) are due to experimental conditions. BHAGAVANTAM* depends on these to bring out a relation between them and certain Raman lines, but this is thought to be unjustified (see p. 519).

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* 'Ind. J. Phys.,' vol. 5, p. 578 (1930).

Extinction coefficient.

As the refractive indices of diamond are unknown in the infra-red, it was not possible to make more than an approximate calculation of the extinction coefficient. Such a calculation gave values for diamonds of Type 1 which showed no significant differences among themselves ; nor did they differ from the values for the same bands in diamonds of Type 2, with the exception, of course, of the region of the absorption at 8 μ.

Region 10 *to* 17 μ.

A special search was made in this region in several diamonds of both Types for the presence of a small band of about 7% intensity, reported by REINKOBER, but no band could be discovered in any diamond examined.

Finer structure of infra-red absorption bands in diamond.

It would have been useful for the allocation of bands to the atomic motions they represent if the band at 4·1 μ situated on the side of the band, which has its centre at 4·8 μ could have been resolved. In spite of many attempts with diamonds of various thicknesses, and with a grating kindly put at our disposal by Professor DONNAN, no definite fine structure of this band emerged.

Definite instances of structure are found in the double peak of the 4·8 μ band, of which the wave number difference is 169 cm.$^{-1}$, while (for the diamonds of Type 1) the band at 8 μ, considered as a triplet, has 83 and 81 cm.$^{-1}$ differences respectively between the peaks. It will be observed that the latter difference is half of that belonging to the band nearer the visible.

INFRA-RED ABSORPTION OF DIAMOND AT LOW TEMPERATURES.

By means of the apparatus of fig. 6 (*a*) and (*b*) diamonds of both types cooled to the temperature of liquid oxygen were examined for their absorption, according to the procedure sketched on p. 480, throughout the spectrum up to 17 μ.

As a result, no change in the position of an absorption band, or in the percentage absorption of the bands could be detected, special attention being given to a diamond of Type 2 (D 2) which still gave no absorption band at 8 μ.

In order to make a direct comparison between the absorption at ordinary and at low temperature at a definite position in a band, the spectrometer was set at positions where a notable absorption was known to occur, whereupon measurements of absorption were made on diamonds at the ordinary temperature, followed in a few minutes by observations when the thermocouple indicated that they had been cooled by liquid oxygen introduced into the Dewar vessel.

The results of these experiments are given in Table IV.

TABLE IV.—Effect of cooling diamonds on absorption in infra-red.

Diamond.	Prism in spectrometer.	Wave-length.	Temperature.	Absorption, %.
D 2	Rocksalt	5 μ	21° C.	90·3 90·3
			Liquid oxygen	90·5 90·2
D 10	Fluorite	7·776 μ	18° C.	82·4 82·2
			Liquid oxygen	85·9 86·8
			Liquid oxygen	83·8 84·9
D 10	Fluorite	7·776 μ	19·5° C.	82·5 81·7
			Liquid oxygen (immediate) . .	85·5 85·5 85·0
			Liquid oxygen, after further 5 minutes	85·4 84·9

It will be seen that in the last two experiments a slight increase in absorption (about 3%) was obtained. This, however, is not thought to be of significance, as it might well have occurred by a small movement of the diamond owing to contraction of the mount on cooling to this low temperature.

Thus cooling down to the temperature of liquid oxygen has resulted in no measurable shift of the bands of diamond in the infra-red region.

ULTRA-VIOLET SPECTROSCOPY OF DIAMOND.

INTRODUCTORY.

As mentioned on p. 466, MILLER, in 1862, had definitely found two types of diamond widely different in transparency in the ultra-violet.

More recently, PETER (*loc. cit.*) found only two of his thirty diamonds which transmitted radiation of less than λ 3000, the absorption constant rising definitely at λ 3130, becoming pronounced at λ 2310, and very high at λ 2260.

WALTHER* found a band in some yellow diamonds at λ 4155, but it was very feeble in green stones. Some other weak bands were reported by him at λ 4710, and in the

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* 'Wied. Ann.,' vol. 42, p. 505 (1891).

violet and ultra-violet regions of the spectrum, these being attributed to rare earths. We can find no other bands reported in the ultra-violet spectrum of diamond.

Our investigations in the ultra-violet region have brought out the following differences :—

Diamonds of Type 1 (fig. 29, Plate 12) have	(*a*) Complete absorption beyond *ca.* λ 3000 ; (*b*) A band system just before complete absorption, persistent at —170° C.
Diamonds of Type 2 (fig. 30, Plate 13) have	(*a*) Complete absorption beyond *ca.* λ 2250 ; (*b*) Just before complete absorption a faint absorptive region with bands, which disappear at —100° C.

APPARATUS.

Absorption at ordinary temperature.

Preliminary experiments having for their object the discrimination of the two types were made with a small portable ultra-violet spectroscope with fluorescent eye-piece and supplied with a copper arc. With this Professor GORDON, at Hatton Garden, found 250 diamonds to be opaque at about λ 3000.

The great difference in transparency possessed by the two types of diamond was then confirmed photographically by means of a nickel iron arc in conjunction with the Hilger spectrograph E 2, but no accurate picture of the presence of absorption bands was possible until a continuous source of illumination was obtained. This consisted of a horizontal tube with a quartz window containing hydrogen at about 15 mm. pressure with large aluminium electrodes in side tubes and was activated by about 2000 volts. The hydrogen was admitted through a heated palladium tube. The glass apparatus was immersed in water to keep the tube cool. Plates 12 and 13 show the essential differences between the spectra of the Types 1 and 2 of diamond.

Absorption at low temperatures.

For observation of the effect of low temperature, the diamond was mounted in the same Dewar apparatus as has been already described for use in the infra-red region (fig. 6 (*a*) and (*b*)) with the exception that the rocksalt windows were replaced by quartz. In these experiments, of which figs. 29 and 30, Plates 12 and 13, are examples, the photographic plates were sensitized by a film of petroleum jelly. The lowest temperature as read by the thermocouple attached to the diamond was —174° C., liquid oxygen being used in the Dewar vessel.

Absorption at high temperatures.

The diamond was held in a graphite mount at the centre of a silica tube, heated electrically, so that the light from the continuous source described above passed directly through the diamond before reaching the spectrograph. The diamond was protected from draughts by plugs of graphite, suitably drilled to allow the passage of the radiation.

Figs. 29 and 30 show the effect of heating the diamond at temperatures up to *ca.* 320° C. for D 10 (of Type 1) and D 2 (of Type 2) respectively.

RESULTS.

In Table V (*a*) will be found the positions of bands that have been observed in diamonds of Type 1, together with the end of the transmission and the effect on these of cooling and of heating the diamond, fig. 29.

In Table V (*b*) are collected data for diamonds of Type 2; the spectrum extends much farther into the ultra-violet and exhibits a region of faint selective absorption at ordinary temperatures. The effects of cooling and of heating (fig. 30) diamonds of Type 2 are also tabulated.

TABLE V (*a*).—Bands found in diamond in ultra-violet region—at different temperatures. Diamonds—Type 1.

		Temp. ° C.	λ. I.	λ. I.	λ. I.	λ. I.	λ. I.	λ. I.	λ. I.	End λ.
Fig. 29.	D 10	– 174	3298 (2)	*3201 (3)	3176 (4)	3154 (10)	3085 (1)	3064 (10)	3034 (10)	3000
	,,	20	—	—	—	3158	—	—	—	3066
	,,	89	—	—	—	3160	—	—	—	3082
	,,	121	—	—	—	3162	—	—	—	3090
	,,	166	—	—	—	—	—	—	—	3090
	,,	206	—	—	—	—	—	—	—	3094
	,,	253	—	—	—	—	—	—	—	3105
	,,	281	—	—	—	—	—	—	—	3105
	,,	316	—	—	—	—	—	—	—	3122
	D 1	20	—	3205 (1)	3178 (3)	3157 (10)	—	—	—	3090
			—	3205 (1)	3180 (3)	3157 (10)	—	—	—	
	D 9	20	3302 (1)	—	—	3157 (3)	—	3067 (2)	3037 (2)	2877
			—	—	—	3158 (3)	—	3068 (2)	3037 (2)	
	D 21	20	—	—	—	3156 (3)	—	3067 (3)	3037 (3)	2960
	D 23	20	—	—	—	3156 (3)	—	3067 (2)	3036 (2)	3015
	D 25	20	—	3203 (1)	3178 (3)	3156 (10)	—	—	—	3105

I = intensity.

* And probably a faint line at λ 3242.

Diamonds of Type 1.—*Table V* (*a*) *and Fig.* 29.

It was found that diamonds of Type 1 gave bands in the spectrum on the long wave-length side of λ 3000, where total absorption set in. At the ordinary temperature not all of these bands were observed, but on cooling the diamonds by means of liquid oxygen, three sequences of one, three, and three bands were obtained, all bands sharpening as the temperature was lowered. Such a sharpening has been observed, for example, by SPEDDING and BEAR,* for samarium ; for benzene by KRONENBERGER†; and for the porphyrins by CONANT and CRAWFORD,‡ and is attributed to the enfeebled interference of neighbouring molecules by reason of movements restricted by the low temperature, or to the Doppler effect being less prominent at low temperatures.

We have not, however, come across any record in the literature of absorption bands of diamond in this region of the spectrum.

A search has been made to see if the wave-lengths of these bands of diamond, of which some of the sequencies occur in all those of the opaque type, can be identified with those of likely impurities. Thus samarium has been stated to be a common impurity, for example, by WALTHER (*loc. cit.*), but none of the bands of that element in the recent work of SPEDDING and BEAR (*loc. cit.*) can be identified with the diamond bands found by us.

In this class of diamonds the position of the bands does not alter with the thickness of the diamond, although the extent of the general transmission does very slightly. The individual bands are not sharp, extending as they do over several Ångström units, although they become sharper with falling temperature, and we have not succeeded in resolving them with greater dispersion. The centres of the bands are given in Table V (*a*), from which the following wave-numbers are calculated for ordinary and for low temperatures, the more important bands being in heavier type :—

At +20° C. (composite figures from Table V (*a*).)—

λ 3302	—	3204	3179	3157	—	3067	3037	
30285	—	31211	31456	**31675**		32605	32927	cm.$^{-1}$

At —174° C. (D. 10)—

λ 3298	3242	3201	3176	3154	3085	3064	3034	
30321	30845	31240	31486	**31706**	32415	32637	**32960**	cm^{-1}

In confirmation of WALTHER'S statement that some diamonds have a band at 4155 A, we have found one diamond (D 20) which shows a band at this place, fig. 33, Plate 14, which is likewise the position of a fluorescence band (see p. 494). In view of the faintness of this band and its absence in most diamonds examined by us, we do not consider it to be normal to the diamond.

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* 'Phys. Rev.,' vol. 42, p. 58 (1932).

† 'Z. Phys.,' vol. 63, p. 494 (1930).

‡ 'Proc. Nat. Acad. Sci. Wash.,' vol. 165, p. 552 (1930).

Diamonds of Type 2.—*Table V* (*b*) *and Fig.* 30.

TABLE V (*b*).—Bands found in diamond in ultra-violet region—at different temperatures. Diamonds—Type 2.

	Temperature, ° C.	Start of faint absorption.	End (beginning of complete absorption).	Bands.	
		λ	λ		
D 2 . . .	– 174 to – 90	None	2250	None	Fig. 30, Plate 13.
,, . . .	– 35 to 20	2351	2254	λ2351 to 2330	
,, . . .	87	—	2359	—	
,, . . .	130	—	2363	—	
,, . . .	168	—	2368	—	
,, . . .	210	—	2375	—	
,, . . .	248	—	2380	—	
,, . . .	281	—	2388	—	
,, . . .	314	—	2393	—	
D 16 . . .	20	2351	2300	—	
D 19 . . .	20	2351	2299	—	
D 22 . . .	20	2351	2257	λ 2351 to 2335	
D 24 . . .	20	2351	2257	—	

Absorption spectra have been obtained with five diamonds of the more transparent type and the effect of cooling and of heating one of them was observed from – 174° to 314° C. Comparison of the spectra of figs. 29 and 30, Plates 12 and 13, shows at once the much greater extension of transparency in the ultra-violet for the spectrum of diamonds of Type 2.

It is a characteristic feature of diamonds of Type 2 that, at the ordinary temperature and somewhat below it, all show a region of faint absorption from λ 2351 for 50 to a 100 Å, and in this region faint bands can be observed from λ 2351 to λ 2330.

Lowering of temperature (see fig. 30) has the effect of obliterating this faintly absorptive region until at about – 100° C. the line which marks the boundary of the spectrum from the region of complete absorption is quite sharp at about λ 2250 and remains so down to – 174° C. In order to determine as closely as possible the temperature at which the faint absorption ends a microphotometric tracing was made for us by Dr. W. H. J. CHILDS, by traversing the plate at a distance of 1 mm. from the end of the spectrum, fig. 31, Plate 14.

In another diamond (not in Table I) which was very thin and transparent to λ 2240, where the cut off was well marked, these bands were more sharply defined and appeared as two groups of two at λ 2300 and λ 2312, and at λ 2359 and λ 2363. The differences in wave-numbers between these are 225 and 72 cm.$^{-1}$.

RAMAN EFFECT IN DIAMOND.

INTRODUCTORY.

Absence of an absorption band in the infra-red in some diamonds seemed to point to the presence of an inactive frequency, such as was predicted in the carbonates and afterwards exactly confirmed by the Raman effect.* A certain analogy between the two cases could be assumed on the ground that while in the CO_3 group the three oxygen atoms move symmetrically in and out with reference to the carbon atom, thus leaving the electric moment of the system stationary, a like movement could be conceived for three carbons at the apices of the tetrahedron towards the central carbon atom.

Experiment, however, disposed of any difference between the two types of diamond : both gave exactly the same Raman difference.

APPARATUS AND PROCEDURE.

At ordinary temperatures.

The investigations of the Raman effect were carried out both with a Hilger quartz spectrograph, and with a specially constructed glass spectrograph of which the dispersing system consisted of two 60° light flint glass prisms of 85 mm. base and 45 mm. high. In the region λ 3650 to λ 4046 the dispersion was about 9A per mm. and it fell to about 30 A per mm. in the neighbourhood of λ 5000. A mercury arc of the hot type in which the mercury is boiled to form a vacuum was used because the arc is thereby concentrated in a length of about 50 mm. The diamonds were fitted into a brass case, constructed so that the greatest possible surface of the diamond could be illuminated, and the edge of the diamond placed close up to the slit of the spectrograph. In this manner, and by covering up the spectrograph, stray radiation was practically eliminated, and only radiation scattered at right angles to the direction of the incident light could enter the spectrograph.

It was ensured that the whole face of the diamond was illuminated by means of a mercury arc, quartz lenses being used for ultra-violet, and a glass condensing system for the visible region.

For experiments on a limited region of the spectrum, and to weaken lines of the mercury arc about λ 5000, liquid cells containing potassium dichromate and cobalt thiocyanate, as suggested by WOOD† were employed. With these filters good photographs were obtained with 30 to 40 hours' exposure ; but without the screens 10 minutes was usually enough for the Raman lines in the region λ 4627, and 20 minutes for the line at λ 4277, with slit widths about 0·02 mm. Ilford Isochromatic plates were found satisfactory. Attempts were made to obtain Raman lines from the mercury line λ 5461 isolated by a Wratten filter, or the yellow sodium lines produced by a specially intense

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* SCHAEFER, MATOSSI, and ADERHOLD, 'Phys. Z.,' vol. 30, p. 581 (1929).

† 'Trans. Faraday Soc.,' vol. 25, p. 792 (1929).

source and neocyanine plates, but no Raman lines originating from these wave-lengths were found even after 60 hours' exposure.

At low temperatures.

In view of the fact that the infra-red spectrum is unaltered at the temperature of liquid oxygen, it was important to examine the Raman spectrum likewise at this temperature. Diamond D 1 was fitted into a Dewar vessel similar to that shown in fig. 6 (*b*), the radiation being condensed on the face of the diamond, and that scattered at right angles being collected by the spectrograph. Suitable diaphragms were arranged around the diamond in order to prevent stray radiation being reflected into the spectrograph.

RESULTS.

In the course of this work we have observed (*a*) Raman lines, (*b*) a diffuse band, and (*c*) a region of continuous spectrum.

(*a*) *Raman lines.*

Nine diamonds, 4 of Type 1 and 5 of Type 2 (see Table I, marked " R ") were examined for the Raman effect. Fig. 32, Plate 14, shows typical photographs of the Raman spectra. Table VI shows all the lines observed.

TABLE VI.—Raman lines of diamond at 20° C.

Exciting lines.		Raman lines.		$\Delta \nu$	Difference from mean value (1333·1 cm^{-1}).
λ air.	ν vac.	λ air.	ν vac.		
2378·3	42034·0	2456·3	40699·0	1335·0	+ 1·9
2534·8	39439·0	2623·5	38105·0	1334·0	+ 0·9
2576·4	38802·0	2667·9	37471·0	1331·0	− 2·1
2652·0	37696·0	2749·5	36360·0	1336·0	+ 2·9
2803·5	35660·0	2912·5	34325·0	1335·0	+ 1·9
2967·3	33689·0	3089·5	32358·0	1331·0	− 2·1
3021·6	33085·0	3148·3	31754·0	1331·0	− 2·1
3125·6	31985·0	3261·3	30653·0	1332·0	− 1·1
3131·7	31922·0	3268·3	30588·0	1334·0	+ 0·9
3341·6	29917·0	3497·1	28587·0	1330·0	− 3·1
3650·2	27388·0	3837·0	26055·0	1333·0	− 0·1
3654·8	27353·0	3842·2	26019·0	1334·0	+ 0·9
3663·3	27290·0	3852·0	25953·0	1337·0	+ 3·9
4046·56*	24705·4	4277·3	23373·0	1332·4	− 0·7
4339·23*	23039·1	4605·5	21707·1	1332·0	− 1·1
4347·50*	22995·3	4614·8	21663·2	1332·1	− 1·0
4358·34*	22938·1	4627·08	21605·7	1332·4	− 0·7

Values with * are taken from diamonds of Type 1; the others are taken from diamonds of Type 2, which also contain those marked *.

At ordinary temperature.

For the 17 Raman lines the mean difference is 1333·1 cm.$^{-1}$ Since they have an appreciable width and it is difficult to judge their exact position, the lines found with the quartz spectrograph (all below λ 3663) are perhaps less accurate than those obtained with the glass instrument. These agree very closely amongst themselves with a mean value of 1332·2 cm.$^{-1}$, and this may be taken as the value for this Raman line of diamonds of both types. BHAGAVANTAM* found this line also and assigns to it the value 1331·9 ± 0·3. These results are practically identical and are well within the limits of error of the method. We made a preliminary statement of these results in *Nature*† simultaneously with RAMASWAMY. Since that date the Raman spectrum of various diamonds has been discussed by RAMASWAMY,‡ and BHAGAVANTAM,§ but our results include many more examples of the line 1332 cm.$^{-1}$ originating from different mercury lines than those reported by these workers. Most lines of the mercury spectrum below λ 4358 appear to be capable of exciting this line, the failure to observe it often being due to the Raman line falling very close to a strongly scattered and unaltered mercury line, or in a region where a continuous spectrum is scattered giving a background on which a faint line would not be seen. It may be stated that photographs of Type 1 diamonds were taken with the quartz instrument, without finding any Raman line below the region—about λ 3000—where these diamonds are opaque.

BHAGAVANTAM (*loc. cit.*) reports six other very feeble Raman lines obtained with two diamonds of 20 and 143 carats respectively. The largest diamond examined by us weighed about three carats, but was quite colourless and clear, and had only natural or cleavage faces, being unworked. We did not observe these feeble lines in any of the diamonds, which were all chosen because of their freedom from colour and transparency to visible radiation so far as could be judged by eye. It may be that the larger diamonds present a better opportunity for scattering very feeble Raman lines.

At low temperatures.

The Raman line at 1332 cm.$^{-1}$ was unaltered in position, sharpness, or intensity when the experiment was made at — 180° C.

(*b*) *A diffuse band.*

In addition to this line 1332 cm.$^{-1}$, we have observed with some diamonds a diffuse band with its centre about λ 4155·5. That this band is a fluorescence band can be seen from fig. 33, Plate 14, where its position is exactly that of a feeble absorption band already described (see p. 490). So far as we have observed this diffuse band it does not

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* 'Ind. J. Phys.,' vol. 5, p. 169 (1930).

† Vol. 125, p. 704 (1930); vol. 126, p. 279 (1930).

‡ 'Ind. J. Phys.,' vol. 5, p. 97 (1930).

§ *Ibid.*, pp. 169, 573.

appear to depend upon the colour of the diamond to any extent, for failure to find this fluorescence may depend upon the optical system used. For example, diamond D 2 does not apparently show this band when a glass spectrograph is used, although D 20 gives the result shown in fig. 33 on the same instrument. If, however, D 2 is photographed with an all-quartz spectrograph, the band can be seen, although not very strongly. This indicates that the fluorescence band may be scattered so feebly that it is absorbed in the lenses and prisms of the instrument. In this connexion it is to be noted that the light produced by bombardment with cathode rays shows an absorption band in exactly this position.* This indicates that there is a natural frequency in diamonds in the violet region of the spectrum, and the failure to observe it in all diamonds is probably due to its extreme feebleness. Since, however, it is a band capable of exciting fluorescence in the same region its origin may possibly be ascribed to some imperfection in the diamond lattice, which may act as an "impurity."

(c) *Continuous spectrum.*

A real continuous spectrum, with limiting edges seems to be scattered as well as the Raman lines and the fluorescent band described. This may be a true fluorescence spectrum, or may be scattered radiation due to the combined effect of possible vibrations of atoms in aggregates. On the other hand, owing to the high refractive index of diamond and imperfections in the gross structure, the possibility of internal reflections cannot be excluded, for the mercury arc has a continuous background of unequal intensity in various parts of the spectrum which it is impossible to exclude entirely by means of filters.

BÄR† has given a full discussion of the question of the continuous spectrum in Raman radiation and arrives at the conclusion that when every care is taken to purify liquids, the continuous spectrum is reduced as purification proceeds, and that finally only a Rayleigh scattering or fluorescence spectrum of the continuous mercury radiation is found.

PHOTO-ELECTRIC CONDUCTIVITY.

INTRODUCTORY.

The important advances by GUDDEN and POHL‡ and their colleagues in the Erlangen Laboratory on photo-conductivity have a special interest since they have worked on diamond.

Shortly after the early work of GUDDEN and POHL appeared a paper on the photo-

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* JOHN, 'Ind. J. Phys.,' vol. 6, p. 305 (1931).

† 'Z. Physik,' vol. 79, p. 455 (1932).

‡ 'Z. Physik,' 1920, *et seq.*; and "Lichtelektrische Erscheinungen," by B. GUDDEN (Springer: Berlin, 1928).

conductivity of diamond by Miss M. LEVI[*], containing several interesting observations. A general account of the subject has recently been made by NIX[†], together with a good bibliography, while WILSON[‡] has dealt with the electronic aspect of conductors and semi-conductors. More recently, FOWLER[§] has presented WILSON's theory in a simple form applied to different models of semi-conductors, and GURNEY[||] has dealt with the internal photo-electric effect in halide crystals. Various views on the nature of the photo-electric effect and on the subject of contacts will be found in the proceedings of a conference held in Leningrad.[¶]

When our attention was called to the work of GUDDEN and POHL, we applied light to both types of diamond and immediately obtained the broad distinction that those of Type 1 were only very feebly photo-conductive, even with high voltages, while those of Type 2 gave measurable currents with small potentials or even with none at all. This feature of the production of a current and a voltage by the imposition of short wave-length light was so striking, and apparently hitherto unreported for diamond, that we decided to investigate the photo-electric effect of diamonds more minutely.

Generally, it may be said that our investigations are in line with the results described by GUDDEN and POHL, but with diamonds of Type 2 certain new effects have been obtained which, if not recognized and as far as possible segregated, tend to mask the more simple phenomena described by these authors.

In the course of this work, four new effects peculiar to diamonds of Type 2 have been recognized :—

1. Production of a current on illuminating diamond with ultra-violet light of short wave-length without an applied field.
2. Activation of diamonds by short wave-length light (about λ 2300) leaving dark current and subsequent increased response to light of longer wave-length.
3. Removal of activation (deactivation) due to λ 2300 by light of wave-length λ 2400 to λ 5000.
4. Large photo-conductivity when light of wave-length greater than λ 5000 is applied to an activated, but not to a deactivated diamond. (Region of adjuvant effect.)

The effect of temperature throughout the range — 160° to 320° C. was also explored.

In the general discussion (p. 533) will be found an attempt to bring the phenomena described in this section into line with those observed by optical methods.

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[*] 'Proc. Roy. Soc. Can.,' vol. 16, p. 241 (1922).

[†] 'Rev. Mod. Phys.,' vol. 4, p. 723 (1932).

[‡] 'Proc. Roy. Soc.,' A, vol. 133, p. 458 (1931), and vol. 134, p. 277 (1931); also 'Nature,' vol. 130, 913 (1932). *Cf.* TEICHMANN, 'Z. Physik,' vol. 78, p. 21 (1932).

[§] 'Proc. Roy. Soc.,' A, vol. 140, p. 505 (1933).

[||] 'Proc. Roy. Soc.,' A, vol. 141, p. 209 (1933).

[¶] 'Phys. Z. Sowjetunion,' vol. 1, p. 5 (1932).

Apparatus.

Light sources.

Owing to the difficulty in finding an intense, steady source of light, continuous in the visible and ultra-violet regions of the spectrum, a hot quartz mercury vapour lamp was used as the most satisfactory source of light for many experiments. When the ultra-violet beyond λ 3000 was not desired, such sources as a pointolite and an ordinary tungsten filament lamp were found to be of service.

By means of a large quartz monochromator, light of specific wave-length was isolated and many effects observed, but as the intensity was too low for some of the work, radiation from the mercury lamp was filtered in various ways. Thus a chlorine filter consisting of a cylindrical container of fused silica, 5 cm. long, filled with chlorine at atmospheric pressure, removed mercury lines between λ 2750 and λ 4000 ; this in conjunction with a 1-mm. layer of saturated tartaric acid solution in water, contained in a cell of fused silica, eliminated practically all lines below λ 4000, except λ 2536 and λ 2652. Light beyond λ 3000 was usually cut off by a sheet of ordinary window glass, 3 mm. thick ; λ 3650 very nearly free from all other lines could be obtained by a combination of glass filters. A so-called infra-red Ilford filter with a source of white light provided radiation of wave-length greater than λ 7000.

For definite exposures of light it was found convenient to use a large aperture photographic shutter, capable of working to 1/100 of a second. The iris diaphragm of this shutter was used in some experiments with monochromator 2 for adjusting the strengths of chosen mercury lines to a constant energy value.

Monochromators.

(1) For the earlier work we were allowed by Professor ALLMAND to use the quartz monochromator* belonging to King's College, London, this instrument having an exceptionally large aperture (about F = 1·8) with a Cornu prism of 17·8 cm. × 11·4 cm. face. By means of a quartz condensing lens of 3-inch aperture and 5-inch focal length, an image of the vertical mercury arc was focussed on the 2-inch slit of this instrument.

The thermopile of the instrument was used for recording the energy of the mercury lines and afterwards when it was desired to determine the photo-conductivity of diamonds, it was replaced by a diamond holder of either of the three types (*a*), (*b*) and (*c*) of fig. 8.

The construction of these holders is sufficiently shown by the figures. That in fig. 8 (*a*) screwed into a Hilger symmetrical slit so that a diamond held as shown between A and B occupied the normal position of a Hilger linear thermopile, which, mounted in a similar

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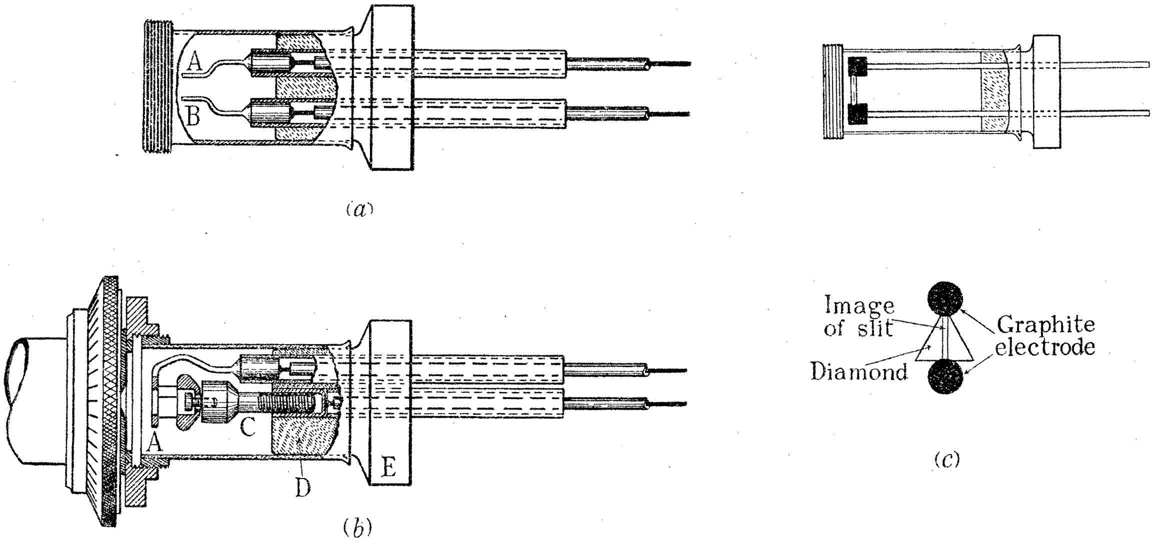
* PERRY, 'Trans. Opt. Soc.,' vol. 33, p. 159 (1931–2).

slit, could be inserted when required. With this holder the incident light was perpendicular to the electric field, but in fig. 8 (*b*) the light was parallel to the field. In this holder the member A has a circular hole 4 mm. in diameter through which the light met the diamond normally to the face. To secure good contact between the diamond and the grips tin-foil was used, and in addition, the rod C was threaded to give a variable gap. A scale was marked on the flange E of the insulating plug D for observation of any desired rotation of the diamond in a vertical plane.



(*a*) (*b*) (*c*)

Fig. 8.—Types of holders.

The relative energies of the mercury lines were determined by means of the thermopile and a Zernicke galvanometer (type Zc) read by means of a telescope and scale at a distance of about 4 metres. From the known characteristics of galvanometer and thermopile, values for the absolute energy associated with any line could be calculated.

(2) A smaller monochromator (Hilger, type D 41) lent to us by Professor Andrade, of University College, was used for later work and proved to be very convenient for observations down to λ 2200. This instrument gave an intensity only slightly less than that of the larger one already described.

Measurement of photo-currents with galvanometer and electrometer triode valve.

Since, when using a monochromator the light intensity available was necessarily low, it was important to use a galvanometer of high sensitivity for measuring the current through the diamond, with or without an applied voltage. Such galvanometers suffered from various disadvantages. For comparatively large currents, galvanometers of low sensitivity and even a microammeter became of service, but for smaller currents the electrometer triode was very useful since under suitable operating conditions the grid-filament resistance was of the order of 10^{15} ohms. This high resistance was achieved by placing the filament between the plate and the grid, great attention being paid to the insulation of the latter electrode. The circuit used is shown in fig. 9.

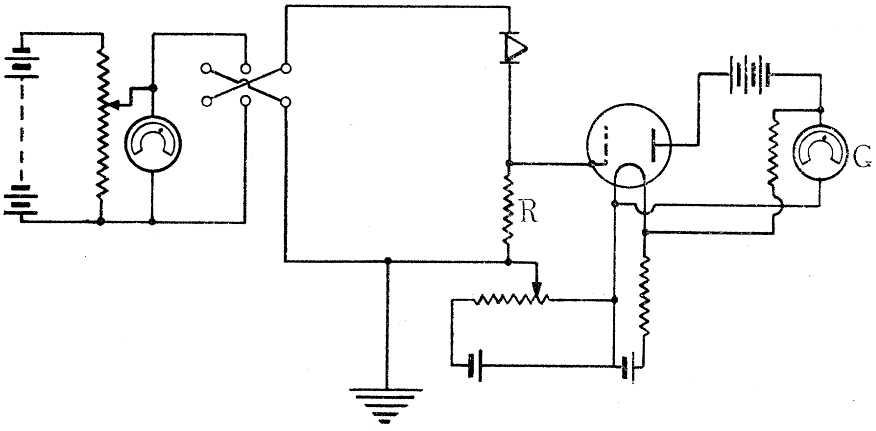


FIG. 9.—Circuit used for measuring current passing through diamond.

The current through the diamond and resistance R (10^7 ohms) in series produced a voltage drop across R which being applied between the grid and the filament of the electrometer valve caused a change of anode current, shown by the galvanometer G of sensitivity 5×10^{-9} amp./mm. The overall sensitivity was $1{\cdot}3 \times 10^{-11}$ amp./mm. and leakage difficulties disappeared when the grid lead was carefully insulated.

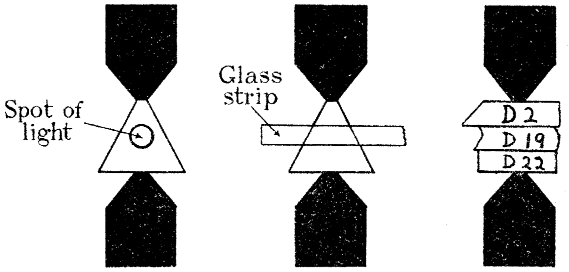
In the earlier work potentials up to 180 volts, obtained from accumulators, were applied to the diamond in either direction at will, as is shown in fig. 9. Later, when we had learnt how to avoid activation of diamonds of Type 2, higher voltages were used, up to 2250 volts, obtained from dry batteries.

Attachment of electrodes.

In the earlier work with the monochromator, the holders already described (fig. 8 (*a*) and (*b*)) were used, but later a modification of (*a*) was adopted. In this the electrodes which held the diamond were of graphite and screwed on to two stout wires passing through an ebonite plug. The manner in which a diamond was mounted and illuminated with monochromatic light is clear from fig. 8 (*c*). The light fell normally on the face of the diamond.

Graphite eletrodes were found to be generally useful, but at different times electrodes of aluminium, tin, copper, brass, lead, Wood's metal, and even illuminated diamond of Type 2 itself were tried and found to be effective. The Wood's metal had the advantage of adhering strongly to the diamond, giving a permanent contact, provided that large temperature changes did not occur.

In order to put aside the possibility that the photo-electric current we obtained on illuminating diamonds might be due to illumination of the electrodes, certain experiments were made. Thus, if a diamond held between electrodes was illuminated by a central small spot of light, fig. 10 (*a*), no current was obtained, the rest of the crystal acting as an insulator. On increasing the diameter of the spot, not necessarily to the extent of the distance between the electrodes, but nearly to this, so that by internal reflection light in the diamond reached these, a current could be got to pass. Also, the current ceased if the diamond near one of the electrodes was obscured.



(*a*) (*b*) (*c*)

FIG. 10.—Different conditions between electrodes.

With specially photo-conductive diamonds it was found that a current would pass the boundaries of a pile of three diamonds, if they were illuminated, see fig. 10 (*c*), but not when a non-conductive diamond was interposed.

It was observed that a current that had been set up by light was quenched if a thin strip of glass was placed across the diamond, fig. 10 (*b*), thus clearly showing that the sheltered part of the diamond acted as an insulator.

Further, to show that a diamond could be rendered conducting in insulating grips, it was illuminated between pieces of ebonite, removed in the dark and then placed between graphite electrodes, whereupon, if it had been caused to glow by ultra-violet light, the glow continued, and by the methods described above, a current could still be made to flow.

Measurements at low temperatures.

For observations down to — 160° C., the Dewar apparatus used in the infra-red and ultra-violet regions, and described on p. 480, was adapted as is shown in fig. 6, (*c*) and (*d*). Springs bearing on graphite electrodes held the diamond inside a highly-polished silver plated tube, provided with suitable openings for inserting the diamond and admitting the light. Insulation of the lower electrode was secured by means of glass tubing. Two leads passed out from the electrodes through the cement used for fixing the bottom plate, and in similar fashion another pair of leads from the thermocouple situated inside the lower electrode.

For this work the Dewar vessel was supplied with quartz windows, and it was well pumped out and sealed off before each set of experiments.

Measurements at high temperatures.

For temperatures up to 300° C., the diamond was heated in the apparatus shown in fig. 11. It was held between graphite electrodes, and over these was slipped a closely-fitting clear silica tube which could be heated electrically. As an appreciable leakage of current was found to occur at 300° C., owing to the much-reduced insulation of silica at this temperature, the heating coils were not wound directly on the silica tubing, but an earthed layer of copper foil was wound round the silica tube. The foil was then covered with asbestos paper, and on this the nichrome heating coils were wound. A space in the middle of the tube was left clear for admitting light to the diamond, and a side tube of fused silica was provided through which a thermocouple could be inserted so as to be in actual contact with the diamond.

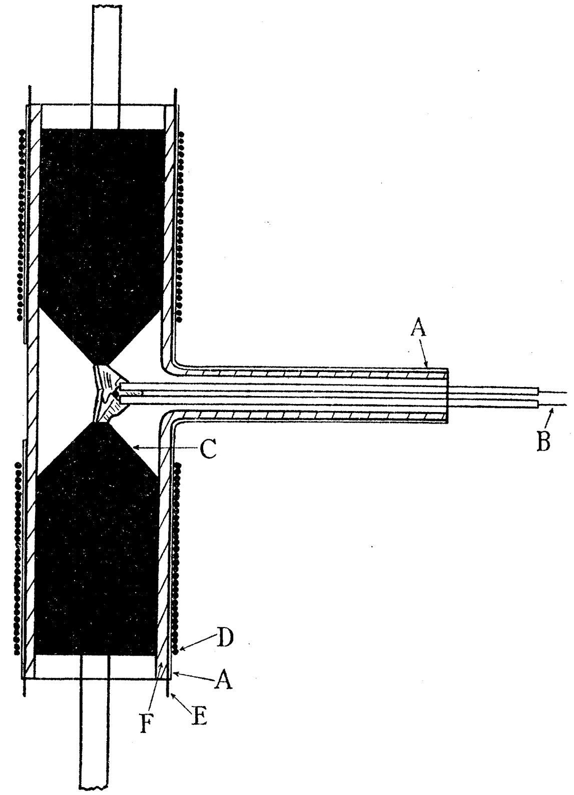


Fig. 11.—Holder for diamond at high temperatures. A, asbestos paper; B, thermocouple; C, graphite electrode; D, heater winding; E, earthed copper screen; F, silica tube.

Results.

Introductory.

Diamonds of Type 1, in general, possess small photo-conductivity, even with applied voltages as high as 5600 volts/cm. In Table VII will be found some results obtained under various conditions of applied voltage and illumination, while in the same table are collected for comparison a few results of diamonds of Type 2. Since in this type several new features emerged, it became necessary to make a more extensive investigation.

TABLE VII.—Photo-currents obtained from Diamond.

Type 1.

Diamond.	Applied voltage.	Wave-length imposed (λ).	Monochromator used.	Current observed (amp.).	Holder.
D 1, D 10, D 20 D 21, D 25	None	Intense light of Hg lamp	None	Too small to be measured	Graphite electrodes.
D 23	"	" "	"	$1{\cdot}0 \times 10^{-10}$	" "
D 1	180	3650	1	$1{\cdot}0 \times 10^{-10}$	Holder (*a*).
"	2250	3650	2	$2{\cdot}1 \times 10^{-10}$	" (*c*).
"	2250	3129	2	$0{\cdot}55 \times 10^{-10}$	" (*c*).
"	2250	2537	2	$6{\cdot}8 \times 10^{-10}$	" (*c*).
D 10	180	3650	1	$1{\cdot}5 \times 10^{-10}$	" (*a*).
"	2250	3650	2	$0{\cdot}26 \times 10^{-10}$	" (*c*).
"	2250	3129	2	$0{\cdot}13 \times 10^{-10}$	" (*c*).
"	2250	2537	2	$2{\cdot}0 \times 10^{-10}$	" (*c*).
D 20	180	3650	1	$1{\cdot}0 \times 10^{-10}$	" (*a*).
D 21	180	3650	1	$1{\cdot}0 \times 10^{-10}$	" (*a*).
D 23	180	3650	1	$7{\cdot}9 \times 10^{-10}$	" (*a*).
Type 2.					
D 2	None	Intense light of Hg lamp	None	$2{\cdot}0 \times 10^{-9}$	Graphite electrodes.
D 16	"	" "	"	—	" "
D 19	"	" "	"	$5{\cdot}0 \times 10^{-9}$	" "
D 22	"	" "	"	$1{\cdot}0 \times 10^{-7}$	" "
D 24	"	" "	"	$2{\cdot}0 \times 10^{-10}$	" "
D 2 (not activated)	2000	3650	2	$9{\cdot}5 \times 10^{-10}$	Holder (*c*).
" "	2000	2652	2	$4{\cdot}0 \times 10^{-10}$	" (*c*).
D 16 "	2250	3650	2	$4{\cdot}2 \times 10^{-10}$	" (*c*).
" "	2250	2537	2	$1{\cdot}9 \times 10^{-10}$	" (*c*).
D 19 (conductive in dark)	—	—	—	—	—
D 22 (not activated)	2250	3650	2	$1{\cdot}0 \times 10^{-9}$	Holder (*c*).
" "	2250	2537	2	$3{\cdot}4 \times 10^{-9}$	" (*c*).
D 24 "	2250	3650	2	$1{\cdot}0 \times 10^{-9}$	" (*c*).
" "	2250	2537	2	$8{\cdot}1 \times 10^{-10}$	" (*c*).
D 22 (activated)	None	3650	2	$2{\cdot}2 \times 10^{-10}$	Holder (*c*).
" "	"	2300	2	$0{\cdot}65 \times 10^{-11}$	" (*c*).
" "	2	3650	1	$2{\cdot}0 \times 10^{-8}$	" (*a*).
" "	500	Intense light of Hg lamp	None	$1{\cdot}0 \times 10^{-2}$	Graphite electrodes.

Diamonds of Type 1.

When diamonds of Type 1 were exposed to monochromatic light of which the energy of various wave-lengths had been determined, it proved that saturation, or attainment of a constant value for current with increasing voltage, was not achieved. Either Ohm's law was obeyed or the current increased even more rapidly than the law required.

High voltages were needed to bring out any conductivity in this type of diamond in any region of the spectrum employed, and the type of relationship between wavelength and the current for equal energy in the spectrum is shown in fig. 12.

Here neither diamond passed any measurable current in the dark with the full voltage applied, and the curves are similar to those obtained by GUDDEN and POHL* for two diamonds of what were apparently Type 1.

The photo-electric yields for D 1 and D 10 are, however, lower than the values obtained by these authors (*e.g.*, $0 \cdot 96 \times 10^{-4}$ coul./cal. at λ 2400 for D 1 (2400 v/cm.) as against $10 \cdot 5 \times 10^{-4}$ coul./cal. at λ 2400 for their "Diamond No. 2" with 16,000 v/cm.), but saturation of current was not secured probably on account of the length of path through the diamonds in the arrangement used by us.

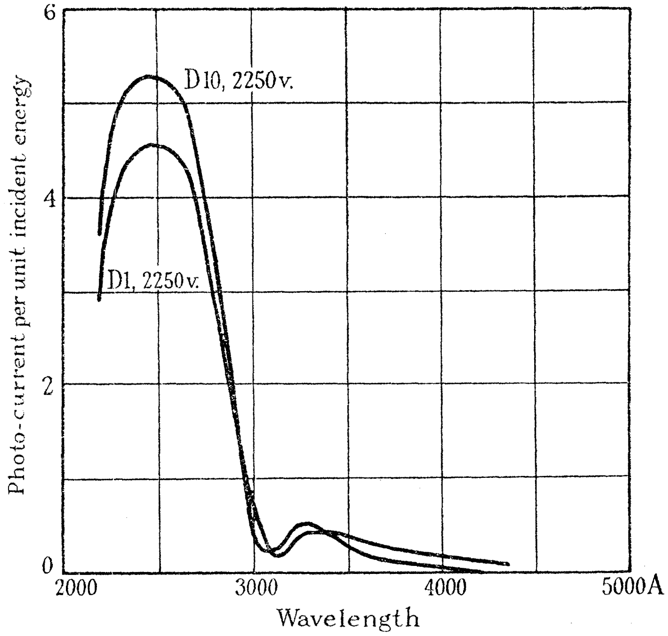


FIG. 12.—Specific photo-electric effect for diamonds of Type 1 at different wave-lengths.
Unity on y-axis $= 2 \times 10^{-5}$ coul./cal. (D 1)
$= 1 \times 10^{-5}$ „ (D 10).

No current was obtained on illumination without an applied voltage, with the exception of a small current given by D 23 when exposed to the full light of the mercury arc. Nor with diamonds of Type 1 did we find any evidence of their being activated by any special frequency, which is one of the characteristic properties of Type 2.

Diamonds of Type 2.

Generally with this type, radiation throughout the spectrum produces much larger currents, and in Table VII are examples of the currents obtained with and without an applied field, and with and without previous activation.

Of the peculiar features of this class of diamond—current without applied voltage,

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* 'Z. Physik,' vol. 3, pp. 127–128 (1920).

activation by short wave-length light, deactivation, and response to red light when activated—it may be said that all the diamonds of Type 2 exhibited them in varying degree.

D 16 and D 24 generate only a small current when illuminated without an applied voltage and are activated but only feebly by light of wave-length λ 2300.

Of D 2, D 19, D 22, D 22 was specially sensitive to irradiation and responded even without an applied voltage to monochromatic light and best at wave-length λ 2300, for unit energy. These diamonds respond powerfully to light of wave-length λ 2300, lose the activation produced by this radiation when exposed to light of rather higher wave-length (λ 2400–λ 5000), and give an exceptionally large photo-current when in an activated state and exposed to light above λ 5000. D 19 differs from the other two in conducting in the dark under all conditions (*cf.* LEVI*), especially at higher temperatures.

Having recognized the need for avoiding activation by light of the region λ 2300, an attempt was made to determine photo-electric yield as was done for diamonds of Type 1, but it was necessary in the case of diamonds of Type 2 to avoid activation by λ 2300. This was specially the case with the very active diamonds D 2 and D 22, but by using short times of exposure (D 16 and D 24) a region from λ 2200 to λ 4500 could be investigated.

The curves (see fig. 13) for the specific photo-electric effect sometimes show subsidiary maxima at λ 3350, as in the case of Type 1 shown in fig. 12, but the maxima are more pronounced, and this feature was observed by Miss LEVI (*loc. cit.*, p. 247) for two diamonds of the transparent type. Full quantum efficiency was never obtained in these experiments.

It is important to remark that the currents generated by the different wave-lengths here and in Type 1, described above, are normal currents developed by light of these wave-lengths without any secondary effect.

When, on the contrary, activation is encouraged by applying light of λ 2300 to D 22, with 120 v. applied, a current can be obtained over fifty times that corresponding to the full quantum efficiency of the incident light.

Those effects mentioned in the Introduction to this Section which we believe have not hitherto been segregated are now considered in more detail. They apply only to diamonds of Type 2.

(1) PRODUCTION OF A CURRENT ON ILLUMINATING DIAMOND WITH ULTRA-VIOLET LIGHT OF SHORT WAVE-LENGTH, WITHOUT AN APPLIED FIELD.

To produce this effect a wave-length about λ 2300 is necessary, and no light of wave-length greater than λ 2400 is of use unless the shorter wave-length has been previously applied or is applied along with it.

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* 'Proc. Trans. Roy. Soc. Can.,' vol. 16, third series, p. 246 (1922).

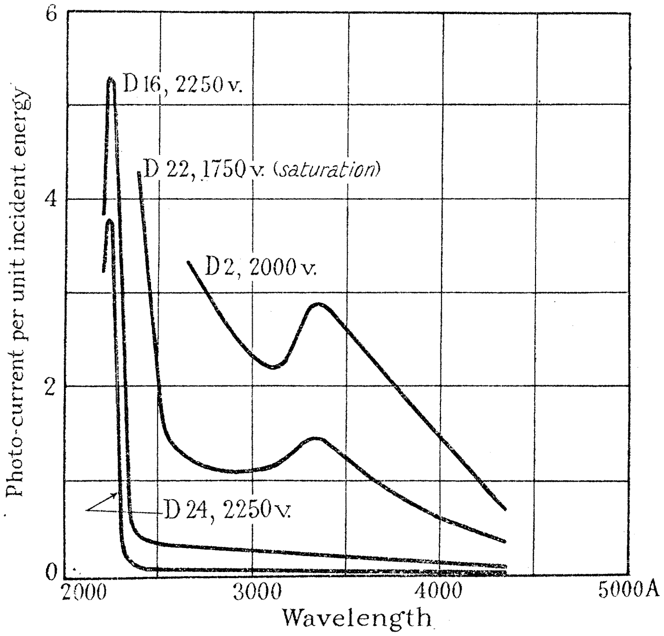

FIG. 13.—Specific photo-electric effect for diamonds of Type 2 at different wave-lengths.

Unity on y-axis $= 2 \times 10^{-5}$ coul./cal. (D 2)
$= 1 \times 10^{-4}$ „ (D 16)
$= 3 \times 10^{-4}$ „ (D 22)
$= 5 \times 10^{-3}$ „ (D 24).

As the direction in which this spontaneous current will actually flow is of interest, some observations have been made by illuminating with the full energy of the mercury arc. Thus the current generated is always opposite to the direction of easy conductivity in the diamond, which exhibits rectifying properties when in an activated state. Differences of conductivity against and with this direction of easy conductivity were as great as 100 : 1 with D 22. The voltage required to neutralize the current generated by this diamond (about 10^{-7} amp.) may be as high as 0·6 v. and the magnitude of the voltage is independent of the intensity of the light.

Definite polarities can indeed be allotted to portions of this diamond, and by experience the direction of the current can be foretold for any given position of the diamond between the electrodes.

Fig. 14 shows the diamond D 22 mounted between electrodes. The corners A, B, C show the polarities positive, negative, positive, respectively. If the diamond is turned in the holder, A and B being interchanged, the direction of the current will be reversed, but if C takes the place of A no change will be observed. If the points concerned are A and

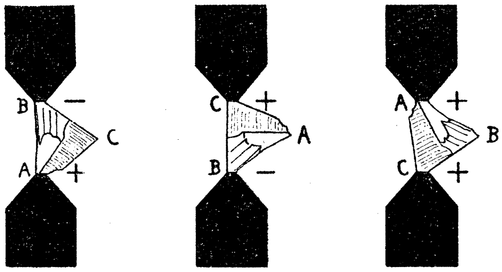

FIG 14.—Polarity of D 22.

C the current obtained may be in either direction, but in any case is very small. In this case in a position such that no current flows on illumination, it is found that if one contact (say C) is shaded, then A is positive and C less positive, and the current in the external circuit flows from A. If the contact at A is shaded then the current flows in the reverse direction. It appears that the best conditions for obtaining a current are when the electrodes are situated at corners between which are discontinuities of structure. Such discontinuities are described and figured (fig. 3) as a penetration of an octahedral into the hexakisoctahedral formation. No such results as are described above could be obtained with the other diamonds, the slightest movement between the contacts being liable to reverse the polarity.

A property possessed by D 22 was that of glowing with a green phosphorescence after exposure to light in the activating region without any voltage being applied. While glowing the diamond was found to have a large conductivity in the dark detectable by the application of a voltage ; both glow and current died away together, the glow being visible for about five minutes at ordinary temperatures after the light was cut off. The dark current persisting when illumination was removed could be detected after much longer periods and was readily measurable after twelve hours. Although after this or a longer period of time the dark current had fallen to a very small value, the notable increase in current produced by imposing red light was nearly as great as when it was applied to a diamond immediately after activation, and could be many times greater even than that produced by the activating light of λ 2300. The green glow immediately after activation was not observed at —100° C. ; at higher temperatures, say, 100° C., the glow was brighter, but died away more rapidly than at ordinary temperatures.

(2) ACTIVATION OF DIAMONDS OF TYPE 2 BY SHORT WAVE-LENGTH LIGHT (ABOUT λ 2300) LEAVING DARK CURRENT AND SUBSEQUENT INCREASED RESPONSE TO LIGHT OF OTHER WAVE-LENGTHS.

Activation, or enhancement of the current by some frequency due to a previous or concurrent illumination with another frequency, was first noticed in D 2. With this specimen it was found that subjection to light of λ 2300 with an applied voltage left the diamond with a detectable dark current and sensitized it for longer wave-lengths so that they produced currents, which might be many times greater than those due to the given wave-length when applied to the unactivated diamond. The necessity for recognizing and avoiding this increase in current due to the higher frequency light for work on the photo-electric yield has been mentioned above.

The following statement gives the course of the phenomena : after one of the diamonds of Type 2 has been activated by light of λ 2300, and the light shut off, a current flows (dark current). On the imposition of wave-lengths between λ 2400 and λ 5000, there is a marked increase in the current, but this is soon quenched together with the dark current, leaving the diamond with only that current due to the specific effect of light of these wave-lengths. Imposition, however, of radiation of wave-length nearer the red to an activated diamond leads immediately to a large and persistent flow of current.

Determination of most effective activating wave-length.

To ascertain the frequency of the radiation producing maximum activation, the spectrum was traversed in small steps by means of monochromator 2. Small voltages and light intensity were used. Exposures of the diamond to the selected portions of the spectrum for one second were usually given when taking readings, in order to avoid undue activation. Presence of much activation in the diamond was found to flatten the curve obtained, but did not alter the position of the maximum. The curves for D 2, D 22, and D 24, fig. 15, were plotted from the observed currents referred to unit incident energy, and show maxima close to λ 2300 for D 2 and D 22, but rather lower (λ 2220) in the case of D 24.

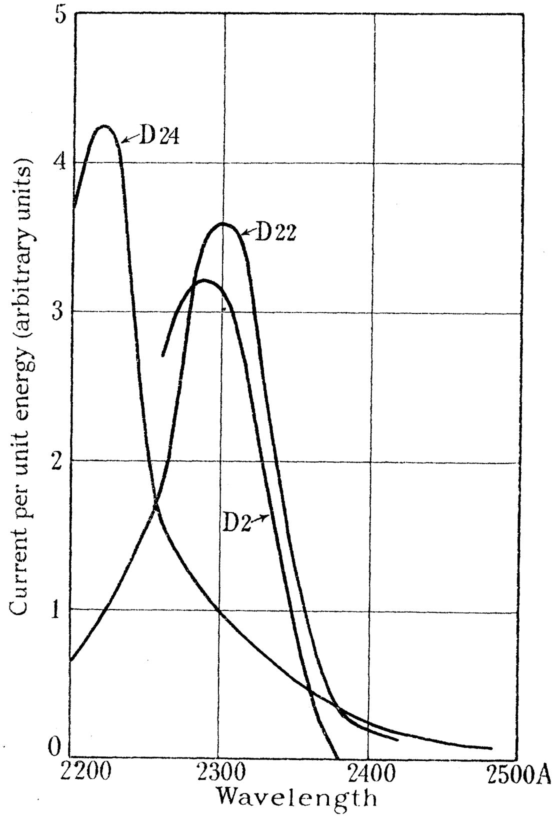

Fig. 15.—Variation with wave-length of currents generated by diamonds of Type 2 in region of activation.

It was observed that the region of greatest activation is similar to that found for D 22 when light of λ 2300 was imposed without any applied voltage.

Features of "dark current."

After diamonds of Type 2 have ceased to be illuminated with light of wave-length λ 2300, a current is detectable but only on applying a voltage. In fig. 16 (*a*) is shown the manner of decay of this current. On continued illumination of D 22 at λ 2300 with 120 v. applied, the current steadily increased. On reaching 24 μ A the light was shut off and the residual current measured for a period of 6 minutes. This curve is typical of many and is readily reproducible.

When no voltage is applied after illumination, the current falls very rapidly; the effect of increasing voltage is to slow down the rate of decay, but after a small critical voltage is surpassed increase in voltage has comparatively small effect on the rate of decay, *e.g.*, at 2 minutes and 0·7 v. only 19% of the initial dark current remained; at 1 v., 17%; at 12 v., 25%; and at 120 v., 23%.

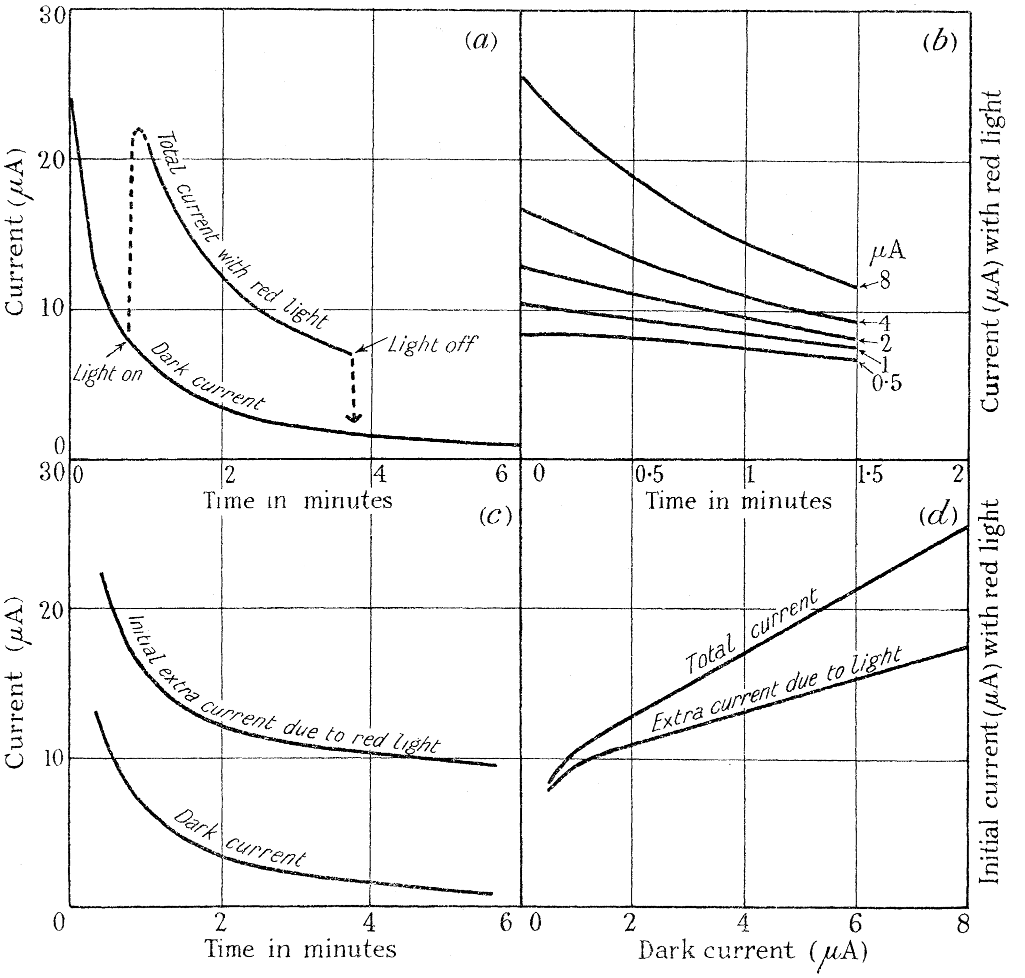

FIG. 16.—Features of current left after illumination of D 22 with λ 2300 :—Decay with and without red light. (*a*) and (*c*)—time after activation; (*b*)—time after imposition of red light.

Most diamonds of this type exhibit the same nature of decay of the dark current, but the rate varies from diamond to diamond, *e.g.*, D 19 is the slowest followed in order by D 22, D 2, D 16, and D 24.

A higher voltage, such as 500 v., when applied to the specially sensitive diamond D 22 which had been caused to phosphoresce with a green glow by light of λ 2300, was found to permit the flow of a large current, accompanied now by a blue glow which disappears at once on withdrawing the voltage; with this higher voltage the rate of decay of the current is much slower than in the examples just quoted.

A peculiarity of D 19 is that it possesses a permanent conductivity apart from previous treatment with light. This diamond is always found capable of passing a current on application of 500 v. accompanied by a blue glow, even although precautions may have been taken to remove possible previous activation.

In the next two Sections will be discussed the phenomena of the quenching of the dark current and the additional current first produced by wave-lengths somewhat longer than λ 2300, and of the persistence of the additional effect at still longer wave-lengths.

(3) REMOVAL OF ACTIVATION—DUE TO λ 2300, BY LIGHT OF λ 2400 TO λ 5000 (DEACTIVATION).

After a diamond of Type 2 has been illuminated by light of λ 2300 it remains in an activated condition for a considerable time when kept in the dark. If light within the above range of wave-lengths is now applied, the conductivity is for a time greatly increased, but the larger part of this photo-conductivity rapidly disappears leaving a small residual photo-current which persists as long as the illumination is continued.

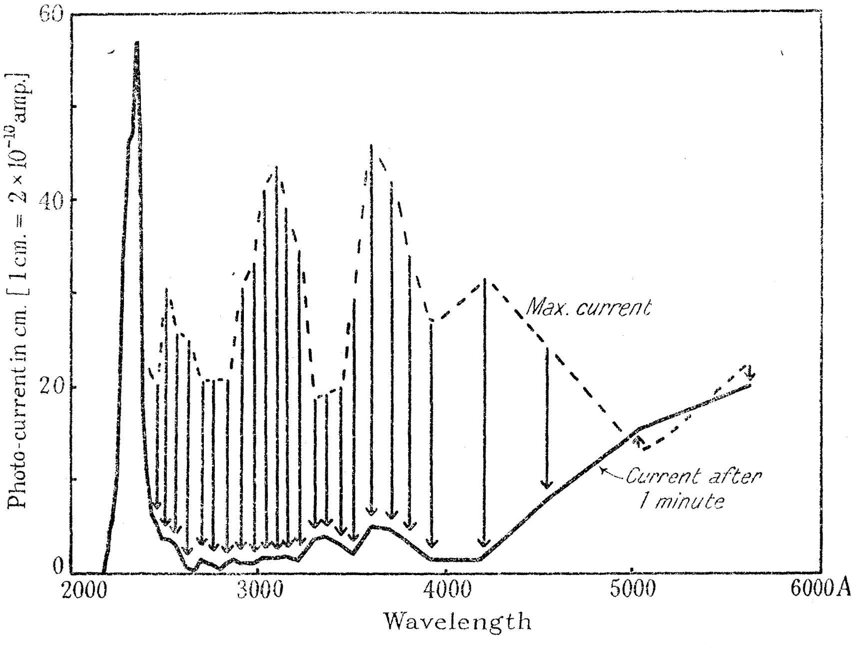

FIG. 17.—Response throughout the spectrum showing regions of activation and deactivation.

These effects were first obtained for D 2, fig. 17, during an attempt to determine its spectral sensitivity. It was observed that after this diamond had been exposed to λ 2300 it exhibited marked photo-conductivity, but on subsequent exposure to longer wave-lengths the considerable current associated with these rapidly fell to a low value but not to zero. To investigate this phenomenon more fully the diamond was activated for 1 minute at λ 2300 before subsequent exposure to each of the higher wave-lengths.

In fig. 17, the maximum current followed by the current flowing after exposure for 1 minute are recorded for each wave-length, and they indicate a region of deactivation extending from about λ 2400 to nearly λ 5000. In this experiment, no correction is made for the greatly varying intensity associated with the different mercury lines of the spectrum.

Determination of most effective deactivating wave-length.

At this stage, many experiments were made to discover at what wave-length the greatest deactivating efficiency resided, while at the same time, the necessity was recognized for referring the effect to constant energy associated with the various mercury lines.

A variable aperture was calibrated for use with monochromator 2 and the mercury lamp, so that certain of the stronger mercury lines could be adjusted to a constant energy value, as measured by a thermopile temporarily occupying the position normally taken by the diamond. The diamond (D 2) was then activated with λ 2300 until a definite current was obtained with 120 v. applied, the monochromator set to the wave-length required, and when one minute had elapsed from the end of the period of activation, the dark current was measured and light of constant intensity, obtained as described from the monochromator, imposed on the diamond. From a comparison of the values of the dark current immediately before exposure and the total current after illumination, it was found that the most effective deactivating wave-length is at λ 2804, for only at this place, after illumination for one minute, was it observed that the total current was smaller than the dark current obtained immediately before exposure to the activating radiation.

With D 22, measurements were made in a somewhat different manner, as it is characterized by giving, after activation, a dark current which decays much more slowly than that given by D 2. Diamond D 22 was activated with λ 2300 until with 120 v. a current of 24 μA was obtained. During the time taken by the dark current to decay from 24 to 8 μA, the monochromator was set to the desired wave-length and intensity, and when 8 μA was reached the diamond was illuminated by the appropriate wave-length and the subsequent current variations noted. A normal decay curve without illumination, was also obtained, and from the two decay curves was found the time t (from 8 μA) before the currents, with and without light, reached the same value, *i.e.*, the time that elapsed before the extra current due to the light was lost.

Table VIII gives the values of t for different wave-lengths, all adjusted to the same intensity. $1/t$ was taken as a measure of the deactivating power of each wave-length, and the variation of $1/t$ with wave-length is shown in fig. 18. As with D 2, the most effective deactivating wave-length is found to be λ 2804.

TABLE VIII.—Variation of time with wave-length.

λ.	t (minutes).	$1/t$.
2300	—	0
2483	0·32	3·1
2537	0·26	3·85
2652	0·19	5·3
2804	0·156	6·4
3022	0·24	4·2
3129	0·24	4·2
3650	0·26	3·85
4047	0·57	1·75
4358	1·50	0·67
5550	12·0	0·08

In several other experiments not recorded here, the results indicated a wave-length of λ 2804 as being most effective for deactivation.

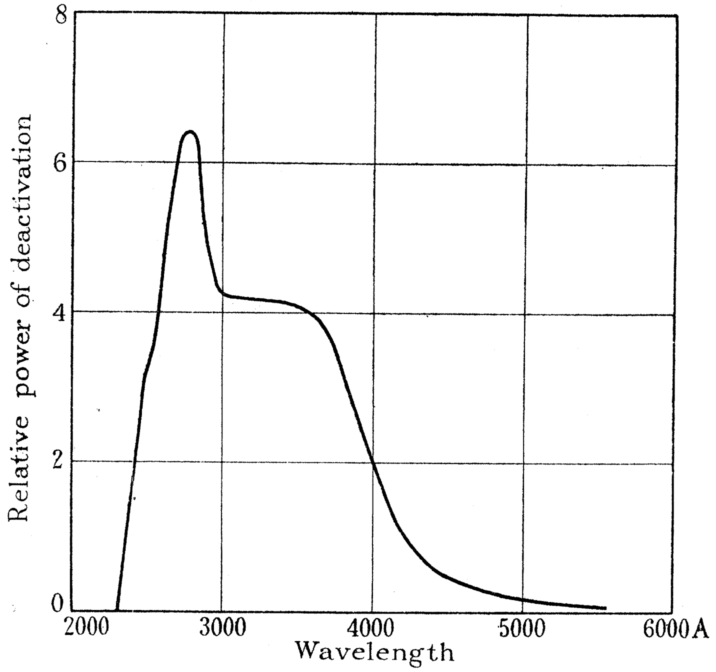

FIG. 18.—Variation of deactivating power with wave-length for diamond D 22.

LENZ,* in his work on the absorption of light of different wave-lengths by a diamond, evidently of Type 2, found a large absorption at about λ 2300 to λ 2400, but also smaller absorptions at λ 2520 and λ 2750.

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* 'Ann. Physik,' vol. 83, p. 941 (1927).

(4) LARGE PHOTO-CONDUCTIVITY WHEN LIGHT OF WAVE-LENGTH GREATER THAN λ 5000 IS APPLIED TO AN ACTIVATED BUT NOT TO A DEACTIVATED DIAMOND. (REGION OF ADJUVANT EFFECT.)

Mention has been made in the foregoing sections of the increase in current when light of wave-length greater than λ 5000 is applied to a diamond that has previously been activated by light of λ 2300, even although it had been kept in the dark for some time, provided in the interval it has not been subjected to light of the deactivating region just described.

An indication of this adjuvant effect was obtained in the early experiment, fig. 17, when subjection to wave-lengths longer than λ 5000 appeared to lead to an increased conductivity, although the absorption by diamond of visible light of wave-length $>$ λ 5000 is known to be very small (*cf.* PETER, *loc. cit.*).

In the course of further work, the features of this additional current emerged. Thus it can persist with scarcely-diminished strength so long as light of the wave-lengths in this region is applied to a diamond whose preliminary activation by λ 2300, as shown by the dark current, had decayed to a constant value; the adjuvant current may greatly exceed even that produced by the activating light, and may be many hundred times the dark current; the adjuvant current in a recently-activated diamond decays, but more slowly than does the dark current; and the most active wave-length is at λ 5850.

(1) *Persistence of the adjuvant current on illumination.*

It has been a frequent experience that when some time has elapsed after the activation of diamond, a current is obtained with light of this region which remains constant so long as this light is applied, or at least decays very slowly. The rate of decay is examined more closely below (see (3)), but it may be said that it ultimately seems to become asymptotic to the time axis.

(2) *Magnitude of the adjuvant current.*

Even 20 minutes after activation, application of red light has been found to produce a current eight times that given by the activating light of λ 2300 itself, and 700 times that of the residual dark current. This was when the intensity of the red light was high, being derived from a 100 candle-power pointolite lamp and Ilford infra-red filter.

(3) *Decay of adjuvant current in a freshly activated diamond.*

The adjuvant current decays rapidly after the activating light has been shut off; the rate then slows down until it becomes nearly constant, as described above (1). In fig. 16 (*a*) are given curves of the decay of the adjuvant as well as of the dark current up to four minutes. Noticeable are the rapid rise and also fall when the red light is applied and cut off respectively.

A strict comparison was made between dark current and the additional effect produced by red light for increasing times after activation. Since, however, the adjuvant current required varied with time in the manner shown in fig. 16 (*a*), it was necessary to extrapolate to zero time with respect to the imposition of red light, as indicated in fig. 16 (*b*), in order to obtain the instantaneous value of the extra current due to the red light. This procedure was adopted for different values of the dark current varying from 0·5 to 8μ A, shown on the right of the curves of fig. 16 (*b*).

In fig. 16 (*c*) are plotted these instantaneous extra currents due to red light, and also the dark current against the time elapsing after activation. Constancy in the difference between these two currents at equal times is to be remarked, leading to a linear relationship between dark current and extra or total current with red light, as is shown in fig. 16 (*d*).

This linear relationship was found also for a different intensity of red light, and leads to the expression $i_r = K(\alpha + i_d)$, where i_r is the total current with red light on, i_d the corresponding dark current, K a constant depending on intensity of red light, and α, one depending on the degree of activation.

(4) *Determination of most active adjuvant wave-length.*

In the foregoing description the term " red light " has been used, as it was by means of a red Ilford filter and tungsten filament lamp that we commonly got the results characteristic of this region. When no account was taken of the energy associated with the different wave-lengths, λ 7220 appeared to be most effective, but when the associated energy was determined by a thermopile for the respective wave-lengths, and allowance made for this, the greatest effect for unit spectral energy was found to be at λ 5850.

In this experiment, fig. 19, the diamond D 22, after having been activated and then

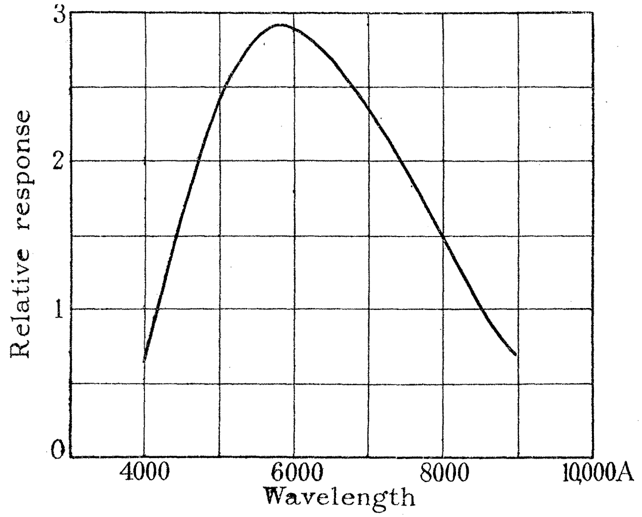

FIG. 19.—Variation of adjuvant current with wave-length for D 22.

left in the dark for 18 hours, was found to have a very small dark current (120 volts). Radiation was then imposed on it between λ 4000 and 9000 from a tungsten-filament lamp and through monochromator 2. The readings corrected for thermopile values were then plotted as shown in the figure.

EFFECT OF TEMPERATURE ON THE PHOTO-ELECTRIC PROPERTIES OF DIAMONDS OF TYPE 2 (FROM – 160° C. TO 300° C.).

Experiments without an applied field.

The currents generated by two diamonds of Type 2 (D 2 and D 22) when exposed to light have been measured over the temperature range – 160° C. to + 300° C. For low temperatures the apparatus and procedure is given on pp. 480 and 500, and for temperatures above normal on p. 500.

Fig. 20 (*a*) shows the variation of the current produced by the unfiltered radiation from the mercury lamp, and also the extra current produced by red light acting in addition to the light from the mercury lamp. In these experiments this can be regarded solely as a source of activating light, since the deactivating wave-lengths are inoperative in the presence of powerful activating radiation, and the amount of red light emitted by the mercury arc is quite negligible compared with the intensity of red light separately available.

Diamond D 22 is most sensitive to light from the mercury lamp at about – 40° C. Above 300° C. little effect remains, and below – 100° C. the current becomes steady at about 20% of its value at room temperature. The extra current due to the red light—which, it should be noted, is almost without effect in the absence of the light from the mercury lamp—is negligible above 200° C., but below this the current increases, in a somewhat irregular manner with fall in temperature, and remains fairly steady below – 100° C.

Diamond D 2 gives results similar to those of D 22, but with D 2 both the current produced by the light from the mercury lamp and the extra current due to the red light show a maximum at – 40° C. Below – 100° C., however, both effects fall off more rapidly than with D 22.

Experiments with an applied field.

Fig. 20 (*b*) shows the variation of current for D 2 over the range – 130° C. to + 320° C., with an applied potential of 10 v. Below – 130° C. the conductivity produced by the light of the mercury lamp was negligible, but above this the current rose with increasing temperature and passed through a maximum at 250° C. At still higher temperatures the current fell off rapidly. The extra current due to red light was found to vary in much the same manner as that produced by the light of the mercury lamp, but the maximum current was obtained at 160° C.

In view of the great activity of D 22, small voltages had to be used, such as 0·165 v., this being half of that needed to balance completely the spontaneous current generated by the diamond itself when exposed to mercury light at room temperature in this experiment. Fig. 20 (*b*) shows that above 77° C. the 0·165 v. was more than enough to balance the spontaneous current, and for the higher temperatures the results follow closely those obtained for D 2, the highest current being observed at 250° C. The curve showing the extra current generated by additional red light is very similar in this case to that obtained for light from the mercury lamp, but falls off somewhat more rapidly for the higher temperatures.

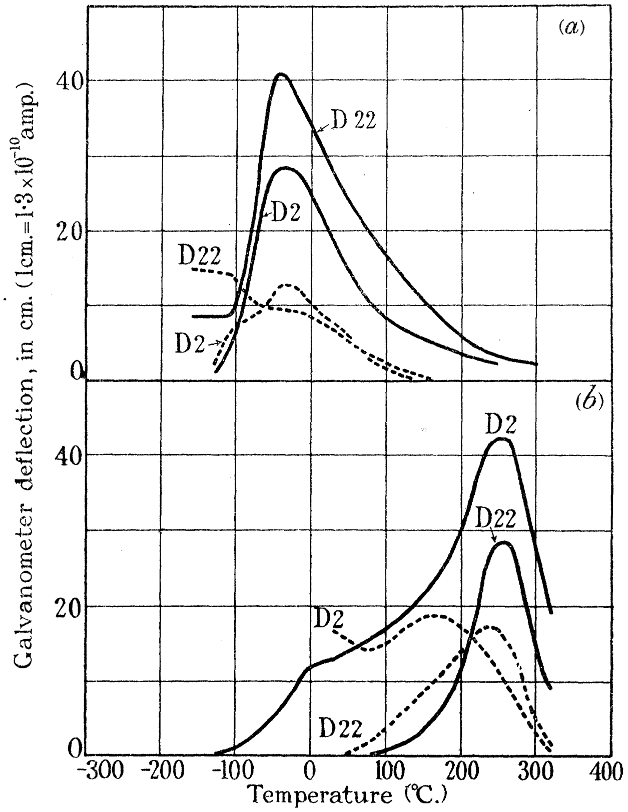

FIG. 20.—Full curves :—Variation with temperature of currents generated by diamonds D 2 and D 22 on imposition of light from mercury lamp, without applied voltage (*a*), and with applied voltage (*b*). Broken curves :—Variation with temperature of extra currents generated by addition of red light, without applied voltage (*a*) and with applied voltage (*b*). The intensity of light used was much reduced in (*b*).

Variation of dark current with temperature.

While measurements on the photo-conductivity of D 2 and D 22, with a small applied field, at the higher temperatures were being made, it was noticed that the decay of the current on shutting off the light became more and more sluggish as the temperature was increased, although the effect was not sufficiently noticeable to interfere with the measurements.

It was considered of interest to investigate the variation of dark current with temperature in D 19, which was found to have considerable conductivity at room temperature even without previous activation by λ 2300. Measurements were accordingly made on this diamond up to 300° C., with a small applied potential of 0·01 v., and the conductivity was found to increase with rising temperature, the value at 300° C. being nearly twenty times as great as at room temperature.

This is in line with the experiments of LENZ,* who finds that while the primary current is not affected by low temperatures, the dark current disappears.

DISCUSSION OF RESULTS.

In order to facilitate reference, the properties of the two types of diamond are tabulated below so as to exhibit those features they have in common, and also those in which they differ.

TABLE IX.—Summary of Features of Types.

	Type 1.	Type 2.
Occurrence	The common type	Rarer.
Form	Derivatives of cubic system	Derivatives of cubic system, but with fine parallel laminations.
Isotropy	Considerable anisotropy between crossed nicols	Nearly isotropic.
Infra-red absorption-persisting at − 170° C.	At 3, 4·1, 4·8 and 8 μ	At 3, 4·1 and 4·8 μ. No band at 8 μ.
Ultra-violet absorption	Not complete till 3000 λ; sequencies of bands near this W.L. increasing in intensity down to − 170° C.	Not complete till 2250 λ. Faint absorption and diffuse bands near this W.L., disappearing at − 100° C.
Photo-electric conductivity	Small with even high voltages	Present with small voltages or none.
X-ray pattern	Normal. Ratio of intensity of 111/222 usually small	Normal. Ratio of intensity of 111/222 usually large.

Electron diffraction	Similar.
Raman difference	Similar (1332 cm.$^{-1}$).
Triboluminescence	Similar.
Dielectric constant	Similar (5·01 and 4·88).
Refractive index	Similar.
Specific gravity	Similar.
Colour	Similar (water-clear).

Discussion of these differences may conveniently be considered under the headings of the respective optical and photo-electric properties.

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* *Loc. cit.* (1927).

OPTICAL.

Orientation of discussion.

It has gradually been impressed upon us, in the course of this work, that diamonds of Type 2 are more nearly perfect. Thus, they are freer from optical strain and are less absorptive of light in both ultra-violet and infra-red regions of the spectrum. We propose, therefore, after considering the properties both types have in common, to discuss the optical properties of diamonds of Type 2 with the inferences to be derived from that discussion, and thereafter to consider in what manner diamonds of Type 1 diverge in these properties from those of the more nearly perfect crystals of Type 2.

On account of the interconnexion of atomic effects, as revealed by the infra-red spectrum, with those in the ultra-violet, more closely associated with electronic levels, it is necessary to consider together the phenomena observed in the infra-red, the visible, the ultra-violet and the X-ray regions of the spectrum.

Problems arising from this work.

Various problems have emerged in the course of this work. Such are :—

(*a*) the atomic vibrations in all diamonds ;

(*b*) the similarity of the Raman effect in all diamonds ; and the calculation of the frequency of the carbon linking in diamond ;

(*c*) the greater optical isotropy of diamonds of Type 2 ;

(*d*) correlation of bands in infra-red spectrum common to all diamonds with modes of vibration ; consideration of the additional band at 8 μ in Type 1 ;

(*e*) transparency of Type 2 diamonds to λ 2250 (with faint absorption bands near this) ; but to λ 3000 only in Type 1, with sequences of lines, and relationship to infra-red spectrum.

(*a*) *Atomic vibrations in all diamonds.*—Both types possess the Bragg structure of diamond as shown by their X-ray pattern, have the same electron diffraction, the same Raman difference, dielectric constant, refractive index and specific gravity. Up to 7 μ they have an infra-red spectrum in common.

Of outstanding importance is the identity of general X-ray pattern in the two types of diamond. This shows that both kinds of diamond have their atoms arranged in space in the same way, namely the system of interpenetrating tetrahedra described by Bragg, the carbon atoms being at the apices of the tetrahedra, and also at the median points. But while this defines the position of the atoms in the space lattice, it takes no account of vibrations about an equilibrium position, nor of electronic changes with which this may be associated. Such information is afforded by infra-red, ultra-violet and Raman spectra.

Further, it was early deduced from its abnormal specific heat at low temperatures (p. 477) that the atoms in diamond had a fundamental frequency of vibration. This frequency proves to be the same as that given by the Raman spectrum — 1332 cm.$^{-1}$ or 7·51 μ (p. 494). That this is a likely order of frequency for carbon vibrating against carbon is discussed later.

Since both types of diamond have the same Raman difference, we may conclude that each has a fundamental frequency of vibration of the carbon atoms, and most simply of a C — C linking, indicating a mode of vibration in which there is no change in the electric moment between the carbon atoms.

From the values mentioned on p. 475, it is clear that the refractive index for the two types of diamond, albeit unrecognized as such, is the same, and in conformity with this we find that the dielectric constants for the two types do not differ more than by a few per cent. Further, when the dielectric constant is calculated from the refractive index at infinite wave-length, a value is obtained of 5·67 (PETER, *loc. cit.*, p. 364), while our determinations are 5·01 (Type 1) and 4·88 (Type 2) (p. 476).

There are thus manifestations, shown in the above-mentioned ways, that in addition to the static condition as revealed by X-rays, there is one mode of vibration of one carbon atom against another, and this we find occurs in all diamonds.

(*b*) *The similarity of the Raman effect in all diamonds ; and calculation of the frequency of the carbon linking in diamond.*—Investigation of various specimens (see Table VI) showed that the Raman difference for diamonds of both types was the same, namely, 1332 cm.$^{-1}$ (or 7·51 μ).

In considering the origin of this Raman difference, the problem cannot be regarded in the same way as was done by DENNISON* for methane, or by its extension in the manner worked out by SCHAEFER and KERN† for carbon tetrachloride, since in these cases the molecules can be considered as separate entities. On the other hand, the frequency calculated from specific heat data by NERNST and LINDEMANN‡ gives a result at 7·51 μ agreeing extraordinarily closely with 1332 cm.$^{-1}$ (7·51 μ).

The most likely origin of this line is in an optically inactive frequency, occurring in both types, this being due to the vibration of two carbon atoms along the line joining their nuclei (ν_1, see below) when such a vibration involves no change in the centre of gravity of the electric moment.

In diamonds of Type 2, no optical frequency occurs in the neighbourhood of 1332 cm.$^{-1}$, the nearest being at 2095 cm.$^{-1}$ (4·8 μ), a band in the infra-red spectrum common to both diamonds.

Near 1332 cm.$^{-1}$, however, in diamonds of Type 1, is an intense infra-red band which embraces it, and within the contour of this band are vibrations at distances of ± 41 cm.$^{-1}$ from it. Thus, the inactive frequency in diamonds of Type 2, is an optically active one in Type 1, and its origin is considered later (p. 520). The small ratio of X-ray

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* 'Astrophys. J.,' vol. 62, p. 84 (1925).

† 'Z. Physik,' vol. 78, p. 608 (1932).

‡ 'Z. phys. Chem.,' vol. 17, p. 822 (1911).

reflection from the 111/222 planes in Type 1 diamonds lends support to the supposition that the electron arrangement is in some way different in the two types.

There is evidence, therefore, supporting our view that diamonds of Type 2 are more free from disturbing vibrations than those of Type 1.

Calculation of frequency of C — C linking.

With the object of seeing if the frequency 1332 cm.$^{-1}$ is a likely one for a C — C linking, some calculations have been made by taking into consideration the strengths of the carbon bonds as determined from the heat of dissociation, and from Raman spectra of simple hydrocarbons. The C — C vibration in ethane is only about 990 cm.$^{-1}$, which is far less than the Raman line of diamond at 1332 cm.$^{-1}$. On the other hand, compounds containing C $\equiv$ C linkage have Raman lines about 2160 cm.$^{-1}$, or rather higher than this.* On the assumption that the force acting between the C atoms in the C $\equiv$ C linkage is three times that of the C — C linkage, and that the frequencies are to a first approximation connected with the binding force by an expression of the type $\nu_0 \approx A\sqrt{\frac{K}{\mu}}$ where A is constant and K is the binding force, the frequencies to be expected would be in the ratio 1 : $\sqrt{3}$, giving for the C — C vibration 1248 cm.$^{-1}$ In the extreme case where the bonds are disrupted, the work of dissociation is 136 calories for C $\equiv$ C in allylene, 155 calories in dimethyldiacetylene, and 68 for C — C in diamond.† Again, assuming 2160 cm.$^{-1}$ as the frequency for C $\equiv$ C, the frequency for C — C is given by 2160 $\sqrt{\frac{68}{A}}$ (A = 136 or 155) or 1528 to 1430 cm.$^{-1}$ Similarly, assuming 1630 cm.$^{-1}$ for the Raman frequency of C = C linkage,‡ and for the heat of its dissociation 104 calories in the case of propylene and 130 in the case of 2 : 4 hexadiene, the corresponding values for the C — C linkage will be 1318 and 1180 cm.$^{-1}$ Allowing for the necessarily approximate character of these calculations, it is seen that the values so calculated are not very far removed from 1332 cm.$^{-1}$, the observed Raman frequency of diamond.

Bhagavantam (*loc. cit.*) has used his observations to calculate the infra-red bands reported by us§ as combinations, taking Reinkober's band at 710 cm^{-1} as a fundamental; but we have failed to observe this band in the infra-red absorption of any diamond (p. 486). Nor are we of the opinion that the very small bands of 1 or 2% intensity assumed to exist by this author (*loc. cit.*, p. 758) actually occur, but think that they are either interference effects|| or irregularities in the curves, of no significance in view of the difficulty in making measurements of absorption with solids such as diamonds closer than 1% or so in this part of the spectrum.

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* *Cf.* Kohlrausch, "Smekal–Raman Effekt," pp. 154 and 327.

† *Cf.* Clopatt, 'Comment. Phys.-Math. Soc. Sci. Fennica,' vol. 6, No. 23 (1933).

‡ Kohlrausch, *loc. cit.*, pp. 154 and 322.

§ 'Nature,' vol. 125, p. 704 (1930)

|| *Cf.* Taylor and Rideal, 'Phil. Mag.,' vol. 4, p. 682 (1927).

We next proceed to discuss the differences of an optical character exhibited by the two types which we now recognize.

(*c*) *The greater optical isotropy of diamonds of Type* 2.—In his later paper, FRIEDEL (*loc. cit.*) sums up his evidence for believing that a paramorphic transformation takes place when diamond cools below 1885° C. (at atmospheric pressure). About 10° below this point his experiments indicate a certain degree of plasticity as shown by the behaviour of the black isotropic bands, but at 1885° ±5° C. the diamond breaks into fragments on account of a rapid change in volume, and birefringence is no longer noticed in the fragments so long as they do not cool below this temperature. He concludes that in cooling from the plastic state the diamond has undergone a discontinuous transformation at a temperature probably much higher than 1885° C. under the influence of strong pressure; and that in passing from the plastic state, it surpasses the elastic limit while crystallizing, being left with a permanent deformation. This appears as the optical anisotropy which FRIEDEL gets with the diamonds he has examined, and which we get with diamonds of Type 1, but scarcely with Type 2 (p. 472).

It may be, therefore, that diamonds of Type 2 have passed through the transformation point under better regulated conditions than obtained for Type 1, such as a gradual fall in pressure, with the result that stresses have had an opportunity to be relieved, as shown by the formation of slip planes or mosaic structure, and generally a more isotropic and less strained condition, as indeed is found in diamonds of Type 2 (p. 473).

(*d*) *Correlation of bands in infra-red spectrum common to all diamonds with modes of vibration; consideration of the additional band at* 8 μ *in Type* 1.—Up to 7 μ in the infra-red region both types of diamond have absorption bands, an optical activity that is a sign of changes in electric moment; beyond 7 μ diamonds of Type 2 have no bands as far as 17 μ, but an intense band at 8 μ appears in Type 1 (see fig. 7). The same Raman frequency, however, occurs at 7·51 μ (1332 cm^{-1}) in both types.

A combination of an inactive frequency with an optically active vibration giving rise to a band has been observed in solids, as for example in calcite, several of whose bands SCHAEFER (*loc. cit.*) identified as combinations of an optically inactive (Raman) frequency at 9·1 μ with optically active fundamentals.

Before considering the allocation of the infra-red bands, since there is the abovementioned evidence for vibrations of the carbon atom in diamond, it may be well to review some of their possible modes. These will be of an oscillatory nature, although from recent work on solids, rotation or at least a nutation is not excluded.*

If it had been that the sole vibrational movement of the carbon atoms was one to and fro along the line joining them, each having the same energy but in opposite phase, then such conditions in a diatomic molecule would lead to the expectation of only one frequency being found and that a Raman frequency, since no change in the position of the centre of the electric moment of the two carbon atoms is involved. In both types of diamond the Raman frequency of 1332 $\mathrm{cm.}^{-1}$ is found, so that it is

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* *Cf.* L. PAULING, 'Phys. Rev.,' vol. 36, p. 430 (1930).

concluded that in both there are carbon atoms vibrating in the above manner with a restoring force due to a C—C linking. This is ν_1 (see below).

But, in addition, the optical data in infra-red and ultra-violet show that there are other modes of vibration and these must be connected with changes in the electric moment.

It is instructive, therefore, to review some possible modes of vibration of the C—C linking, having regard to the direction of the forces applied to each of these two carbon atoms along their lines of connexion with adjoining carbon atoms in the Bragg model, making the simplifying assumptions that the resolved components are equal in magnitude and that for a first approximation two tetrahedra can be considered alone. Each of these in a next approximation would naturally in turn be affected by forces still farther removed.

Different modes of vibration may be illustrated as in fig. 21 :—

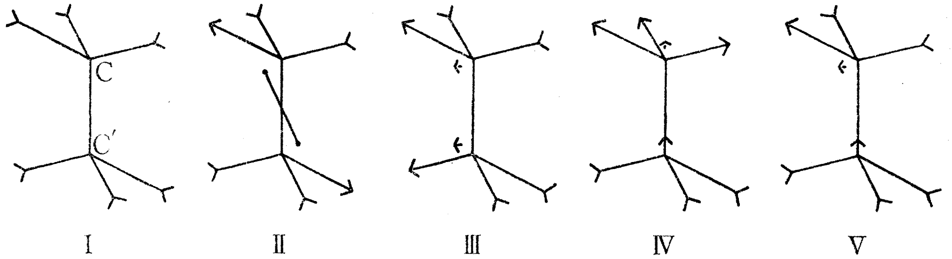

Fig. 21.—Modes of vibration of C — C.

In I it is assumed that three equal resolved components are applied to each of the two carbon atoms C and C^1 in opposite phase. The central position of the electric moment is unaffected and as the frequency is optically inactive, and obviously a most probable vibration, it may be identified with the Raman frequency 1332 cm.$^{-1}$. This may be called ν_1.

In II there is also a symmetrical arrangement of resolved forces, but those applied to one atom are not all in the same phase, each being in opposite phase from its counterpart on the other atom. While this should produce three vibrations of the carbon atoms, there would be no change in the centre of the electric moment and so no optical frequency.

In III, three variants of a mode of vibration are indicated, characterized by an unsymmetrical application of the resolved forces to each of the two carbon atoms. The effect is to move the centre of the electric moment to the side of the line joining the carbon atoms and in the plane of the unequal force. An active frequency should result (ν_2 or ν_3—see below).

In IV each of the resolved forces on each atom is in the same direction, but unlike I, where the three oppose each other, here they reinforce one another. Such a vibration involves a change of the electric moment in space, with the production of an optical frequency (ν_2 or ν_3—see below).

In V is found a combination of III and IV.

From this review of the modes of vibration of the carbon atoms in the C—C link, it would appear that there is clearly one—and that the simplest—which should be optically inactive, but with a Raman frequency (I), another also optically inactive (II), which might also be expected to give rise to a Raman frequency, although only one has been found by us.

The torque applied to the central position of the electric moment as exemplified in the less symmetrical arrangement in V might be considered as made up of III and IV, and such a combination with I may give rise to the optical combination bands about 3 μ.

The observed infra-red bands of Type 2 diamonds may be arranged as a series of optical frequencies, including the Raman frequency as a fundamental, together with combinations of these and the Raman frequency. We may consider 2481 and 2095 cm.$^{-1}$ to be the active fundamental frequencies, for the degree of absorption in these regions is consistent with fundamental active vibrations, and models III and IV would allow for these active frequencies. For another active frequency we take that at 84 cm.$^{-1}$ as being either a much slower vibrational frequency much farther in the infra-red, or a "nutational" frequency. Such an assumption is in accordance with the usual assignment of frequencies in infra-red bands which have double peaks, the two limbs here being B α and B β 2095 ± 84 cm.$^{-1}$. The whole infra-red band system of Type 2 and of Type 1 up to 7 μ may then be made up of the fundamentals, and combinations of these as shown in Table X.

TABLE X.—Allocation of frequencies in all diamonds up to 7 μ.

$$\begin{array}{l}\text{Fundamental}\\ \text{Frequencies}\end{array}\begin{cases} \nu_1 = 1332 \text{ cm.}^{-1} \text{ (Raman).}\\ \left.\begin{array}{l}\nu_2 = 2095\text{ cm.}^{-1}\\ \nu_3 = 2481\text{ cm.}^{-1}\end{array}\right\}\text{ Model III or IV.}\\ \nu_4 = 84 \quad \text{cm.}^{-1} \text{ — I.R. difference from } 4\cdot 8\ \mu \text{ band.}\end{cases}$$

Combinations.			Calcd. cm.$^{-1}$.	Observed cm.$^{-1}$.
Branches of Band at 4·8 μ	Bα	$\nu_2 + \nu_4$	2179	2176
	Bβ	$\nu_2 - \nu_4$	2011	2007
Band at 3 μ	Aα	$\nu_1 + \nu_3$	3813	3790
	Aβ	$3\,\nu_1 + \nu_2 - \nu_3$	3610	ca. 3600
	A dip	$\nu_1 + \nu_2$	3427	ca. 3400
	Aγ	$3\,\nu_1 + 2\,\nu_2 - 2\,\nu_3$	3224	ca. 3160

The band about 3 μ is here represented as a much more complicated combination system than the others. Such combinations are less likely to occur than the simpler ones, and the band would therefore be anticipated to have comparatively small intensity and to be rather ill-defined, as is indeed found (see fig. 7). Allowing for this, the calculated frequencies for the 3 μ band are as good as can be expected. It is also to be noted that the centre of the 3 μ band (the dip) is quite a simple combination of ν_1 and ν_2, thus serving to fix this centre more accurately, and to afford an additional reason for regarding the parts of these bands as combinations.

As there is no change in the structure of the bands at low temperatures (see p. 486), the ground state must be unique, or, in other words, a diamond at normal temperatures does not have nutational energy, but only acquires it, together with vibrational energy of a higher order when it absorbs radiation.

The structure of the diamond bands cannot be regarded as similar to those of gaseous molecules having P and R branches, in which the P branch would tend to disappear at low temperatures.

The 8 μ *band in diamonds of Type* 1.—We have still to consider the reason for diamonds of Type 1 showing the strong band at 8 μ. In the first place, the strong peak of the band at 1289 cm.$^{-1}$ is near the Raman frequency 1332 cm.$^{-1}$ and differs from it in frequency in the same manner as has been observed between Raman lines and infra-red bands in other substances (*cf.* benzene, calcite, ammonia*). The less prominent peaks at C α and C γ at 1372 and 1208 cm.$^{-1}$ are then derived very simply from the band at 1289 cm.$^{-1}$ by adding or deducting ν_4. The actual values are 1373 and 1205 cm.$^{-1}$ so that the peaks of the band at 8 μ of Type 1 diamonds would, on this view, represent different energy levels not found in diamonds of Type 2. Furthermore, the ultra-violet bands of these diamonds can be arranged to include a frequency 1289 cm.$^{-1}$ (see below) which is C β and another frequency of 84 cm.$^{-1}$ which also occurs in the bands about 8 μ. In view of the strained condition of Type 1 diamonds as indicated by the optical anisotropy, we may consider these different energy levels to be connected with the strain, and associate the 8 μ band with this condition. This conception is novel, but we believe not entirely impossible of belief.

(*e*) *Transparency of Type* 2 *diamonds to* λ 2250 (*with faint absorption band near this*); *but to* λ 3000 *only in Type* 1, *with sequences of lines, and relationship to infra-red spectrum.*—Figs. 29 and 30, Plates 12 and 13 show at once the striking difference in ultra-violet transparency of the two types of diamond. Type 2 transmits as far as λ 2250, while Type 1 only as far as about λ 3000. It is also to be remarked that the photographs which were taken by the aid of a continuous source of illumination (see p. 488) show no band system for Type 2, such as is brought out in Type 1 in the neighbourhood of λ 3000.

Type 2 diamonds are of greater " optical " purity as they are much more transparent in the ultra-violet and infra-red regions. This seems to us to be consistent with the absence of optical strain in this type of diamond. A feature of the transmission spectrum of diamonds of this type is a faint selective absorption from λ 2351 to λ 2330 containing two very diffuse bands. Unlike the bands found in diamonds of Type 1, the effect of

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* KOHLRAUSCH, *loc. cit.*, pp. 329, 343, 353; ROBERTSON and FOX, 'Proc. Roy. Soc.,' A, vol. 120, p. 165 (1928); SCHAEFER and MATOSSI, "Das Ultrarote Spektrum" pp. 345 and 272 (1930).

lowering temperature is not to sharpen these bands but to suppress them. The connexion of this suppression and fall in photo-conductivity is dealt with later (see p. 533).

Fig. 30 shows the effect of raising the temperature from 17° to 314° on the absorption of Type 2 diamonds. The shift towards the red is about 20 cm.$^{-1}$ per 10° C., namely, from 42463 to 41788 cm.$^{-1}$, and there is a sudden increase in the sharpness of the absorption edge when the region of the diffuse bands is left behind. This may be seen from a comparison of the absorption at 17° and 87°, where the diffuse band at room temperature is seen to be obliterated at the higher temperature. This increase in absorption of 675 cm.$^{-1}$ corresponds to about 1900 calories, a quantity of absorbed heat comparable with that to be expected from the rapid change in specific heat of diamond on raising it through the range of temperature indicated.

Thus if we consider as a first approximation that the heat involved is concerned with the C—C linkage of diamond, the value found corresponds to about 80 calories per gram, a value corresponding approximately to a specific heat rather less than 0·3. It is to be noted that MAGNUS* finds for the specific heat at 11° C. 0·11 and at 327° 0·33.

Turning now to the sequencies of bands which by the aid of the continuous source described we have discovered in the spectrum of diamonds of Type 1, although their number is small they would appear to fall into a scheme given generally by an expression of the usual kind for bands of polyatomic molecules,

$$\upsilon = \upsilon_e + v_a \times 1289 - v_a^2 \times \text{const.} \pm v_b \times 84,$$

where υ_e is the electronic frequency of the transition; 1289 cm.$^{-1}$ represents a vibrational frequency (namely C β) of the diamond in an excited state, and not far removed from the Raman frequency in the unexcited state (1332 cm.$^{-1}$); $v_a^2 \times$ const. is a correcting factor for anharmonicity; and in $v_b \times 84$ the number 84 is the ν_4 fundamental derived (see p. 522) from the consideration of the peaks of the infra-red band at 4·8 μ, and it also occurs as the differences in the peaks of the 8 μ band, while v_a and v_b are whole numbers or zero. Some measure of the anharmonicity can be deduced from the differences of 1385 and 1254 cm.$^{-1}$ from 1289 ± 84 corresponding to Cα (1372) and C γ (1208 cm.$^{-1}$). While it is not possible to consider a rotational frequency of 84 cm.$^{-1}$ in a solid, there is no reason to suppose that a slow oscillation of a carbon atom cannot occur in a direction at right angles to the line of union of the carbon atoms of the lattice.

If it is permissible to arrange the bands in such a scheme as that proposed, it follows that the carbon atom in the diamond when the structure is strained can be excited to energy levels represented by 30321, 31706 and 32960 cm.$^{-1}$, the strong components of the sequencies found (see p. 490); and it is clear from the marked absorption of all ultraviolet radiation less than λ 3000 in Type 1 diamonds that the electrons are capable of responding to such radiation, although the effect is shown as pronounced general absorption and not as individual bands.

It is to be noted that the differences of those more prominent bands 32960—31706=

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* 'Ann. Physik,' vol. 70, p. 221 (1923).

1254 cm.$^{-1}$, and 31706—30321=1385 cm.$^{-1}$, are near peaks C γ and C α of the 8 μ band (see p. 483). It is thus indicated that the physical condition of Type 1 diamonds giving rise to the 8 μ band is likewise concerned in the ultra-violet bands of those structurally " impure " diamonds.

The feebler bands between these stronger ultra-violet bands would appear to arise from rather lower energy states of the carbon atom in diamonds of this type.

Apart from the system of bands just discussed, we were able to obtain with one diamond a fairly strong wide band with its centre about λ 4155, fig. 33, Plate 14, and it is to be noted that this is in the same place as the fluorescence band observed in photographs of the Raman effect in some diamonds. That the band and fluorescence are closely allied in these specimens is obvious when they are examined with the iron arc photographs as fiduciary spectra. In the colourless diamonds at our disposal this band was observed strongly in one specimen only, although indications were obtained in two or three other diamonds in the scattered radiation while photographing the Raman lines.

It was hoped that the band system which we have found in all the diamonds of Type 1 examined in the ultra-violet region might have been connected with systems of C_2 bands already known in emission,* but while at first sight some resemblances appeared to emerge in the energy differences, closer study failed to establish a definite connexion. This resemblance might perhaps be the less likely since the C_2 molecule is probably bound by double bonds, while C — C in diamond has a single bond.

In fig. 29 the effect of raising the temperature of Type 1 diamonds to 316° C. is seen. There is a continuous shift of the end of the spectrum towards the longer wave region (see also Table V (*a*)) and at the same time the bands lose their sharpness. The rate of increase of the total absorption is again about 20 cm.$^{-1}$ per 10° C. The increase in continuous complete absorption at the higher temperatures and suppression of the finer bands indicates that the energy absorbed is no longer quantized, or, in other words, the electrons having been brought up to a continuous energy level fall back continuously.† Over the region 20° to 316° the increase in absorption 32616 to 32030 cm.$^{-1}$, namely, 586 cm.$^{-1}$ corresponds to about 1700 calories. If we again consider the heat to be taken up in acting on the union C—C, approximately 70 calories per gram is indicated, a value of the expected order of magnitude for the specific heat.

It will have been observed that while lowering of temperature causes a diminution of absorption in the ultra-violet, and raising the temperature an increase, no such effect was found in the infra-red. Such an antithesis would dispose of an explanation that effects in the ultra-violet are simply due to the suppression or promotion of different levels in the ground state with change in temperature.

This subject cannot be dismissed without a reference to the vague suggestions (see above) referring the origin of the bands and the pronounced absorption to impurities

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* See JEVONS's " Report on Band Spectra of Diatomic Molecules," 1932, p. 282.

† *Cf.* WILSON, 'Proc. Roy. Soc.,' A, vol. 134, p. 277 (1931).

such as samarium or other rare earths. It is known that diamonds contain traces of mineral matter, but the differences found in the two types of diamonds cannot be referred to traces of foreign substances for the reason that Type 1 diamonds of widely different geographical occurrence all have the same band about 8 μ, with the same structure and similar high intensity. Furthermore, all these diamonds exhibit the same bands and the same sharp cut off at the same place in the ultra-violet region of the spectrum. If impurities (other than " structural impurities ") are to be invoked it will be necessary to assume that diamonds found in different countries all have exactly the same impurity to the same degree of concentration. Such diamonds should also exhibit enhanced photo-electric effects due to the action of impurities in liberating electrons or producing ionic centres from any metal ion. In fact, Type 1 diamonds show much less photo-electric effect, so that on this view alone the assumption of impurities must fail to account for the observations. On the other hand, if Type 2 diamonds are assumed to owe their properties to impurities of rare earth character, we would have to suppose that the impurities have conferred transparency on the diamonds in infra-red and ultra-violet regions of the spectrum. Such a view cannot, of course, be reconciled with the known effect of impurities in causing absorption of radiation in all other cases. The possibility is not excluded, however, that a trace of a foreign substance may have a marked influence on the ease of liberation or movement of electrons in the lattice of the diamond, thus helping to produce fluorescence or phosphorescence. In this limited sense alone can the effect of foreign substances be considered as having any influence on the physical properties here recorded. It should however be noted that in very few of the diamonds described was there any marked phosphorescence or fluorescence.

PHOTO-ELECTRIC.

It may be said at the start that the novel feature we have met with in our study of the photo-conductivity of diamonds is the activation of diamonds of Type 2 by light of short wave-length (λ 2300). In some a current is observed even without an applied voltage, and we find subsequent effects of light of longer wave-lengths to be diverse according to the region of the spectrum selected.

It should also be stated that we are in agreement with the work of GUDDEN and POHL in regard to the phenomena of what they term the " primary " photo-electric current whose quantum relationship they demonstrated, and we also agree as to the production of " secondary " currents when an unactivated diamond is subjected to high voltages.

It is to the study of the effects due to activation of certain diamonds that we have devoted much attention.

Orientation of the discussion.

In order to present the principal effects of light on the two types of diamond in a succinct manner, they are assembled in Table XI, followed by fig. 22 embodying their chief aspects. The effect of temperature is then summarized in Table XII. A reference is then made to previous results, with a note on the mosaic structure of diamonds of Type 2, leading to a discussion on the photo-electric properties of diamonds generally with special reference to the feature of activation by light of short wave-length and its *sequelæ*. Remarks follow on the bearing of these characteristics.

TABLE XI.—Effect of light of varying wave-lengths.

Diamonds of Type 1.		**PAGE**
Feeble response; no activation and no dark current; no current without an applied field		502
Diamonds of Type 2.		
Applied wave-length.	*Effect.*	
λ 2300 (optimum)—to diamond in any condition	*Activation,* with or without applied voltage—leaving dark conductivity which decays at continually decreasing rate	506
λ 2400 to λ 5000—to unactivated diamond	*Response*—with quantum efficiency as a maximum; no dark current	503
λ 2400 to λ 5000—to previously activated diamond	*Initial response,* followed by *deactivation* with light on. Only preceding effect left. Dark conductivity removed. Optimum for deactivation at λ 2800	509
λ 5000 to λ 9000—to unactivated diamond	*Response*—presumably of quantum efficiency; value here very small	—
λ 5000 to λ 9000—to previously activated diamond	*Maintained response*—may be many hundred times value of dark current; varies with intensities of initial activation and of light of λ 5000–λ 9000. Optimum at λ 5850 (for this adjuvant effect)	512

The above effects have been found for all the diamonds of Type 2, except for a slight variation in optimum for activation (λ 2220 to λ 2300) and difficulty in quenching D 19.

Some of these effects are illustrated diagrammatically in fig. 22.

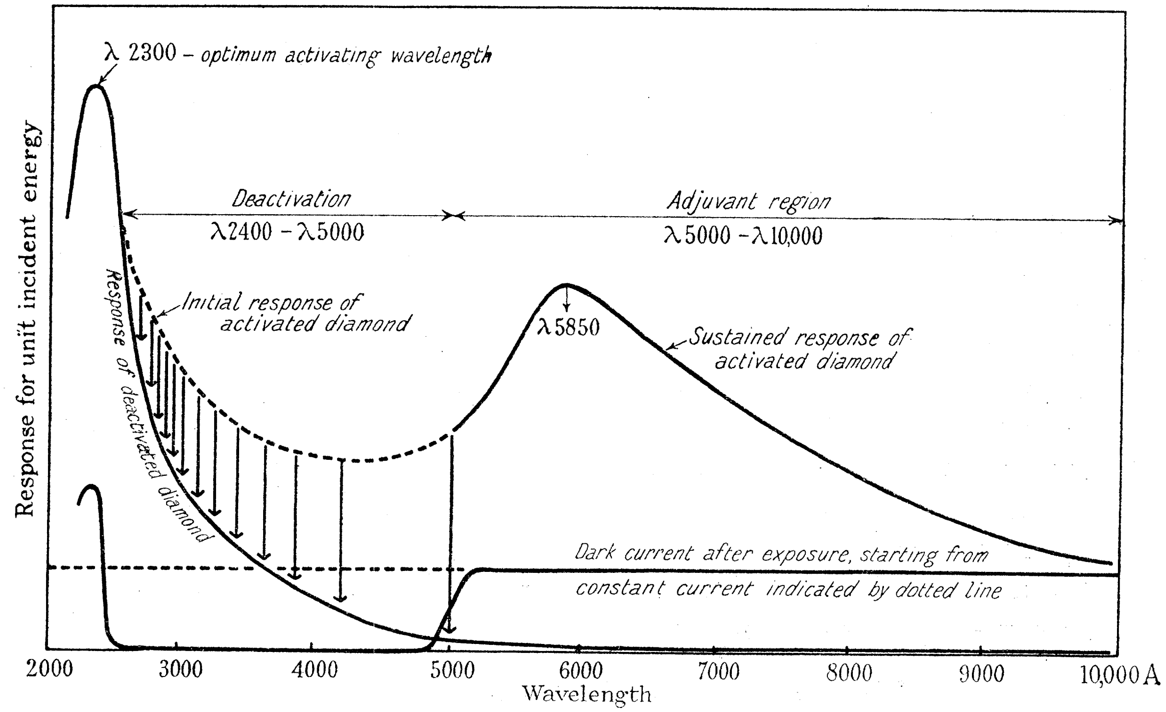

FIG. 22.—Diagram showing effects of radiation on diamonds of Type 2, indicating activation, deactivation, adjuvant effect and dark current.

TABLE XII.—Effect of temperature on photo-electric phenomena.

Range — 160°C. to 300°C.

Without applied voltage.	
Activating light	At − 100° C., effect small or vanishing. At − 40° C., maximum. At + 200° C., effect vanishing.
Additional red light	At − 100° C., effect small or increasing. At − 40° C., maximum. At + 200° C., effect vanishing.
With applied voltage.	
Activating light	At + 250° C., maximum. At 0° and 300° C., small.
Additional red light	Follows activating light.

(See fig. 20.)

Previous results on photo-conductivity.

GUDDEN and POHL[*] demonstrated that for a particular diamond recognizable as of Type 2 one quantum of absorbed light of any wave-length between λ 2260 and λ 4358 always liberated one electron. The number of electrons liberated by a flash of light was found by working under conditions of saturation, when every liberated electron was recorded; and the light energy absorbed was obtained with the aid of PETER'S absorption measurements for the diamond used (*loc. cit.*).

It was found by GUDDEN and POHL that when diamond is irradiated for a brief time with short wave light near the low-frequency side of the absorption band a certain quantity of electricity flows through the galvanometer; if thereupon this irradiation is followed by illumination with red light (which does not give rise to photo-current in a crystal not previously illuminated with short-wave light), an extra quantity of charge flows through the circuit, which, in limiting cases, was found equal to the previous quantity observed at the time of irradiation by short wave light.[†]

The current produced by the short-wave light is called, by GUDDEN and POHL, the negative part of the primary current, while the charge which flows at the time of the subsequent illumination with long wave (red) light is called the positive part of the primary current.

LENZ[‡] measured the steady photo-electric current in diamond over a range of temperatures and found that the current was considerably reduced as the temperature fell. GUDDEN and POHL explained this by assuming that a large positive space charge formed at low temperatures as a result of the slow dissipation of the positive charges. This large positive space charge at low temperatures largely nullified the applied potential. Further, the absorption band of the diamond presumably narrowed and shifted towards shorter wave-lengths at low temperatures, so that less active short wave light was then

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[*] 'Z. Physik,' vol. 17, p. 331 (1923).

[†] 'Z. Physik,' vol. 16, p. 174 (1923).

[‡] 'Ann. Phys.,' vol. 77, p. 449 (1925).

absorbed by the diamond and a smaller photo-current was only to be expected. Later, LENZ allowed for these disturbing factors and claimed that the initial negative part of the primary current was independent of temperature down to − 250° C.

Many of the effects found by GUDDEN and POHL we have been able to reproduce in both types of diamond in a greater or less degree, but an entirely different condition emerges when we get the phenomenon of activation as in certain diamonds of Type 2. It is true that GUDDEN and POHL recognized departures from the simple effects and termed them "secondary." For such "secondary" effects they require, at least so far as diamond is concerned, high voltages,[*] such as 16,000 v. per cm.

Physical condition of diamonds capable of being activated.

In the description of the morphology (p. 467), the isotropic condition (p. 472), and the X-ray intensities of the diamonds of Type 2 (p. 474), attention has been directed to the mosaic character of this type. In the distinctly laminar condition of D 2 and D 22, for example, those which are most active photo-electrically, it may be assumed that the electronic system of the marginal carbon atoms is different from that for atoms in the body of the diamond substance. It is further likely that the marginal carbon atoms will have electrons bound less tightly than those surrounded uniformly on all sides by other complete atoms as in the BRAGG model.

Photo-electric properties of diamond.

(i) *Conditions for liberation of electrons.*—Postulating the condition just indicated, it would seem likely that only when the electronic structure is less stable than in the perfect lattice, diamonds respond to light. This is in accordance with the views of GUDDEN and POHL who consider that the separation of electrons from certain centres, *i.e.*, "abnormal" atoms, gives rise to the primary photo-electric current, and the view of HUGHES and DUBRIDGE[†], who hold also that the normal atoms of the lattice are inactive photo-electrically.

So far as we have examined diamonds, those of Type 1 in which neither GUDDEN and POHL nor ourselves have obtained more than very feeble photo-electric currents, it would seem that these have few of the above "centres."

It is with diamonds of Type 2, *e.g.*, D 2 and D 22, that we find ready activation by λ 2300 and its consequent effects.

In a given diamond such as that studied by GUDDEN and POHL, we must suppose that by reason of imperfections in the crystal, numbers of atoms are available in which an electron is comparatively loosely bound, the degree of looseness varying from atom to atom, and the number having any given degree of looseness becoming smaller as they depart more and more from normality. This scheme is in keeping with the

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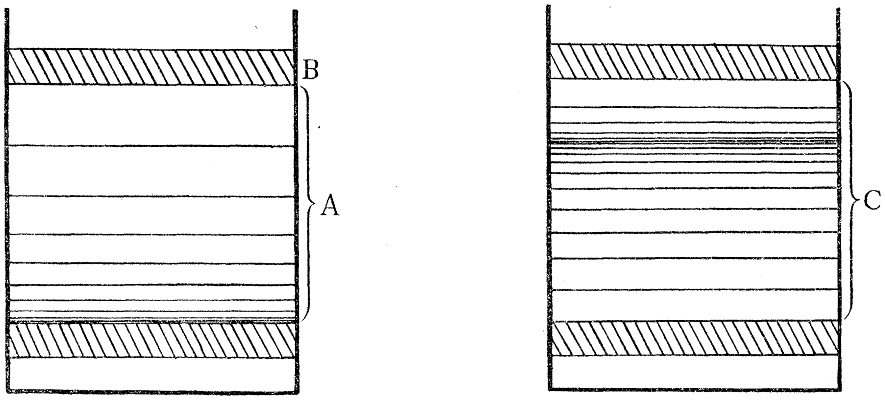
[*] *Cf.* 'Z. Physik,' vol. 7, p. 69 (1921).

[†] *Cf.* "Photo-electric Phenomena," pp. 306–7 (1932).

observed photo-electric effect which decreases with increasing wave-length, fewer and fewer atoms being able to respond as the frequency of the light is reduced.

The number of atoms involved in such photo-electric effects is small and can be shown by calculation to be roughly about one centre in 10^{11} atoms.

Diamonds capable of being activated are assumed to have " abnormal " atoms, and when activation is avoided, they are in bands of energy levels, A of fig. 23 (*a*), and give the normal photo-electric effect whereby they are raised to the ionizing potential level B. On being subjected to radiation of the activating region λ 2300 the electron binding in these atoms is loosened and the atoms with the loosened electrons are in a metastable band of energy C, fig. 23 (*b*), from which they can fall back to A only very slowly, still as abnormal atoms. From atoms in this metastable state, " red " light is capable of ejecting the loosely-held electrons, other electrons entering to take up the positions of those ejected, so that a continuous adjuvant effect results so long as red light is applied. The maximum of the adjuvant effect will then depend upon the distribution of metastable levels available in C.



(*a*) (*b*)

FIG. 23.—Energy levels of diamond. (*a*) shows allowed bands of energy levels (shaded areas) in actual diamond in inactivated state, together with intermediate levels due to crystal imperfections. (*b*) shows energy levels in the same diamond when activated. Here many of the intermediate levels are metastable.

The effect of radiation within the deactivating range λ 2400-λ 5000 is to disturb the condition of the metastable atom whereby the carbon nucleus and the electrons associated with it are changed into the condition of the abnormal atom, the energy of the radiation being partly used up to effect this and partly appearing as heat or fluorescence ; in other words, condition C reverts to condition A. It might be recalled that for every wave-length in the deactivating region there is a corresponding wave-length in the adjuvant region of half the energy (*cf.* λ 2400 to maximum λ 2800 and finish λ 5000, with λ 5000 to maximum λ 5850 and finish λ 9000). It is tempting to suggest the partition of the energy in the deactivating region into halves—one engaged in ejecting an electron and the other restoring the metastable to the abnormal condition.

Since it is evident that no diamond is a perfect crystal, but contains numerous submicroscopic cracks, more developed in Type 2, the above considerations are in line with those of GURNEY, who points out that in the "quantum mechanical model of an insulating crystal there are bands of electron levels separated by wide zones of disallowed energies" (*loc. cit.*, p. 215). The activation and deactivation observed by us show that other levels exist.

(ii) *Behaviour of liberated electrons.*—It may be worth while to consider some cases of the subsequent behaviour of the electrons liberated from atoms in diamonds varying in the character of their response, with and without an applied field.

For those diamonds not liable to activation (see above), no appreciable current is observed when light is applied without a voltage, indicating that the electron is ejected with such a small velocity that it moves only a short distance through the diamond. On the application of a voltage, however, the electron acquires a velocity from the field which enables it to resist capture over an appreciable distance, and this distance increases with rising voltage, until finally the electron is drawn across the diamond.

For diamonds capable of being activated, the liberated electron, if ejected from a metastable atom formed by the action of light of λ 2300, has sufficient velocity even in the absence of an applied field to carry it some way through the diamond before recapture. Even when light of long wave-length is applied to diamonds in this active condition electrons are liberated, but require an applied field for them to be detected as a current. In these diamonds, very large currents can be obtained on the application of quite small voltages, due to an abundant supply of metastable atoms, readily capable of losing electrons on collision with swiftly-moving free electrons. This is an effect comparable with the action of light on selenium which readily gives large secondary currents, the small primary current having been detected by GUDDEN and POHL* only when special precautions were taken.

Owing to the simplicity of effects when light of the adjuvant region (λ 5000 to λ 9000), termed for this purpose "red light," is applied to a diamond which had been activated, there being then no complication due to deactivation, an opportunity is afforded to account for the linear relationship between the total current and dark current (see p. 513).

Suppose that some time after activation by λ 2300 there are n free electrons and r metastable atoms from which the electrons can be released by red light. Let i_d be the value of the dark current and suppose that it is proportional to the number of free electrons, so that $i_d = kn$ where k is a constant. Let i_r be the value of the current when red light is applied, and suppose that the intensity of red light is such that at a given instant a fraction c of the metastable atoms has parted with an electron, then $i_r = k(n + cr)$, or $i_r = i_d + kcr$.

This expression, however, does not fit the observations, and it is necessary to modify

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* 'Z. Physik,' vol. 35, p. 243 (1925).

the scheme by supposing that the red light not only liberates electrons from metastable atoms, but also facilitates the transport of free electrons through the diamond, an effect which can be allowed for by supposing the normal mean free path (in the dark) λ_d to be increased to λ_r when red light is applied. Then

$$i_d = k'\lambda_d n\,; \quad \text{and} \quad i_r = k'\lambda_r\,(n + cr),$$

$$i_r = i_d\left(\frac{\lambda_r}{\lambda_d}\right) + k'cr\lambda_r = \frac{\lambda_r}{\lambda_d}[i_d + k'\lambda_d cr].$$

This last expression can be compared with the empirical expression $i_r = \mathrm{K}\ (i_d + \alpha)$ (see p. 513), where K depends only on intensity of red light used, and α depends solely on degree of activation of diamond.

λ_r/λ_d can be identified with K, but $k'\lambda_d cr$ is dependent on the intensity of red light while α is not. This difficulty can be avoided if we assume that with the great intensity of red light used in our experiments electrons are liberated from all the metastable atoms so that $c = 1$. Then $k'\lambda_d cr$ is independent of red light intensity for high intensities and can be identified with α.

Increase in free path can then be associated with the experimental results obtained when red light is applied to a diamond previously activated by λ 2300, and with a voltage. While red light alone is incapable of giving an appreciable current, even with an activated diamond in the absence of a voltage, experiment shows that the same conception of increased free path affords an explanation for the extra current produced by red light in conjunction with λ 2300 (p. 514).

Before completing a consideration of the effects produced by red light, it may be profitable to consider some of these in connection with the variation of currents generated by diamonds of Type 2 with temperature, in absence and presence of an applied field (fig. 20 (*a*) and (*b*)).

From (*a*) it will be seen that while the current produced by ultra-violet light falls rapidly as the temperature is reduced below — 40° C., the extra current produced by simultaneous illumination of red light falls much less rapidly (D 2), or may even rise (D 22). The smaller current produced by ultra-violet light at low temperatures such as — 100° C. is partly accounted for by the decrease in the number of electrons liberated, this being in line with the smaller absorption of light observed spectroscopically (see p. 491), and partly by the reduction of mean path of the electrons, presumably due to the small thermal agitation of atoms and positive ions in the diamond. That thermal agitation is small at — 100° C. is shown by the low value of the specific heat, the value of Cp interpolated from the results of NERNST, LINDEMANN, WEBER and MAGNUS being only 0·4 as compared with 1·35 at 11° C. and 3·97 at 327° C.

The small current produced by ultra-violet light at — 100° C. (fig. 20 (*a*)) can be increased in two ways, either by rise of temperature up to — 40°, which increases the vibrations of atoms and positive ions in the crystal, and so hinders the capture of free electrons, or by the influence of red light which, by disturbing the positive ions, also retards electron capture. Above − 40° C. increasing temperature reduces the current, for the violently vibrating atoms increasingly interfere with the passage of electrons of small velocity, unless there is a directing force resulting from an applied field (see fig. 20 (*b*)) which enables them to proceed across the diamond in spite of the interference of the vibrating atoms. At the highest temperatures used (*ca.* 300° C.), when the value of C_p has reached two-thirds of its maximum value, the atomic disturbances are so great that even an applied field cannot ensure the passage of electrons.

The effect of red light also diminishes at high temperatures, since in comparison with the violent heat motion then in force the mild ionic agitation produced by the red light is negligible and little extra current is obtained.

It must be kept in mind that the above hypotheses are put forward only in explanation of the photo-electric observations, and do not apply to the variations with temperature of the dark current (see p. 515).

CORRELATION OF ABSORPTION AND PHOTO-CONDUCTIVITY.

Generally in the diamonds we have examined those which are least absorbent in the ultra-violet (Type 2) are also most photo-conductive, although it must be stated that those of Type 1 exhibit some photo-conductivity if the potential applied is sufficiently high.

It has been shown that at −100° C. the diffuse ultra-violet bands of Type 2 diamonds disappear, fig. 30, and that when there was a green glow (p. 506) it was likewise absent. That there is a definite connexion between the photo-electric effects and the absorption of light is brought out by the curves for D 2 and D 22 in fig. 20. About −100° C., where the diffuse bands vanish, the photo-conductivity becomes constant and the additional effect of red light first becomes greater than the normal effect. At this temperature, therefore, those electrons active in absorbing the energy to produce the faint selective absorption are so held that they cannot respond to radiation. Only those photo-electrons remain which arise from the persistence of abnormal atoms in certain centres.

In Table V (*b*) (p. 419) and fig. 30, it is shown that the ultra-violet transmission ceases abruptly at λ 2250 : at low temperatures the sharpness of the absorption edge is extraordinary. This has a counterpart in the photo-conductivity of Type 2 diamonds, fig. 13, for the maximum photo-conductivity per unit incident energy is greatest just at this region of the ultra-violet spectrum. The curves of photo-current against wavelength are not sufficiently precise to enable a statement to be made as to the exact coincidence at λ 2250 of the optical and photo-electric effects, but the difference in position, if any, is certainly very small.

We have many acknowledgments to make. In the first place we are indebted to the Diamond Corporation, Ltd., for lending us most of the stones, to Professor GORDON for the use of some from his own collection, and to Messrs. VAN MOPPES for some industrial diamonds; to the Director of the Geological Survey for the loan of some specimens; to Mr. J. L. JONES, who assisted us in the early stages of the work when the difference in infra-red absorption of the two types of diamond was discovered; to Professors ALLMAND and ANDRADE for the use of ultra-violet monochromators; to Professor DONNAN for use of an infra-red grating; to Dr. BOWDEN for the design of a lamp giving a continuous spectrum in the ultra-violet; to Dr. H. H. THOMAS and Mr. A. F. HALLIMOND for examining the birefringence of the stones; to Professor G. P. THOMSON for examining some diamonds for electron diffraction; to Mr. B. ROBINSON for his X-ray examinations; to Dr. W. H. J. CHILDS for his microphotometric measurements; and to Sir WILLIAM BRAGG, Professor R. H. FOWLER, Dr. C. D. ELLIS, Dr. A. MÜLLER, Mr. J. D. BERNAL, Dr. C. P. SNOW, Dr. W. JEVONS, and Dr. R. C. JOHNSON for assistance in discussions; to Mr. R. H. S. ROBERTSON for sketches of diamonds; and we are much indebted to Mr. F. S. BENGE, our mechanic, for his ingenuity in the construction of apparatus and his enthusiasm in using it.

SUMMARY.

1. From an observation that a diamond failed to give a prominent absorption band at 8 μ in the infra-red region of the spectrum where a great number of diamonds gave this, a similar exploration was undertaken in the ultra-violet region where a difference in absorption in the same sense was found.

More examples were found and two types were recognized, the more common or opaque Type 1 (band at 8 μ and complete absorption at λ 3000) and Type 2 (no band at 8 μ and complete absorption at λ 2250).

2. Other properties were investigated: the crystalline condition which indicated a fine oscillation lamellation more particularly associated with Type 2, a mosaic condition in that Type being confirmed by X-rays. Type 2 was found to be more isotropic optically than Type 1, but specific gravity, refractive index, and dielectric constant showed no difference between the types; nor did the Raman effect which gave one fundamental frequency at 1332 cm.$^{-1}$ for both types.

3. From the band system in the infra-red up to 17 μ and the new carbon bands found about λ 3000 in the ultra-violet, together with the Raman frequency a picture is sketched of the various modes of vibration of carbon against carbon in the diamond structure, for which the frequency of the fundamental vibration is also calculated.

4. An explanation founded on the consideration of the phenomena after molten carbon has frozen is put forward to account for the existence of the transparent type. Arguments are advanced against the assumption that the less usual type owes its properties to common impurities.

5. A remarkable difference in the response to light of the two types has emerged.

While most diamonds give some response to light when the passage of the dislodged electrons is assisted by an applied potential, it has been disclosed that some diamonds (of Type 2) generate a current without the application of any voltage. When these diamonds have been activated by light of λ 2300 they acquire a condition in which light of certain wave-lengths can quench the photo-conductivity while others augment it. The bearing of these effects on the conditions produced in the crystal is discussed and some correlation attempted between them and the optical effects. The comparatively easy production of photo-electric currents in Type 2 diamonds is probably connected with the mosaic structure, the atoms at the boundaries of the irregularities losing electrons more readily than those in the perfect lattice.

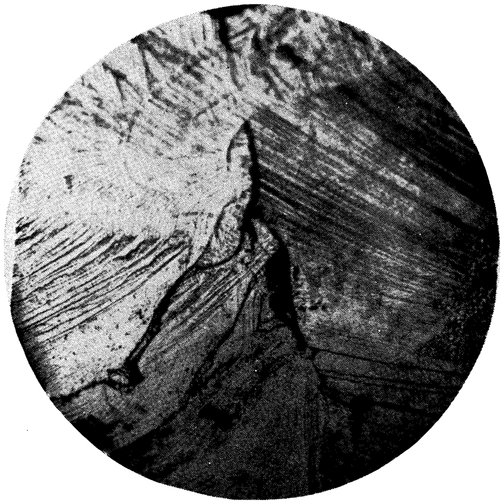


Fig. 24.

Fig. 25.

Fig. 26.

Fig. 27.

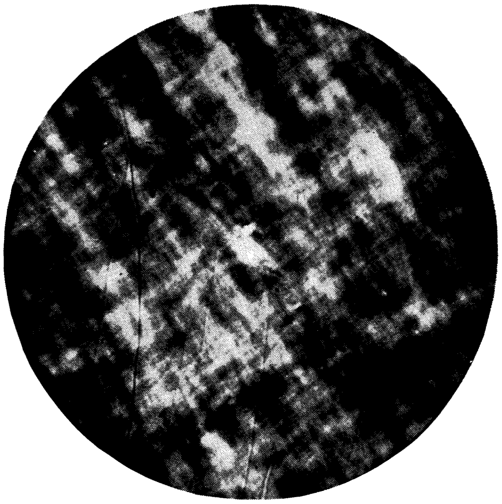


Fig. 28.

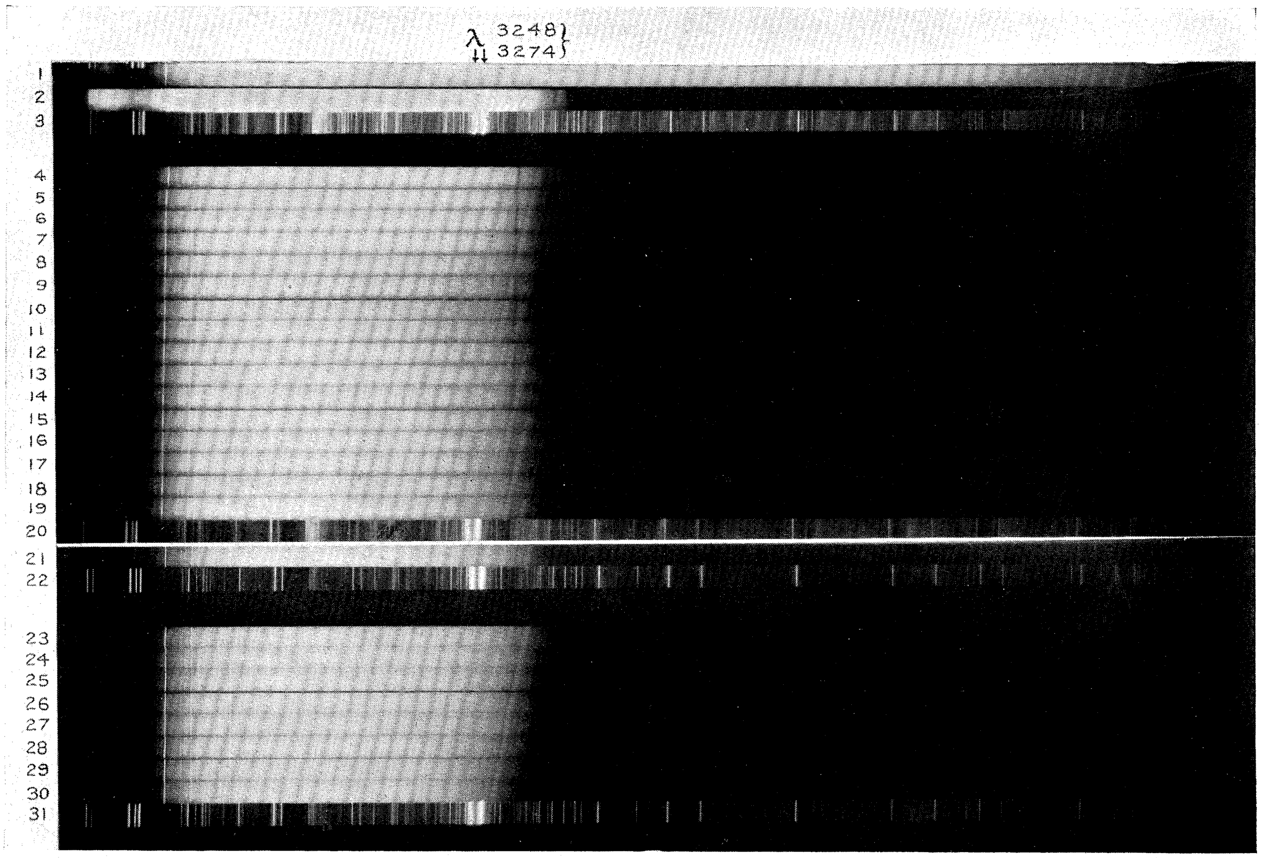


Fig. 29.—Absorption spectrum of Type 1 Diamond.

1. Hydrogen spectrum (1 min.).
2. — 174° long exposure.
3. Cu. arc.
4. — 174° C.
5. — 151° C.
6. — 131° C.
7. — 109° C.
8. — 91° C.
9. — 71° C.
10. — 51° C.
11. — 35° C.
12. — 27° C.
13. — 17° C.
14. — 10° C.
15. 0° C.
16. 4° C.
17. 8° C.
18. 14° C.
19. 17° C.
20. Cu. arc.
21. 20° C.
22. Cu. arc.
23. 20° C.
24. 89° C.
25. 121° C.
26. 166° C.
27. 206° C.
28. 253° C.
29. 281° C.
30. 316° C.
31. Cu. arc.

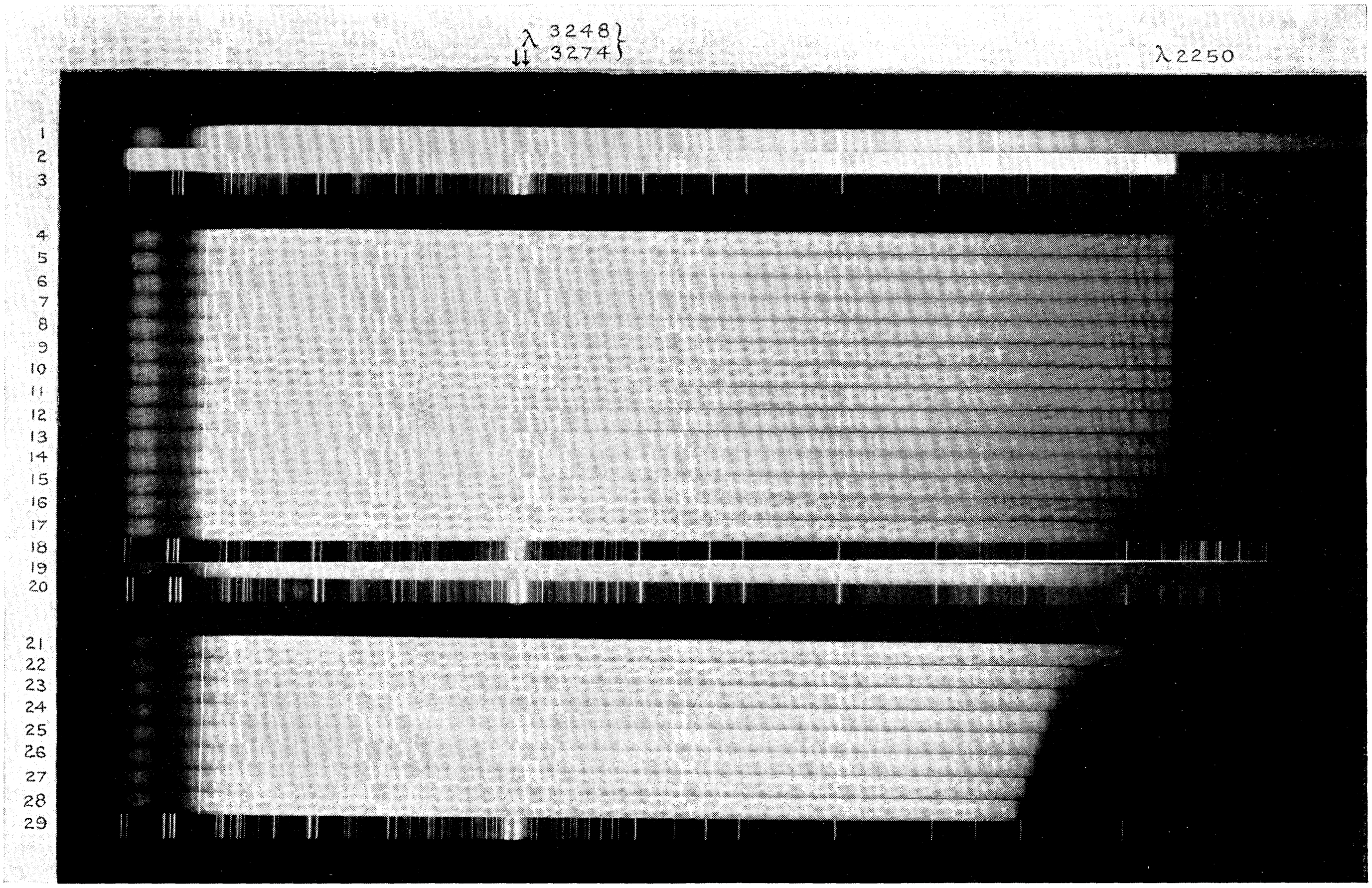


FIG. 30.—Absorption spectrum of Type 2 Diamond.

1. Hydrogen spectrum (1 min.).
2. – 174° C. long exposure.
3. Cu. arc.
4. – 174° C.
5. – 154° C.
6. – 135° C.
7. – 119° C.
8. – 104° C.
9. – 90° C.
10. – 77° C.
11. – 64° C.
12. – 54° C.
13. – 43° C.
14. – 35° C.
15. – 16° C.
16. – 1° C.
17. 12° C.
18. Cu. arc.
19. 17° C.
20. Cu. arc.
21. 17° C.
22. 87° C.
23. 130° C.
24. 168° C.
25. 210° C.
26. 248° C.
27. 281° C.
28. 314° C.
29. Cu. arc.

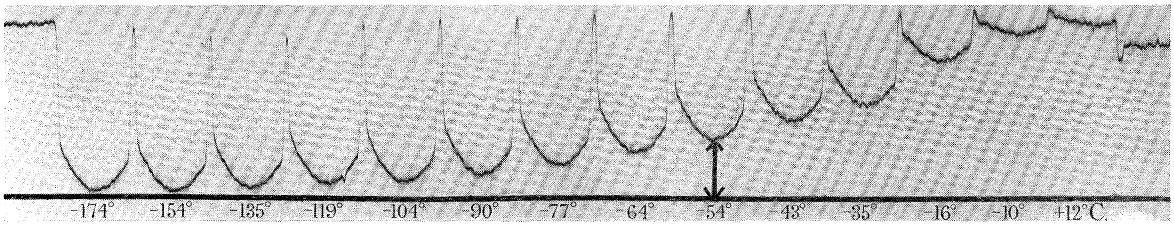


FIG. 31.—Microphotometric tracing showing onset of faint absorption about − 100° C.

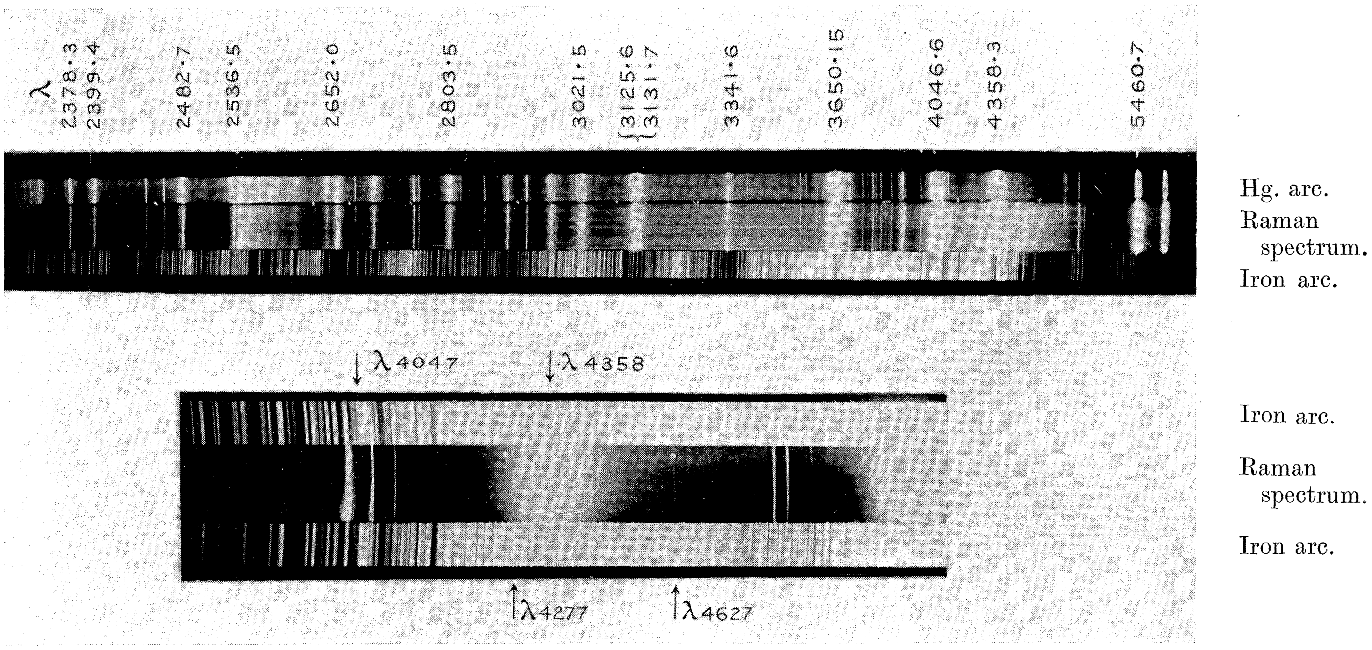


FIG. 32.—Raman spectra of Diamond. Upper Fig. with quartz spectrograph. Lower Fig. with glass spectrograph.

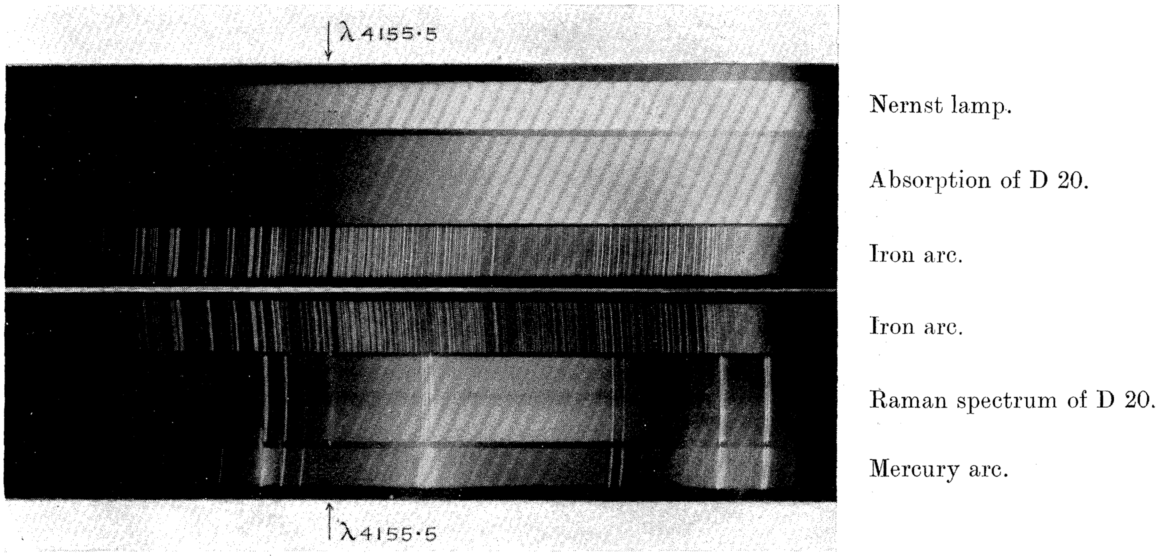


FIG. 33.—Absorption and Fluorescent bands of Diamond.

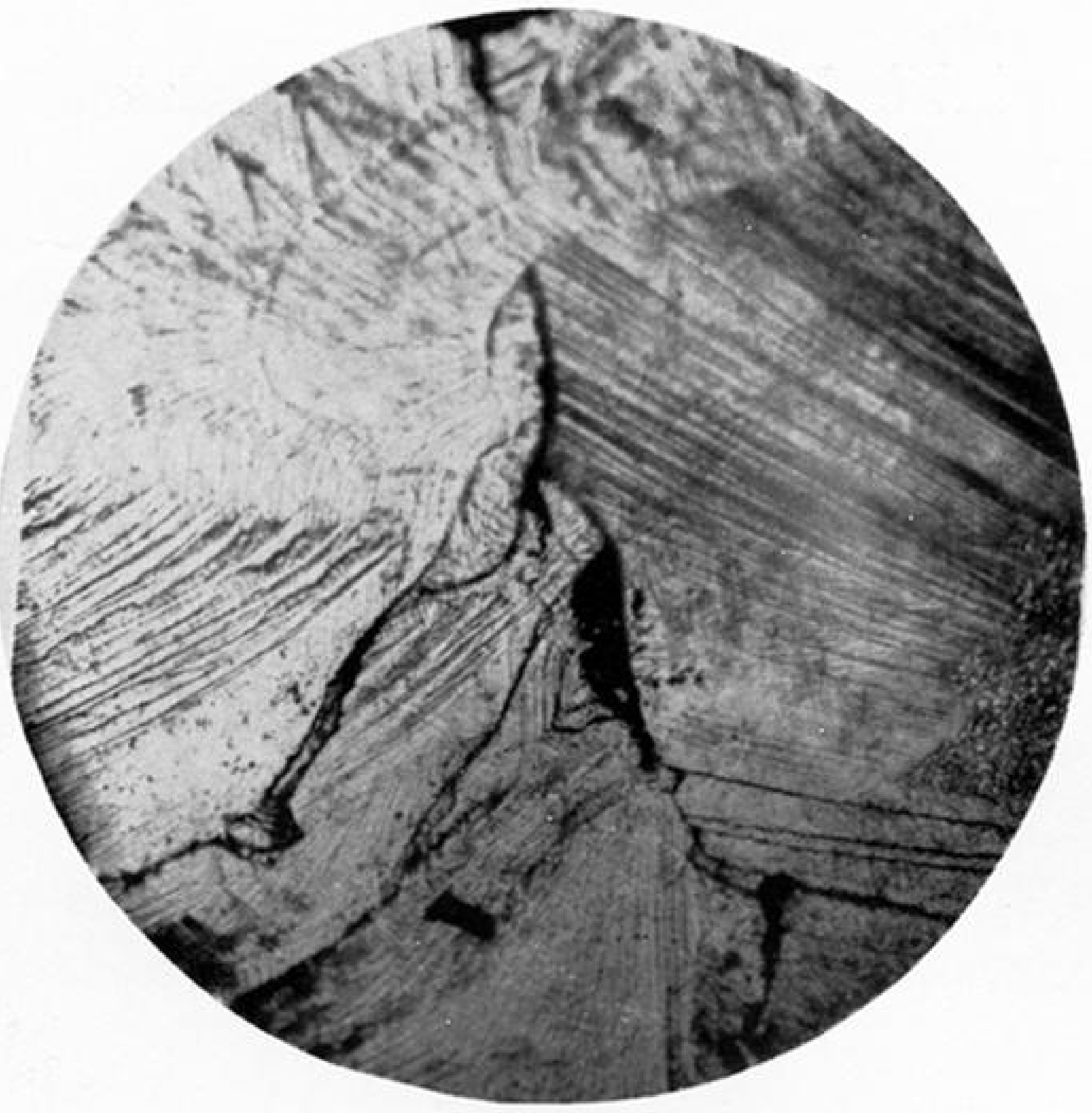


FIG. 24.

FIG. 25.

FIG. 26.

FIG. 27.

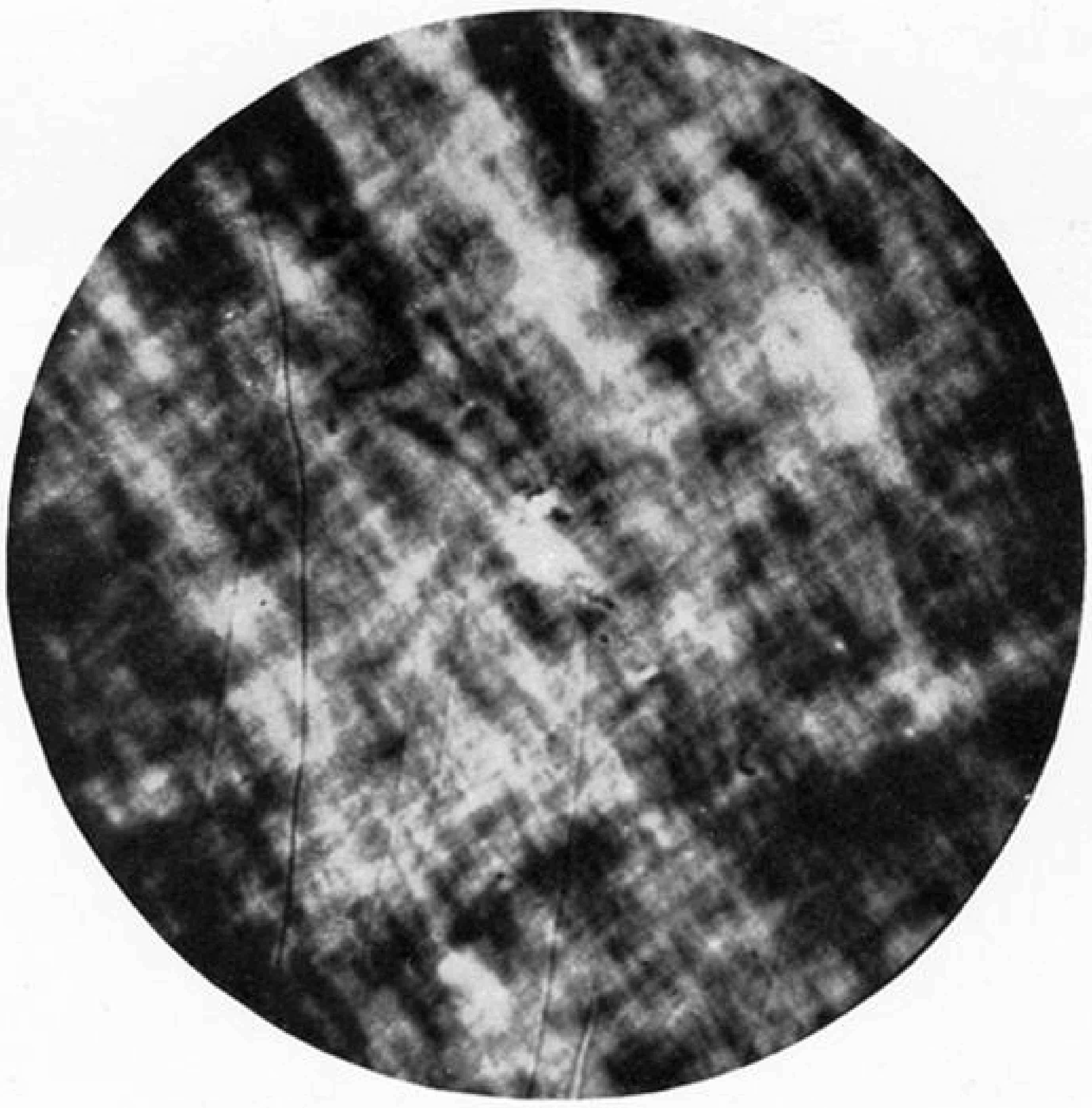
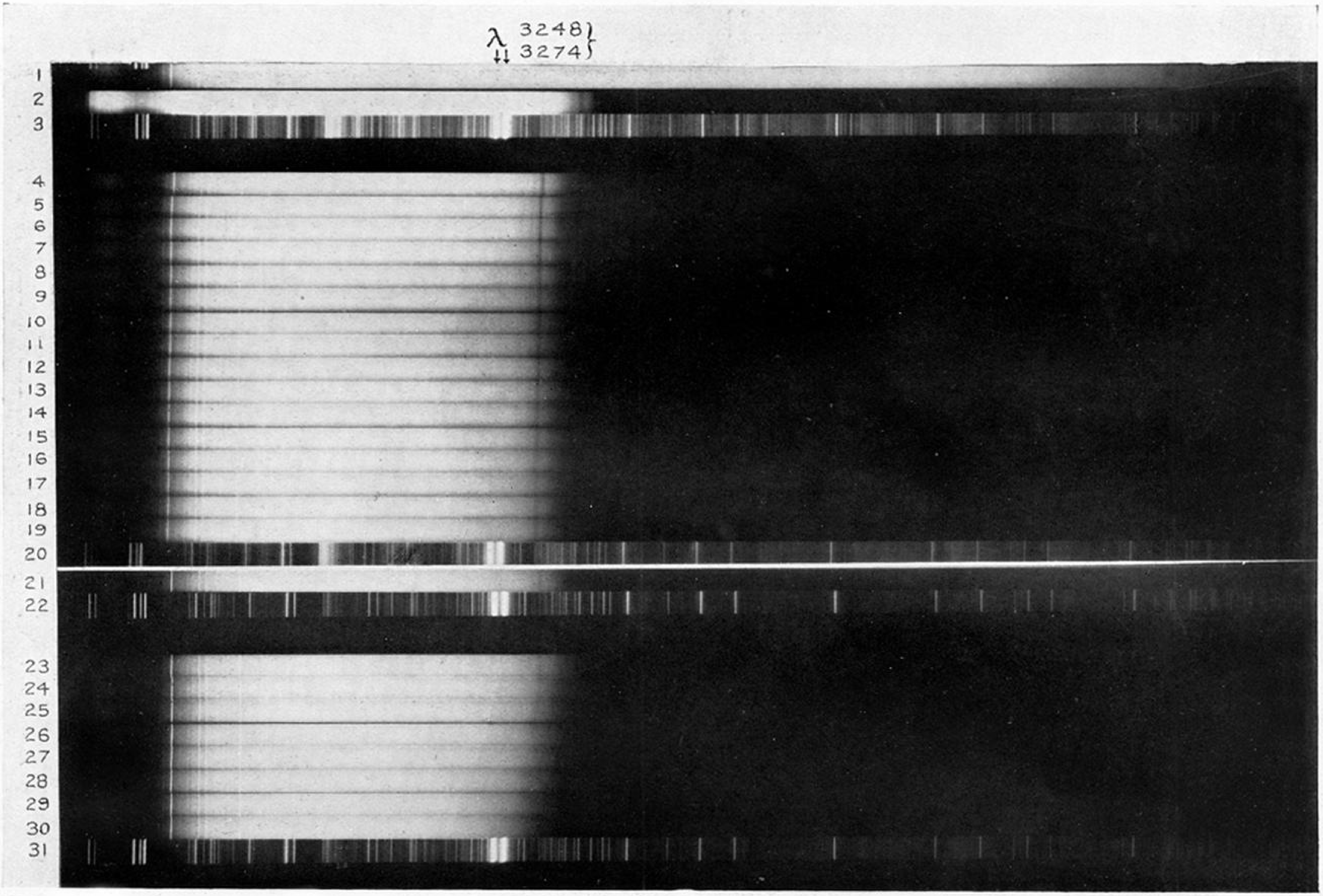


FIG. 28.



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2. — 174° long exposure.
3. Cu. arc.
4. — 174° C.
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6. — 131° C.
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10. — 51° C.
11. — 35° C.
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13. — 17° C.
14. — 10° C.
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28. 253° C.
29. 281° C.
30. 316° C.
31. Cu. arc.

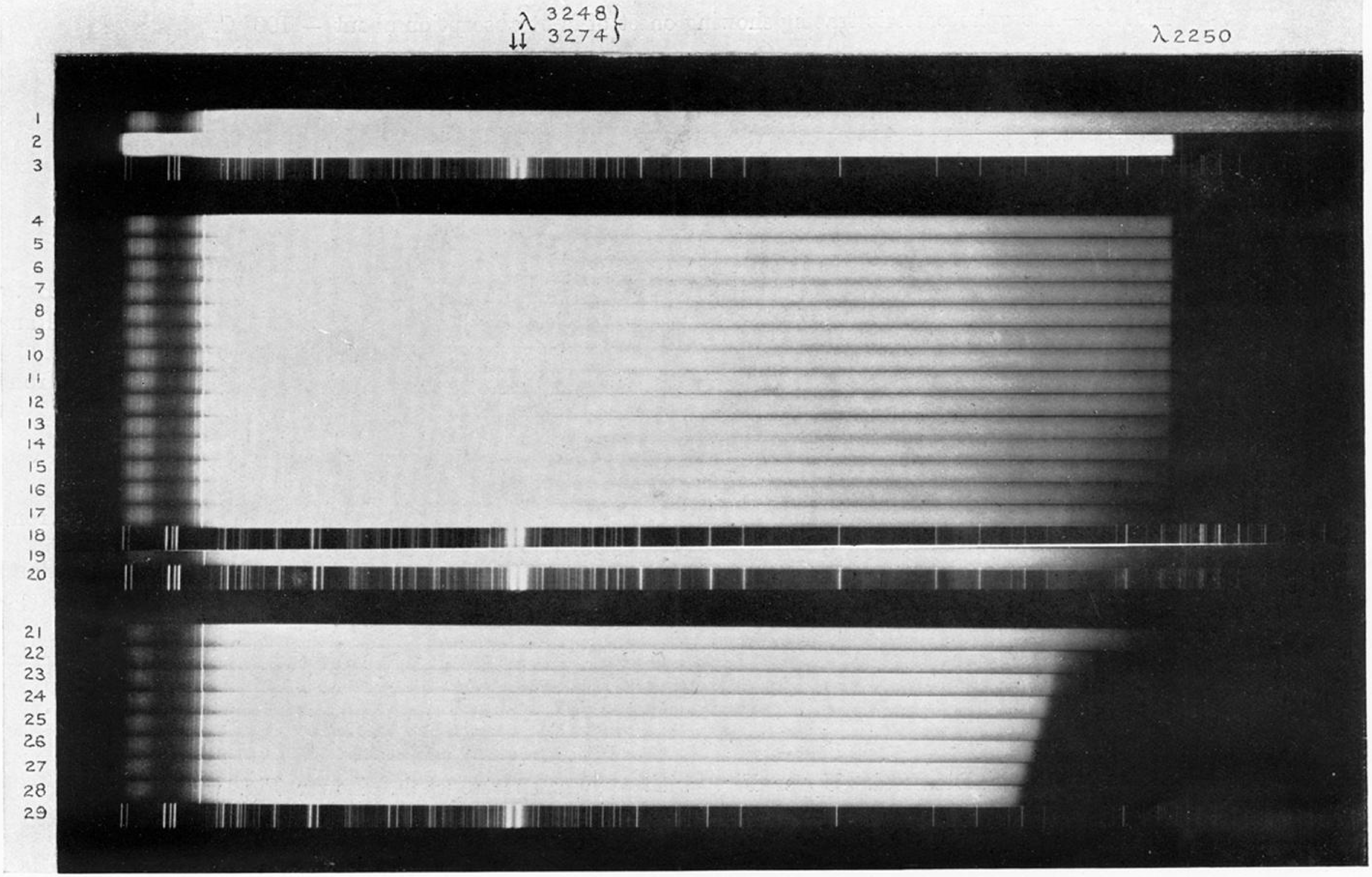

Fig. 30.—Absorption spectrum of Type 2 Diamond.

1. Hydrogen spectrum (1 min.).
2. — 174° C. long exposure.
3. Cu. arc.
4. — 174° C.
5. — 154° C.
6. — 135° C.
7. — 119° C.
8. — 104° C.
9. — 90° C.
10. — 77° C.
11. — 64° C.
12. — 54° C.
13. — 43° C.
14. — 35° C.
15. — 16° C.
16. — 1° C.
17. 12° C.
18. Cu. arc.
19. 17° C.
20. Cu. arc.
21. 17° C.
22. 87° C.
23. 130° C.
24. 168° C.
25. 210° C.
26. 248° C.
27. 281° C.
28. 314° C.
29. Cu. arc.

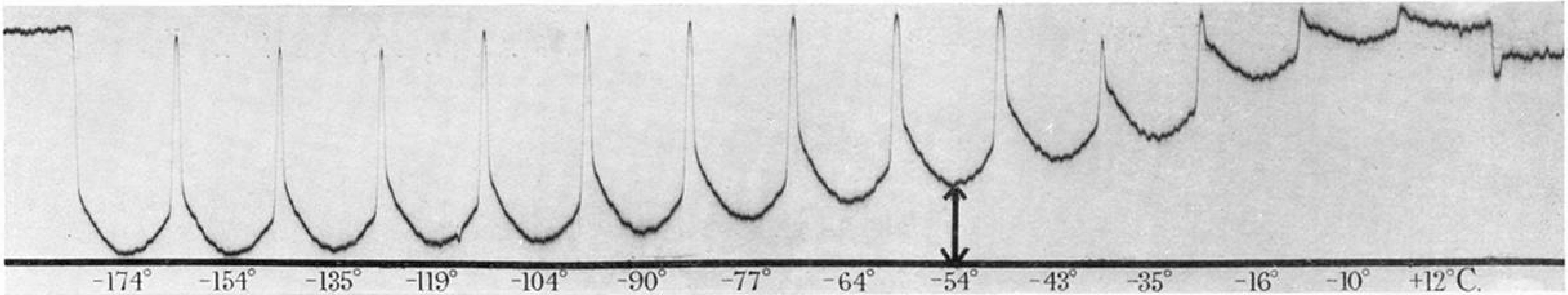

Fig. 31.—Microphotometric tracing showing onset of faint absorption about − 100° C.

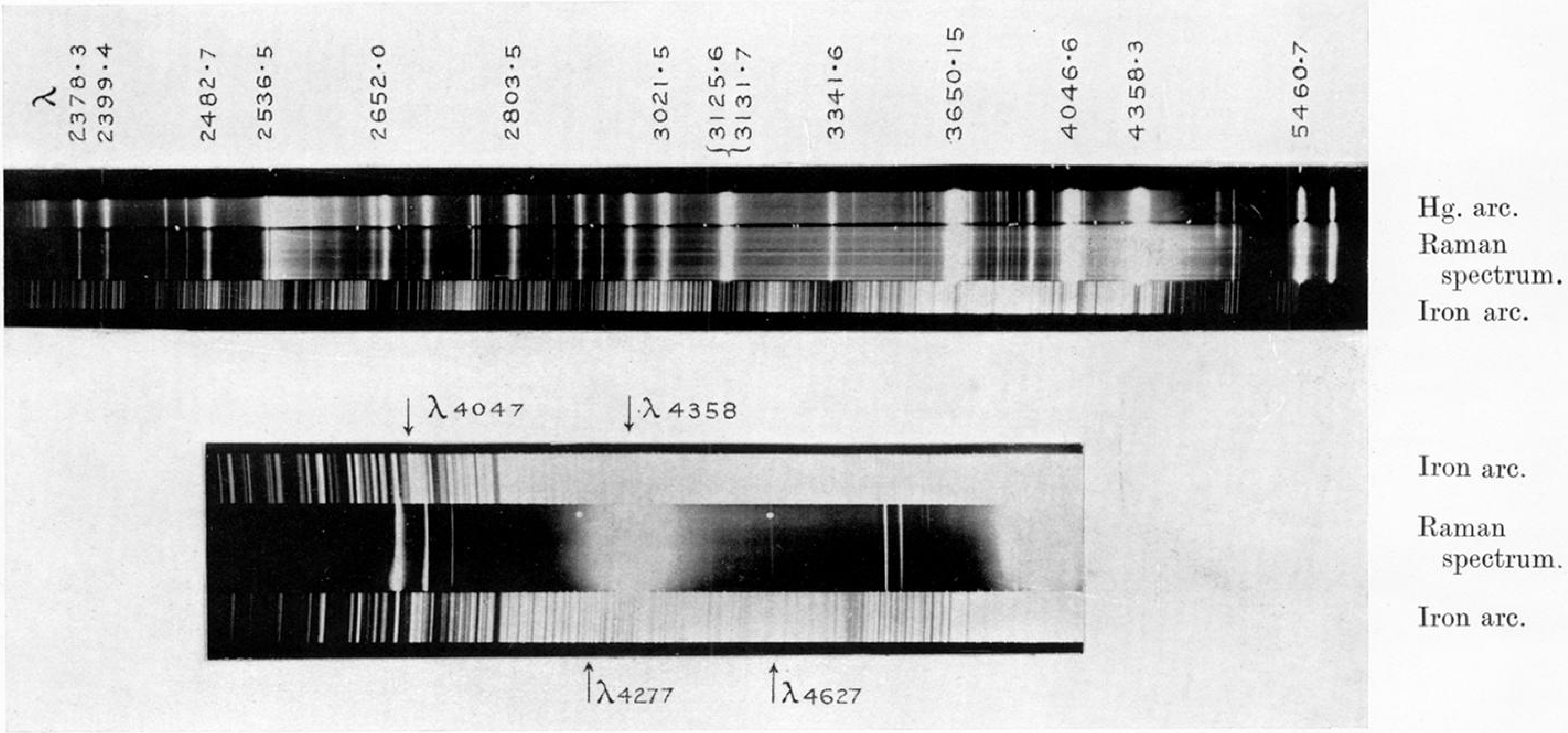

FIG. 32.—Raman spectra of Diamond. Upper Fig. with quartz spectrograph. Lower Fig. with glass spectrograph.

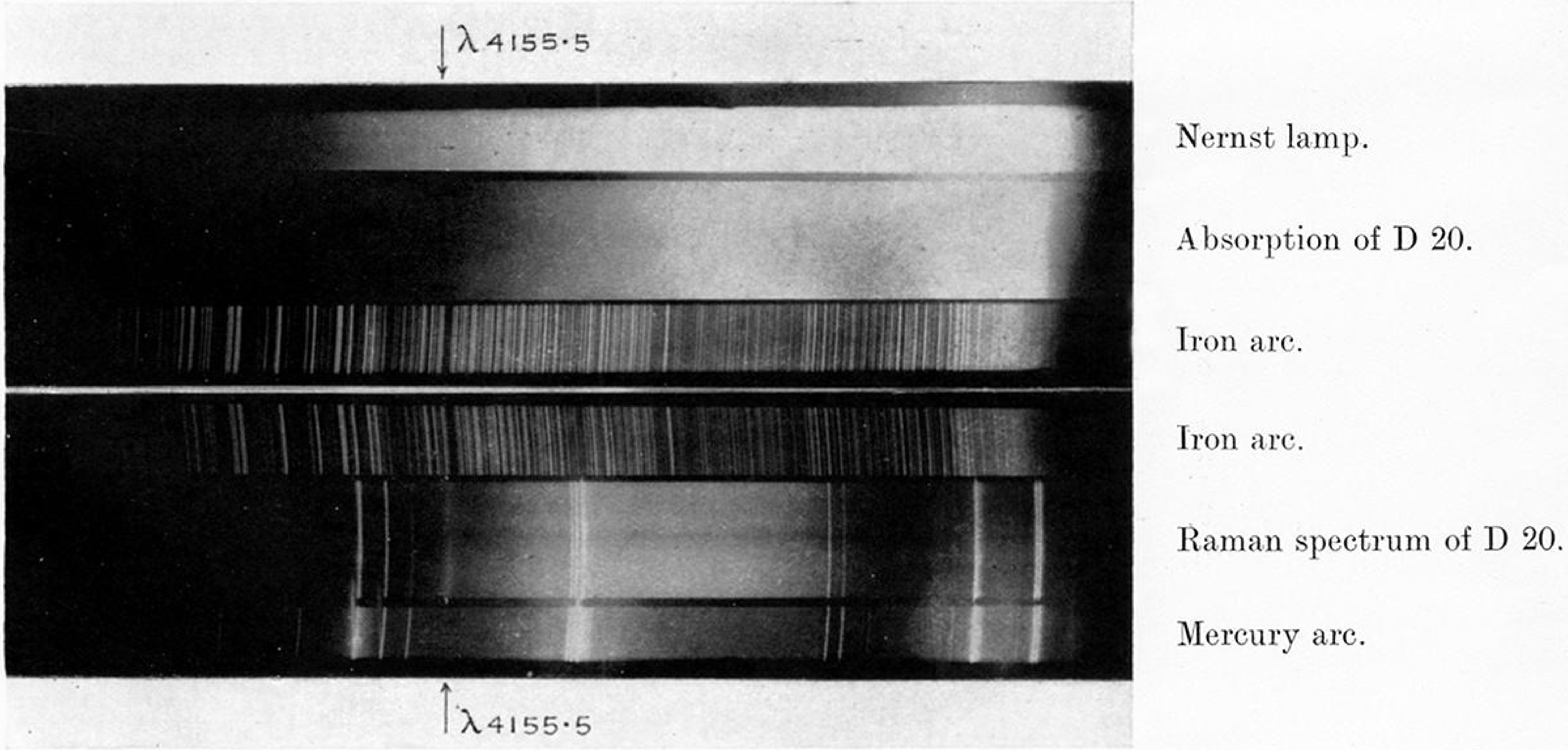

Fig. 33.—Absorption and Fluorescent bands of Diamond.