THE FLUORESCENCE AND ABSORPTION SPECTRA OF DIAMOND IN THE VISIBLE REGION

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1. *Introduction*

The luminescence of diamond has long been familiar knowledge, but spectroscopic studies of it have not been very numerous. E. Becquerel (1859) and W. Crookes (1879) were amongst the earlier observers. The latter noticed some bright lines in the spectrum of the cathode luminescence of diamond and ascribed them to the presence of foreign atoms. Walter (1891) who studied the absorption of light by diamond and noticed a dark band at 4155 A.U., also ascribed it to the presence of impurities. The luminescence of diamond appears in the spectrum along with the scattering of light when the Raman effect is studied, thus directing attention to itself [Ramaswamy (1930), Bhagavantam (1930), Robertson and Fox (1930), and Robertson, Fox and Martin (1934)]. The important observation was made by these authors that a bright line appears in luminescence which coincides with the dark line at the same wave-length noticed in absorption by Walter. John (1931) observed the cathode luminescence spectrum of diamond and found it to be very similar to that excited by ultra-violet irradiation.

Dr. P. G. N. Nayar (1941 *a*, *b*, *c*, *d*; 1942 *a*, *b*) made a notable advance by his comparative studies of the luminescence and absorption spectra of diamond over a wide range of temperatures. His investigations at liquid air temperatures, in particular, yielded highly interesting and valuable results. His most important findings were, however, made with one single strongly blue-luminescent diamond. It is well-known that diamond may also emit luminescence of other colours and that the intensity of such luminescence may vary over a wide range of values. It is therefore of importance that the investigation of the luminescence and absorption spectra should be extended to specimens showing the widest range of behaviour. Such studies may be expected to throw light on the question of the reason for such difference of behaviour and ultimately also on the general question of the nature and origin of the luminescence of diamond.

The present paper describes a detailed investigation of the fluorescence and absorption spectra of 32 diamonds from Sir C. V. Raman's collection, so selected to be as widely representative as possible of the behaviour of this substance. To enable this wide range of specimens to be successfully studied, a spectrograph of high light-gathering power combined with good resolution was found to be necessary. A two-prism Hilger glass spectrograph (E 328) was used which gave a dispersion of 28 A.U./mm. in the 4358 A.U. region and 63 A.U./mm. in the 5500 A.U. region. To study the absorption spectra under high dispersion in a few cases, a spectrograph of three-metre focal length (Hilger E 185) having a dispersion of 2 A.U./mm. in the 4200 A.U. region and 6 A.U./mm. in the 5200 A.U. region was employed.

Except with regard to the spectrographs employed, the technique of the investigation was generally similar to that followed by Nayar. A specially designed demountable Dewar flask was used to hold liquid air, and the diamonds were mounted in copper blocks screwed on to the bottom of its inner metal tube. This ensured the specimen reaching and remaining at the liquid air temperature. The source of ultra-violet light was a small carbon arc run at 5 amperes, the light from it being filtered through a plate of Wood's glass. The fluorescent light was focussed on the slit of the spectrograph by a short-focus cylindrical lens. The light-source for the absorption studies was a gas-filled incandescent lamp with a straight filament run at 30% more than the usual voltage. In every case, the diamonds were set so that the maximum thickness was employed. The spectra were photographed on Ilford selochrome plates in the blue region of the spectrum, on Ilford HP_2 plates in the green, and on Kodak extra-rapid infra-red plates in the red.

The fluorescence spectrum of each diamond was recorded both at room and at liquid air temperature, while the absorption spectrum was similarly recorded in each case with a graded series of exposures. In all, some 67 fluorescence spectra and 590 absorption spectra were obtained. Except where specifically mentioned, however, the data given in the paper always refer to the measurements of the plates taken at liquid air temperature.

2. *Description of the Diamonds*

As mentioned above, the 32 specimens chosen for examination covered a wide range of behaviour. Four of them were totally non-fluorescent; sixteen showed a blue luminescence with intensities ranging from extreme brilliance to almost complete invisibility; seven showed a greenish-blue and five a greenish-yellow fluorescence, in each case with widely different

intensities. By placing all the diamonds together under the ultra-violet lamp they could be sorted out, and those in each class of luminescence arranged in order of their apparent brightness. Table I shows the catalogue numbers of the 32 diamonds arranged in the order of decreasing intensity of luminescence as visually observed. The twelve diamonds with catalogue numbers between D1 and D30 were crystals from Panna in their natural state. Ten of the other diamonds were cleavage plates with their faces polished flat, while the rest had been fashioned into different shapes for use as jewellery.

TABLE I

List of Diamonds Studied

Diamonds which were non-fluorescent : (4)

D39	D206	D207	D227	
6·6	7·2	6·8	11·2	millimetres

Diamonds showing a blue fluorescence : (16)

D223	D224	D40	D226	D34	D27	D32	D3	
4·4	8·7	4·6	3·8	9·2	7·0	11·5	7·0	millimetres
D8	D38	D33	D43	D42	D36	D221	D31	
6·0	7·6	7·6	7·8	7·7	8·4	8·2	10·0	millimetres

Diamonds showing a greenish-blue fluorescence : (7)

D225	D4	D15	D10	D11	D7	D47	
10·3	7·9	6·7	8·9	6·2	6·7	4·4	millimetres

Diamonds showing a greenish-yellow fluorescence : (5)

D13	D12	D19	D1	D197	
6·5	5·0	5·0	9·8	9·4	millimetres

The great majority of the non-fluorescent and blue-fluorescent stones were colourless as seen in daylight. The exceptions were the following: in the non-fluorescent class, D227, a rod-shaped diamond with a slight brownish tinge; in the blue-fluorescent class, D226, a small brilliant with a lively pink colour; D27, a grey hexakis-octahedron from Panna; D32, a heart-shaped diamond with a distinct yellow tinge.

On the other hand, the majority of the diamonds with a greenish-blue or greenish-yellow fluorescence showed various shades of brown or yellow or yellowish brown difficult to describe exactly. The exceptions were D47, a small colourless octahedron with an extremely feeble bluish-green fluorescence, and the two diamonds D225 and D13 which exhibited a greenish tint by daylight, possibly due to their fluorescing with that colour.

The maximum linear dimension (in millimetres) of each diamond has been entered under it. This is of importance, as it influences the observed results, especially in the case of the absorption spectra.

3. *General Results of the Investigation*

Nayar's published studies (*loc. cit.*) relate to the class of diamonds which exhibit a blue fluorescence of greater or less intensity. Such diamonds show a bright band in luminescence at 4156 A.U. and a dark band in absorption at the same wave-length. A summary of the results obtained by him with regard to the fluorescence and absorption spectra of such diamonds appears in the preface to his doctorate thesis. It is useful to quote the same here *in extenso,* in view of its bearing on the present investigations and to enable it to be better appreciated how the latter have advanced our knowledge of the subject.

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"The fluorescent band at 4156 Å varies enormously in intensity between different diamonds, but is nevertheless found to be present with every one of the specimens examined, and is thus evidently characteristic of diamond. The 4156 band occurs also in absorption, the peak of intensity coinciding exactly with that observed in fluorescence, and the intensity varying with the specimen studied in precisely the same fashion. Both in absorption and fluorescence, the 4156 band sharpens at liquid air temperature, shifting to 4152 Å and appears resolved into a close doublet. On the other hand, at higher temperatures, there is a shift to greater wave-lengths, the band becomes progressively more diffuse, and fades off to invisibility above 600°K.

"The 4156 Å band in the spectrum is accompanied by subsidiary bands between 4156 Å and 4900 Å in fluorescence, and between 4156 Å and 3600 Å in absorption. These are present strongly in crystals in which the 4156 band is intense. The bands in absorption exhibit a perfect mirror image symmetry about the 4156 frequency with respect to the bands observed in fluorescence. When the diamond is cooled to liquid air temperature, and the bands are examined under high dispersion, they appear resolved into a spectrum of discrete frequencies. The frequency shifts from the principal band at 4152 Å in fluorescence and in absorption are found to be exactly equal but of opposite sign. They lie in the infra-red range, indicating that the subsidiary bands arise from a combination of certain infra-red or atomic vibrations with the electronic frequency manifesting itself both in emission and absorption at 4152 Å.

"The 18 discrete infra-red frequencies ranging from 137 cm.$^{-1}$ to 1332 cm.$^{-1}$ deduced as explained above from the fluorescence and absorption spectra of diamond at low temperature, are interpreted as the characteristic

vibration frequencies of the diamond lattice. This interpretation is confirmed by the agreement of the frequency shifts with the Raman effect data reported by Bhagavantam, and with the infra-red absorption frequencies reported by Julius, Reinkober and by Robertson *et al.* The fact that the lattice spectrum of diamond consists of 18 discrete frequencies covering such a wide range, is evidently irreconcilable with the assumptions on which the Debye theory of specific heats is based."

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The present investigation shows the appearance of a *second system of subsidiary bands which may be designated as the* 5032 *system* to distinguish it from the 4152 system described in Nayar's thesis. As will be set out later in the paper, this 5032 system is related to a line observed at 5032 Å, appearing at longer wave-lengths in emission and at shorter wave-lengths in absorption in a manner generally analogous to, but differing in important details from the relation between the 4152 system and the 4152 Å line. The important point is that both the 4152 and 5032 systems appear in the fluorescence and absorption spectra, but that their relative as well as their absolute intensities vary enormously from diamond to diamond. The great differences in the intensity and colour of the light emitted by different stones as perceived by the unaided eye arise from these variations. These points are illustrated by the five fluorescence spectra reproduced as Fig. 8 in Plate X appearing at the end of the paper. The spectra were those obtained with two diamonds of the blue-fluorescing type, two of the greenish-blue and one of the yellowish-green fluorescing type.

Another important result of the present investigation has been to show that besides the 4152 and 5032 lines and the bands which accompany them in luminescence and in absorption, there are numerous other lines which are quite sharply defined at liquid air temperature and of which the positions as observed in emission and in absorption coincide. These are interpreted as electronic frequencies. No fewer than 36 such lines have been recorded in the present investigation, their wave-lengths ranging between 3934 and 6358 Å. They may roughly be divided into two groups, the behaviour of which in respect of intensity is similar to that of the 4152 and 5032 systems respectively in the spectra.

The present investigation also shows that the relations between emission and absorption observed by Nayar in respect of the 4152 line and its associated bands are much more general, and extend also to the lines and bands of the 5032 system and to the numerous other electronic frequencies mentioned above. A particular case of this correlation which is of great importance is that of the non-fluorescent diamonds. It has been found that

these show no trace of any absorption lines in the visible spectrum even under the most favourable conditions, namely with the longest possible absorption paths and the exposures most suitable for their detection. No trace of any emission lines, either, appears with such diamonds even after prolonged exposures.

Still another interesting result of the present investigation is that the doublet structure of the 4152 line detected in *absorption* by Nayar in a particular diamond is observable also in the *emission spectra* of numerous diamonds. Further, it has been found that the width and separation of the components of the doublet varies from diamond to diamond in a manner generally related to the intensity of the luminescence of the specimen.

4. *The Colour of Fluorescence and its Spectrum*

The 22 diamonds whose fluorescence spectra have been studied may be arranged in the order of the *relative* intensities of the band systems accompanying the 4152 and 5032 lines, beginning with those in which the former is the principal feature while the latter is barely recorded, and ending with those in which the 5032 system is much more prominent than the 4152 system. It should be mentioned that in no case does the 5032 system appear in the spectrum without the 4152 system being also recorded.

TABLE II

Order of Relative Intensities of the 4152 *and* 5032 *Systems in Emission*

D33,	D8,	D27,	D36,	D38,	D34,	D40,	D42,	D223,	D224,	D32,
D12,	D226,	D3,	D225,	D7,	D4,	D47,	D15,	D1,	D13,	D19

Examining this list and comparing it with Table I, it will be noticed that all the diamonds which appear earliest in Table II are those classified as blue-luminescent in Table I, while those which appear last are mostly those shown in it as having a greenish-yellow luminescence. The diamonds shown in Table I as giving a greenish-blue fluorescence appear somewhere midway between the beginning and the end of the list in Table II. There are a few anomalies, *e.g.*, D12 appears high up in the list instead of towards the end. The order in which the blue-fluorescent diamonds appear in Table II is also not the same as that in which they are shown in Table I. It is quite clear, however, on a comparison of the two tables that the difference in the relative intensities of the 4152 and 5032 band systems in the spectrum is the origin of the differences in the colour of the fluorescence as visually observed.

5. *Relation between Fluorescence and Absorption*

The intensity of the luminescence of diamond varies enormously. An idea of the range of this variation may be obtained by phtographing a

group of stones with a series of graded exposures and counting the number rendered visible by their luminescence. Such photographs also enable a large group of diamonds to be sorted to small groups of approximately equal brightness and their relative intensities to be estimated microphotometrically. The figures obtained in this way for a group of 88 South African diamonds are:—

5(0), 2(1), 4(3), 9(10), 16(20), 4(30), 14(50), 7(100), 6(200), 4(400), 3(700), 2(1,000), 6(1,800), 3(3,000), 1(5,000), 1(10,000), 1(12,000).

It will be seen that the majority of the diamonds have small intensities of fluorescence, while a few exhibit intense luminescence or else are entirely non-fluorescent.

The diamonds whose emission and absorption spectra have been studied in the present investigation exhibit similar variations in their intensities of luminescence. While the spectra of the most intensely fluorescent diamonds were recorded in a few minutes, to photograph the emission spectrum of the weakly fluorescent diamonds, long exposures of the order 15 to 20 hours were found to be necessary even when thinner plates of Wood's glass and broader slits were used, and the source of light was brought much nearer the diamond.

Accompanying these large differences in the intensities of luminescence, we have corresponding differences in the intensity of absorption of the electronic lines, especially those at the wave-lengths 4152 and 5032. There is also a corresponding increase in the intensity of the subsidiary absorption bands associated with these two electronic lines and appearing towards shorter wave-lengths. It should be mentioned that if the diamonds are arranged in the order of the relative intensities of the two systems of bands as they appear in absorption, the list would be the same as Table II. The absolute intensities of absorption would, however, depend on the length of the absorbing column and cannot therefore be directly compared unless the latter is equal.

Figs. 9 and 10 in Plate XI illustrate the 4152 and 5032 systems respectively, as seen in absorption in a sequence of seven diamonds in one case, and a sequence of five in the other. We have only to compare the spectra of D36 and D224 in Fig. 9 or those of D1 and D197 in Fig. 10 to realise that great differences in the strength of absorption go hand in hand with the differences in the intensity of luminescence. It is not unlikely that the absorption coefficients for the electronic lines are proportional to the intensity of their emission and that the subsidiary band-systems also vary proportionately in intensity. No quantitative measurements have, however, been made to test these points.

It is important to remark that the intensity with which *the 4152 and 5032 electronic lines* are actually recorded in emission would be affected by the absorption of these same radiations before they emerge from the diamond. Hence, the apparent intensities of these lines as recorded in the spectra would not be proportional to the intensity of the luminescence as visually observed, especially when considerable thicknesses are involved. The subsidiary bands accompanying the electronic lines are a better criterion for the visually observed intensity of luminescence. The effect of self-reversal in reducing the intensity of the 4152 and 5032 lines compared with that of the band systems accompanying them is clear on an inspection of several of the spectrograms reproduced in Figs. 1, 7 and 8 in Plates VIII and X. This is also startlingly evident in the emission spectrum of D32 reproduced in Fig. 7, where the 4152 line has completely disappeared due to self-reversal in passing through a thickness of over one centimeter of diamond.

6. *The Electronic Frequencies*

In the fluorescence spectra taken at liquid air temperature, the presence is noticed of several sharply defined lines, besides those at 4152 and 5032 Å and the emission band-systems associated with these which appear at longer wave-lengths. The absorption spectra of luminescent diamonds similarly show several sharply defined dark lines other than 4152 and 5032 and the absorption band-systems associated with these toward shorter wave-lengths. When the absorption and emission spectra are compared, the positions of the bright and dark lines respectively noticed in them are found to coincide, and their identification as distinct electronic frequencies is thereby confirmed.

It must not be supposed, however, that an electronic absorption line would necessarily be observable in the same position in the spectrum as every electronic emission line. The effective absorption dependson the luminescent intensity of the diamond, the intrinsic strength of the electronic absorption and the length of the path available, and when these factors (or all of them working together) make the effective absorption very small, the absorption line in the spectrum would be overpowered by the transmission on either side of it and become unobservable. In general, therefore, a weak electronic line would be more easily observed in emission than in absorption, and only the strongest electronic lines could be expected to be recorded with very weakly luminescent diamonds, unless very long absorption paths are available. Another inherent difficulty in observing weak electronic lines arises when the region in which they appear coincides with the regions in which the subsidiary bands associated with the 4152 and 5032 lines appear.

The latter regions are fortunately different in emission and in absorption, and the relative intensity with which the two systems appear differs greatly with different diamonds. These facts and the sharpness and intensity of the electronic lines are an aid to their discrimination from the background of the band-system on which they may appear superposed.

The foregoing remarks will enable the results shown in Appendices I and II at the end of the paper to be better understood. These appendices give a list of the electronic lines observed in the emission and absorption spectra of the 28 diamonds investigated. Where a column has been left blank under either emission or absorption, it is to be understood that the same has not been studied. The figures recorded in these tables reveal the following features:—

(*a*) The most strongly luminescent diamonds show the largest number of electronic lines, and the number of such recorded in emission is generally greater than in absorption, for the reasons already explained.

(*b*) The blue-fluorescing diamonds show characteristic electronic lines at the wave-lengths 4090, 4109, **4152, 4189, 4197, 4206, 4959** and **5032** Å.

(*c*) The yellow-fluorescing diamonds show characteristic electronic lines at the wave-lengths 4060, 4123, **4152, 4194,** 4222, 4232, **4277, 4907,** 5014, **5032, 5359,** 5658, 5695, **5758,** 6177, 6265 and 6358 A.U.

The more intense lines are printed in heavy type. They may be recognised in the spectrograms reproduced in the Plates. Fig. 11(*a*), (*b*) and (*c*) indicate diagrammatically the changes of the electronic spectrum occurring in the transition from yellow to blue fluorescence. While the diagram represents the facts generally both as regards the positions of the lines and (qualitatively) also their relative intensities, individual diamonds show peculiarities of behaviour, as will be seen from the data given in Appendices I and II. For instance, D42 shows 4907, 6177, 6265 and 6358 but not 4959, 5359 or 5758. Then again, D13 shows strong lines at 4388 and 4833, D32 a strong line at 5895, and D47 strong lines at 4175 and 6043 which are not usually observed in other diamonds. A remarkable observation worthy of special mention is the appearance of an extremely sharp and intense absorption line at 3934 Å with D225 and D36.

7. *Structure of the* 4152 *and* 5032 *Lines*

In one particular diamond, the 4152 line in absorption was observed by Nayar to exhibit a doublet structure. In the present investigation it is

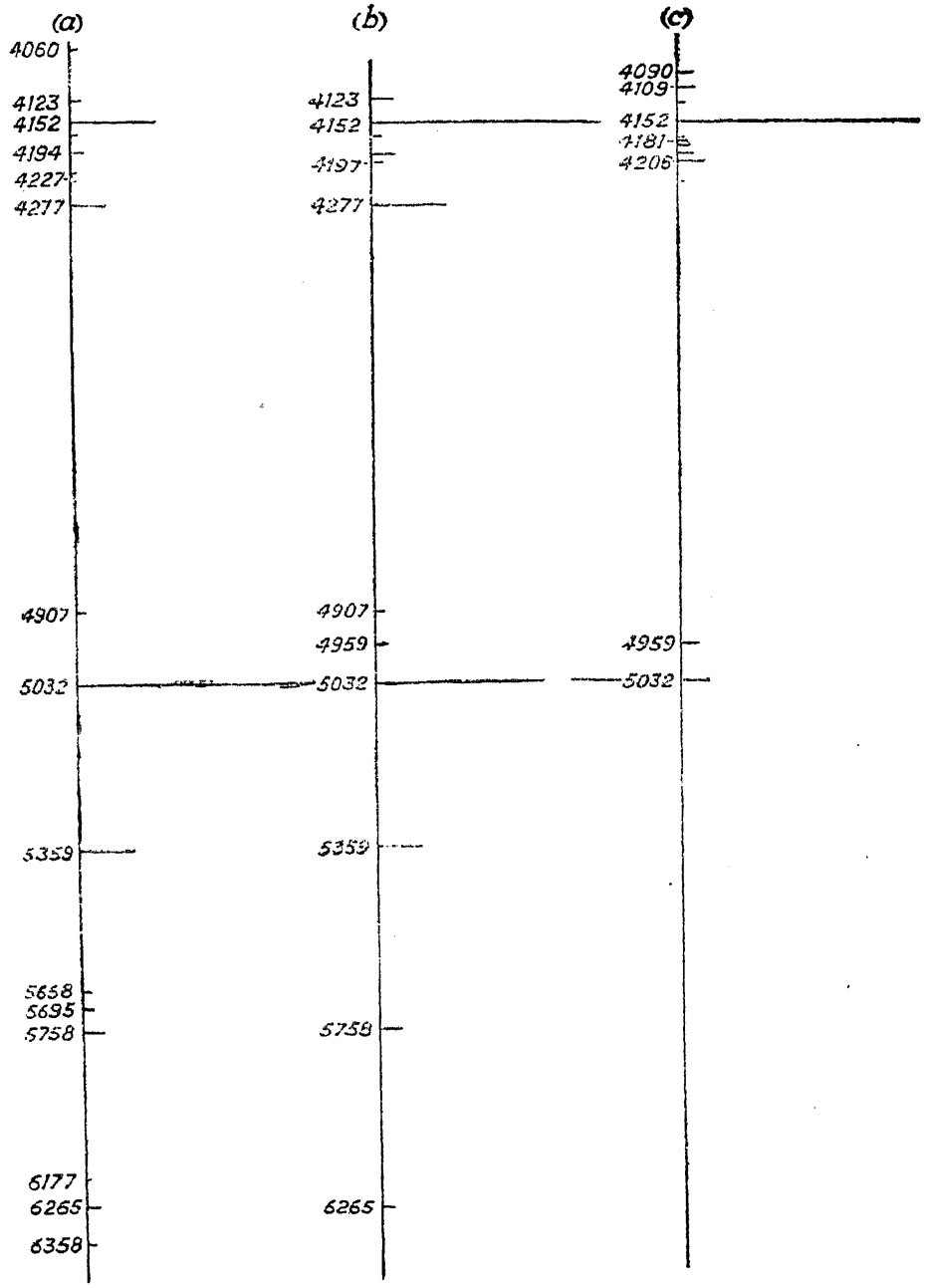

Fig. 11

FIG. 11. Electronic Spectrum of Diamond for (*a*) yellow, (*b*) green and (*c*) blue fluorescence.

found that in most diamonds the 4152 line appears as a doublet with widely separated components in both emission and absorption. The width and separation of the components generally increases with the intensity of luminescence. In very weakly fluorescent diamonds, the doublet is so close as to be scarcely resolved. With increasing intensities of luminescence, the separation as well as the width of each component increases, so that in the most intensely fluorescent diamonds the 4152 line is the most diffuse and the separation of the components the largest. This is strikingly illustrated in Fig. 13, Plate XII, where the microphotometer tracings of the 4152

line for 6 diamonds of increasing intensities of blue luminescence are reproduced. Table III gives the wave-lengths, width and separation of the two components of the 4152 line for 13 diamonds. It will be noticed that the two components always appear centred about the mean wave-length at 4152 A.U. and that the line is thus symmetrically split with regard to the positions of the two components. The intensity and the width of the component of longer wave-length are, however, larger than those of the component of shorter wave-length.

TABLE III

Structure of the 4152 Line

Number of Diamond	Component I		Component II		Separation in A.U.
	Wave-length in A.U.	Width in A.U.	Wave-length in A.U.	Width in A.U.	
D223	4155	3	4149	3	6
D224	4156	3	4150	2	6
D27	4155	3	4149	2	6
D40	4155	2	4149	2	6
D226	4155	5	4150	4	5
D42	4154	3	4149	2	5
D225	4154	3	4150	2	4
D34	4154	3	4151	3	3
D3	4153	2	4151	2	2
D38	4153	2	4151	2	2
D15	4153	2	4151	2	2
D13	4153	2	4151	1	2
D4	4153	2	4151	1	2

The four diamonds D3, D33, D34 and D226 appear to be exceptions to the general rule stated above as existing between the intensity of luminescence and the structure of the 4152 line. In D3, D33 and D34, the separation of the components is not as high as we might expect from their luminescence intensity. In D226 the two components of the 4152 doublet are extremely broad and more diffuse than in D223 or D224. It is likely that D226 owes its pink colour to some extraneous impurities and that these are responsible for the observed diffuseness of the line. It should be remarked however,

that in the case of diamonds showing a tinge of yellow or brown colour, impurities if present, appear to have no effect on the sharpness of the electronic lines.

In the case of two diamonds D223 and D225, it was observed that different portions of the same diamond give the 4152 line respectively as a well-separated doublet and as a single line. In D223, where the 4152 appears as a line, it is accompanied by two wings of high intensity extending to 4 A.U. on either side. D225 showed in the same spectrogram the upper portions of the doublet clearly split, while in the lower portion the two components were very close to each other. These observations become intelligible when it is remembered that in many cases diamonds show definite regions of both high and low luminosity and patterns of blue and green fluorescence. The weakly blue-fluorescent portions of the same diamond will show 4152 as a close doublet or a single line, while with the strongly fluorescent parts it will appear as a well-separated doublet.

Under the high dispersion of the three-metre spectrograph and at liquid air temperature the 4152 line in D42 appears as a triplet, the central line at 4152·2 A.U. being very much sharper and fainter than the two outer components. Absorption photographs of the 4152 line taken at room temperature and at liquid air temperature respectively on the three metre spectrograph are reproduced in Fig. 3(*a*) and (*b*) Plate VIII.

The principal electronic line appearing in fluorescence and absorption at 5032 A.U., on the other hand, does not alter in its width and structure with variations in the intensity of luminescence. As will be noticed in the photographs of the 5032 system for different diamonds reproduced in Fig. 8 (emission) and Fig. 10 (absorption), there is no marked broadening of the line as the intensity of yellow luminescence increases, the width of the line in the strongest and weakest fluorescing diamonds being approximately the same, *viz.*, 7 to 8 A.U. In all yellow-fluorescing diamonds, with the exception of D1, D13 and D15 where it appears as a very close doublet, 5032 is present as a single line. Absorption spectra taken on the three-metre spectrograph also failed to reveal any clear splitting of the 5032 line. No definite relationship thus seems to exist between the intensity of yellow luminescence and the structure of the 5032 line. In D226, the 5032 line as well as the other electronic frequencies at 4206, 4388 and 4959 are broader than in other diamonds. This, as mentioned before, is to be ascribed to probable impurities in this diamond.

8. *The Lattice Spectrum of Diamond*

(*a*) *The 4152 System.*—The wave-lengths, intensities and frequencies of the principal electronic line at 4152 and the associated subsidiary bands

in both fluorescence and absorption are given in Table IV. Column 6 gives the descriptions of the lines and bands, and columns 5 and 9 the frequency differences of the subsidiary bands from 4152 in fluorescence and absorption respectively. The microphotometer tracing of the 4152 system in emission for D4 is reproduced in Fig. 14, Plate XIII, and the prominent lattice frequencies indicated by their frequency shifts. The bands are numbered from II to XI, extending to 4825 A.U. in fluorescence and to 3730 A.U. in absorption. The continuous spectrum in fluorescence lies between 4110 and 6500 A.U. A number of new lines have been observed in the present investigation, *viz.*, 4158, 4164, 4169, 4189, 4215, 4248, 4279, 4373, 4386 and 4401 in fluorescence and 4140, 4135, 4123, 4116, 4109, 4092, 4060, 3952 and 3930 in absorption. The bands X and XI in fluorescence could not be obtained in absorption, owing to the lack of sensitiveness of the selochrome plates in the 3500–3700 Å region.

An examination of the 4152 system in both emission and absorption reveals that though the intensity of the subsidiary bands relative to that of 4152 varies from diamond to diamond, the relative intensities of the lattice bands among themselves are constant. The only exception to this rule is the first subsidiary band II which generally consists of two faint lines at 4164 and 4169 in fluorescence and at 4140 and 4135 in absorption. In D47 this appears as a fairly intense band with limits at 4158 and 4169 and is observed in D3, D4, D19, D40 and D225 but weakly. This band is however present in fluorescence and absorption with identical frequency shifts in both the 4152 and 5032 systems and hence 34, 70 and 98 cm.$^{-1}$ are classed as genuine lattice frequencies.

The lattice lines at 4060, 4109, 4175, 4189, 4197 and 4304 coincide with electronic lines present at the same wave-lengths and this is evidently responsible for the observed small variations in the relative intensities of these lines.

A number of lines which could not be classified with any certainty as either lattice or electronic lines are listed separately in Table V.

D32 exhibits the lattice spectrum in absorption also at wave-lengths greater than 4152. The bands in absorption at longer wave-lengths disappear at low temperatures and are therefore probably thermally excited. D32 also exhibits three broad bands in absorption with approximate limits at 4494 and 4538, 4602 and 4701 and 4758 and 4794 A.U., which are apparently unrelated to either the 4152 or 5032 systems. The last one at 4776 A.U. is the most intense of the three and appears in the fluorescence spectrum as a dark band.

TABLE IV

Lattice Spectrum in the 4152 System

No.	Fluorescence				Description of the Bands	Absorption		
	Wavelength in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency differences from 4152 in cm.$^{-1}$		Wavelength in A.U.	Frequency in cm.$^{-1}$	Frequency differences from 4152 in cm.$^{-1}$
I	4152	20	24077	..	Intense line	4152	24077	..
II	4158	½	24043	34	Sharp edge	..	..	..
	4164	½	24009	68	Discrete line	(4140)	24148	(71)
	4169	½	23980	97	Discrete line	(4135)	24177	100
III	4175	½	23945	132	Sharp limit	4130	24206	131
	4183	½	23900	177	Discrete line	(4123)	24247	(170)
	4189	½	23865	212	Discrete line	(4116)	24288	(211)
	4197	1	23820	257	Discrete line	(4191)	24330	(253)
	4215	1	23718	359	Discrete line	(4092)	24431	(354)
	4230	1	23634	443	Sharp limit	4077	24521	444
IV	4246	3	23545	532	Very sharp edge	4062	24611	533
	4248	4	23534	543	Discrete line	4060	24624	544
	..	..	..	..	Discrete line	4057	24642	565
	4273	5	23396	681	High int. edge	4038	24758	681
	4279	5	23363	714	Discrete line	4032	24795	717
	4292	6	23293	784	Sharp edge	4021	24862	785
V	4304	½	23228	849	Discrete line	4011	24924	847
	4322	1	23131	946	Discrete line	3995	25024	947
	4334	3	23067	1010	Discrete line	3984	25093	1016
	4349	4	22987	1090	Discrete line	3973	25163	1086
VI	4357	3	22945	1132	Sharp edge	3966	25207	1130
	4360	4	22929	1148	Discrete line	3963	25226	1149
	4373	4	22861	1216	Discrete line	(3952)	25296	1219
	4380	5	22825	1252	Discrete line	3947	25328	1251
	4386	5	22793	1284	Discrete line	3942	25360	1283
	4395	6	22747	1330	Discrete line	3935	25406	1329
	4397	5	22736	1341	Sharp edge	3933	25419	1342
VII	4401	2	22716	1361	Sharp line	3930	25438	1361
	4406	2	22690	1387	Sharp limit	3927	25457	1380
	(4461)	1	22410	(1667)	Limit approx.	(3890)	25700	(1623)
VIII	(4490)	2	22265	(1812)	Limit approx.	(3865)	25865	(1788)
	(4511)	3	22162	(1915)	Peak approx.	(3850)	25967	(1890)
	(4547)	3	21986	(2091)	Limit approx.	(3827)	26123	(2046)
IX	(4611)	2	21681	(2396)	Limit approx.	(3782)	26434	(2357)
	(4635)	2	21569	(2508)	Peak approx.	(3758)	26602	(2525)
	(4667)	2	21421	(2656)	Limit approx.	(3742)	26716	(2639)
X	(4678)	1	21370	(2707)	Limit approx.	..	..	..
	(4700)	1	21271	(2806)	Peak approx.	..	..	..
	(4710)	1	21225	(2852)	Limit approx.	..	..	..
XI	(4760)	1	21002	(3075)	Limit approx.	..	..	..
	(4795)	1	20849	(3228)	Peak approx	..	..	..
	(4825)	1	20719	(3358)	Limit approx	..	..	..

N.B.—The figures within brackets refer to lines which are doubtful or to those whose frequencies could not be measured accurately.

The sharpness of the lattice lines in the 4152 system is closely associated with the structure of the 4152 line. In strongly fluorescing diamonds where the 4152 is broad and diffuse, the lattice lines are broad and the edges of the bands slightly diffuse, while in weakly fluorescent diamonds, where the 4152 is sharp, the lattice lines and edges are correspondingly sharp. This is clearly seen in the spectra of D3, D1, D42 and D225 in the Plates and may more readily be noticed in the case of the lines at 4334 and 4349 which are a prominent feature of every spectrum. In D226, these two lines are scarcely observable owing to their diffuseness. In D3 and D1 they are seen to be very sharp. The variations in the breadth of the lattice lines with the broadening and splitting of the 4152 line suggest that both components of the doublet are capable of exciting the lattice frequencies. Therefore the procedure adopted in Table IV of considering neither of the components but the central wave-length at 4152 as responsible for exciting the lattice spectrum appears justified.

TABLE V

Unassigned Frequencies

No.	Wave-length of lines in		Diamonds in which present	Frequency in cm.$^{-1}$
	Emission	Absorption		
1	5128	..	D225	19495
2	4200	..	D3	23803
3	4310	..	D223	23195

(*b*) *The* 5032 *System.*—Preliminary investigations by Nayar on the yellow luminescence and absorption of diamond had shown that the fluorescence spectrum is similar to that in the blue and consists of a principal band accompanied by subsidiary bands at longer wave-lengths in fluorescence and at diminished wave-lengths in absorption. A photograph of the 5032 system in emission and absorption taken by Nayar is reproduced in an article by Sir C. V. Raman in *Current Science* for January 1943.

At room temperature the principal electronic line lies at 5038 A.U. and is about 15 A.U. broad. The subsidiary bands, as will be seen in Fig. 5(*a*), are correspondingly broad and diffuse. As the temperature is lowered, both the main and subsidiary bands become more intense and sharper and shift towards shorter wave-lengths. The peak of the band at liquid air temperature as determined by a microphotometer curve was found to be at 5032·0 A.U. Descriptions of the bands, their wave-lengths, intensities

and frequencies are given in Table VI for both emission and absorption. Columns 5 and 9 give the frequency shifts of the subsidiary bands from 5032 in fluorescence and absorption respectively. A microphotometer tracing of the 5032 system in emission is reproduced in Fig. 15, Plate XIII.

TABLE VI

Lattice Spectrum in the 5032 System

No.	Fluorescence				Description of the Bands	Absorption		
	Wavelength in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$		Wavelength in A.U.	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$
I	5032	20	19867	..	Intense line	5032	19867	..
II	5040	4	19836	31	Sharp limit	..	..	..
	(5049)	4	19800	(67)	Fall in intensity	(5015)	19934	(67)
	(5056)	2	19773	94	Diffuse limit	(5009)	19958	(91)
III	(5062)	2	19750	(117)	Diffuse limit	(5002)	19986	(119)
	(5080)	4	19680	(187)	Rise in intensity	(4985)	20054	(187)
	(5100)	7	19602	(265)	Further rise in intensity	(4966)	20131	(264)
	(5130)	7	19488	(379)	Fall in intensity	(4930)	20278	(411)
	(5144)	3	19435	(432)	Diffuse limit	(4920)	20320	(453)
IV	(5170)	3	19337	(530)	Diffuse limit	(4900)	20402	(535)
	(5180)	5	19300	(567)	Rise in intensity	(4890)	20444	(577)
	..	..	..	..	..	..	..	..
	(5216)	5	19166	(701)	Fall in intensity	..	..	..
	(5230)	3	19115	(752)	Diffuse limit	(4840)	20655	(788)
V	(5260)	2	19006	(861)	Diffuse limit	(4825)	20720	(853)
	(5284)	3	18920	(947)	Rise in intensity	..	..	..
	(5304)	3	18848	(1019)	Fall in intensity	(4788)	20880	(1013)
	(5320)	2	18792	(1075)	Diffuse limit	(4768)	20967	(1100)
VI	(5335)	1	18739	(1128)	Fairly sharp limit	(4762)	20994	(1127)
	5341	2	18718	1149	Sharp line	4757	21016	1149
	5372	3	18610	1257	Sharp limit	4733	21122	1255
	5381	2	18579	1288	Sharp limit	4727	21149	1282
	5393	2	18537	1330	Sharp limit	4716	21198	1331
	(5397)	1	18524	(1343)	Fairly sharp limit	(4713)	21212	(1345)
VII	(5420)	2	18445	(1422)	Limit approx.	(4692)	21307	(1440)
	(5455)	2	18327	(1540)	Peak approx.	(4673)	21394	(1527)
	(5492)	2	18203	(1664)	Limit approx.	(4645)	21522	(1655)
VIII	(5520)	1	18110	(1757)	Limit approx.	(4611)	21681	(1814)
	(5560)	1	17980	(1887)	Peak approx.	(4588)	21790	(1923)
	(5602)	1	17846	(2021)	Limit approx.	(4566)	21895	(2028)
IX	(5639)	1	17729	(2138)	Limit approx.	..	..	..
	..	..	..	..	Peak approx.	(4468)	22375	(2508)
	..	..	..	..	..	..	..	..

The bands are numbered from II to IX and extend to 5700 A.U. in fluorescence and to 4400 in absorption. The continuous spectrum in this system extends to 6500 A.U., and beyond 5600 A.U. is as intense as the subsidiary bands whose limits could not therefore be located with any certainty. The relative intensities of the subsidiary bands as in the 4152 system are always constant with the exception of the band II which is generally weak, but appears with fairly high intensity in D225 (see Fig. 7*c* and Fig. 8*c*).

(*c*) *Lattice Frequencies.*—An examination of Tables IV and VI shows that the frequency shifts of the subsidiary bands in both the 4152 and 5032 systems are identical within the limits of accuracy of measurement and that these bands arise from a combination of the lattice frequencies of the diamond lattice with the electronic frequencies at 4152 and 5032 respectively. The intensity and structure of the bands in the two systems are, however, very different. In the 4152 system, the bands II to VI consist of sharp lines or bands with extremely sharp edges, while in the 5032 system all the bands with the exception of VI are broad and diffuse. The lattice bands in the 4152 system alternate in intensity, II, V, VII, IX and XI being weaker than IV, VI and VIII. In the 4152 system VI is the most intense band and III one of the weakest. On the other hand in the 5032 system, the bands progressively decreasing in intensity as we proceed away from 5032, III is the most intense band of the group and VI one of the weakest.

The lattice frequencies derived from fluorescence and absorption measurements may be classified into ten groups: 34–98, 132–443, 532–784, 848–1088, 1131–1341, 1361–1667, 1800–2090, 2400–2660, 2700–2850 and 3100–3350 cm.$^{-1}$ The principal discrete frequencies are listed below:—

34, 70, 98, 132, 178, 212, 258, 359, 443, 533, 543, 565, 681, 716, 784, 848, 946, 1013, 1088,1131, 1149, 1218, 1252, 1284, 1330.

9. *Effect of Temperature Variation on the* 5032 *System*

The general effect of cooling the crystal from room temperature to liquid air temperature is to increase the intensity of fluorescence and absorption in the whole region of the 5032 system. The bands become considerably sharper and shift towards the blue, the general behaviour being analogous to that of the 4152 system. The changes in absorption in every case are parallel to those in fluorescence. In Table VII are given the wave-lengths and frequencies of the principal electronic line and the lattice bands of the 5032 system at room temperature and at liquid air temperature respectively. In column (3) are shown the shifts of the bands in cm.$^{-1}$ as the temperature is lowered from 25° C. to − 189° C. In column (6) the changes in

TABLE VII

Effect of Temperature Variation on Electronic and Lattice Lines

No.	25° C.		−189° C.		Wave-numbers shift	Shift per 1000 cm.$^{-1}$
	Wave-length in A.U.	Frequency in cm.$^{-1}$	Wave-length in A.U.	Frequency in cm.$^{-1}$		
I	5038	19844	5032	19868	24	1·2
III	5123	19514	5115	19545	31	1·6
IV	5204	19210	5198	19233	23	1·2
V	5292	18891	5286	18912	21	1·1
VI	5367	18627	5359	18655	28	1·5
VII	5455	18327	5451	18340	13	0·71
XI	5701 5768	17536 17332	5695 5758	17554 17362	18 30	1·0 1·7
1	4156	24057	4152	24077	20	0·83
2	3450	28975	3447	28999	24	0·83
3	3304	30257	3299	30303	46	1·5
4	3159	31648	3154	31699	51	1·6
5	Raman line	1332·1	Raman line	1333·8	1·7	1·3

frequencies in each case are shown as a shift per 1000 cm.$^{-1}$ In the lower half of the table are given similar data for the prominent electronic lines in the 4152 system and in ultra-violet absorption along with those of the 1332 line in Raman effect (taken from Nayar's tables). An examination of the last column shows that the shifts per 1000 cm.$^{-1}$ are more or less of the same order and about the same as that of the 1332 line in Raman effect.

In conclusion, the author wishes to express her respectful thanks to Professor Sir. C. V. Raman for his constant guidance and encouragement during the course of this work.

10. *Summary*

A detailed study of the fluorescence and absorption spectra of 32 diamonds of widely different intensities and colours of luminescence has been made at room temperature and at liquid air temperature, using a two-prism spectrograph of good resolution and large light-gathering power. A clear relation is observed to exist between the fluorescence and absorption spectra in the visible region and this is shown to extend both to the

general character of the spectra and to their intensities. In spite of the enormous variations in the intensity and colour of luminescence, the spectra in all diamonds consist mainly of the 4152 and 5032 systems which consist of (*a*) a set of lines appearing as bright and dark at the same wave-lengths respectively in fluorescence and absorption, (*b*) subsidiary or lattice lines appearing at greater wave-lengths in fluorescence and at diminished wave-lengths in absorption, associated with the principal electronic lines at 4152 and 5032 Å respectively. In blue-fluorescing diamonds the 4152 system is more prominent than the 5032 system. In yellow-fluorescent diamonds the reverse is the case. More generally, the two systems appear with comparable intensities. The intensity and colour of luminescence is thus determined by the absolute and relative intensities of the two systems.

Thirty-six electronic lines other than 4152 and 5032 are found to be present in the visible region. Of these the lines at 4060, 4123, 4194, 4222, 4232, 4277, 4907, 5359, 5695, 5758, 6177, 6265 and 6358 are characteristic of yellow fluorescence while those at 4090, 4109, 4189, 4197, 4206 and 4959 are characteristic of blue fluorescence.

The 4152 line appears in most diamonds as a doublet in both emission and absorption, the width and separation of the components increasing with the intensity of blue luminescence. The 5032 line shows no such variation with changes in the intensity of yellow fluorescence.

The frequency differences between the principal electronic lines at 4152 and 5032 and the lattice lines associated with them are the same in fluorescence and absorption, and lie in the infra-red range; they thus represent the vibration frequencies of the diamond lattice. Their values as derived from the 4152 and 5032 systems are identical, but the degree of sharpness and the intensity distributions are different in the two systems. From the observed frequency differences 25 monochromatic frequencies, *viz.*, 34, 70, 98, 132, 178, 212, 258, 359, 443, 533, 543, 565, 681, 716, 784, 848, 946, 1013, 1088, 1131, 1149, 1218, 1252, 1284 and 1330 have been obtained as constituting the lattice spectrum of diamond.

APPENDIX I

List of Electronic Lines

Observed in Diamond	Wave-lengths in A.U. and intensities (on a scale of 20) of the lines present in	
	Fluorescence	Absorption
D3	4152 (20), 4189 (0), 4197 (1), 4206 (2), 4959 (5), 5032 (6)	4152 (20), 5032 (4), 4959 (2)
D7	4152 (20), 5032 (3)	
D8	4152 (20)	
D12	4152 (20), 4206 (2), 5032 (1)	
D27	4152 (20), 4206 (4), 4222 (2)	
D31		4152 (20)
D32	4152 (–), 4197 (6), 4206 (6), 4227 (15), 5895 (20)	4152 (20), 4189 (1), 4197 (1), 4206 (2), 4304 (1), 4380 (1), 4252 (1), 4959 (1), 5032 (1)
D33	4152 (20), 4197 (3), 4206 (2)	4152 (20)
D34	4152 (20), 4189 (1), 4197 (1), 4206 (2), 4959 (2), 5032 (1)	
D36	4152 (20), 4197 (1), 4206 (3), 4227 (1), 5032 (0)	4152 (20), 3934 (5),
D38	4152 (20), 4206 (2), 4227 (2), 5032 (4)	
D40	4152 (20), 4189 (0), 4197 (0), 4206 (1), 4227 (1), 4959 (2), 5032 (6), 5233 (1)	
D42	4152 (20), 4189 (1), 4197 (2), 4206 (4), 4907 (2), 5032 (8), 6177 (1), 6265 (2), 6358 (1)	4152 (20), 5032 (4)
D42+D43		4152 (20), 4206 (1), 5014 (1), 5032 (3)
D221		4152 (20)
D223	4090 (1), 4109 (1), 4152 (20), 4175 (2), 4189 (1), 4197 (2), 4206 (3), 5233 (2)	
D224	4090 (2), 4109 (1), 4152 (20), 4189 (2), 4197 (3), 4206 (4)	4152 (20)
D226	4152 (20), 4206 (2), 4388 (5), 4959 (2), 5032 (7)	4152 (20), 5032 (5)

APPENDIX II

List of Electronic Lines

Observed in Diamond	Wave-lengths in A.U. and intensities (on a scale of 20) of the lines present in	
	Fluorescence	Absorption
D1	4060 (1), 4123 (1), 4152 (20), 4194 (2), 4222 (1), 4227 (0), 4232 (1), 4277 (3), 4907 (2), 5014 (0), 5032 (20), 5359 (4), 5658 (1), 5695 (1), 5758 (2), 6177 (0), 6265 (0), 6358 (0)	4152 (20), 4907 (2), 5014 (1) 5032 (20), 5359 (4)
D4	4152 (20), 4175 (1), 4206 (2), 4907 (3), 4959 (1), 5032 (7), 5359 (1)	4152 (20), 5032 (6)
D10		4152 (15), 4907 (2), 5032 (20), 5359 (3)
D11		4152 (5), 4907 (1), 5032 (20), 5359 (4)
D13	4123 (1), 4152 (20), 4175 (1), 4194 (3), 4222 (1), 4227 (0), 4232 (1), 4277 (5), 4388 (6), 4590 (1), 4606 (2), 4833 (4), 5014 (0), 5032 (20), 5359 (3), 5658 (0), 5695 (0), 5758 (2), 6177 (0), 6265 (0), 6358 (0)	
D15	4123 (1), 4152 (20), 4194 (3), 4222 (1), 4227 (0), 4232 (1), 4277 (6), 4907 (2), 4959 (1), 5032 (15), 5359 (6), 5658 (0), 5695 (0), 5758 (1), 6177 (0), 6265 (0), 6358 (0)	4152 (15), 4907 (2), 5032 (20), 5359 (5)
D19	4152 (10), 5032 (20), 5359 (3)	
D47	4152 (20), 4175 (4), 4959 (1), 5032 (12), 5233 (2), 5359 (2), 5758 (2), 5895 (1), 6043 (4)	
D197		4060 (1), 4152 (6), 5014 (1), 5032 (20)
D225	4152 (20), 4189 (2), 4197 (3), 4206 (4), 4959 (18), 5032 (12)	3934 (10), 4152 (20), 4245 (1), 4295 (2), 4304 (1) 4959 (6), 5032 (10)

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DESCRIPTION OF PLATES VIII TO XIII

FIG. 1. Fluorescence spectra, (*a*) at room temperature, and (*b*), (*c*), (*d*) at liquid air temperature. In these, 4152 appears at the extreme left and 5032 at the extreme right. The latter is much brighter than the former for D1 which is a yellow-luminescing diamond, while the reverse is the case for D3 and D42 which are blue-luminescing diamonds. 4152 is clearly seen as a doublet in Fig. 1 (*d*). The electronic frequency at 4959 is seen with D3 but not with D1. Note other electronic frequencies at 4194, 4222, 4232, 4277 in (*c*) and 4189, 4197 and 4206 in (*b*).

FIG. 2. Fluorescence and absorption spectra juxtaposed after inverting the latter to exhibit the mirror-image symmetry of the lattice lines about the electronic frequency at 4152.

FIG. 3. The 4152 line of D42 in absorption at room temperature and at liquid temperature with the three-meter spectrograph.

FIG. 4. The 5032 system of D1 in emission and absorption at liquid air temperature, showing mirror-image symmetry. Note the two prominent electronic lines at 5359 and 5758 A.U.

FIG. 5. (*a*) The 5032 system in emission at room temperature ; (*b*) and (*c*), the same in emission and absorption at liquid air temperature, with the latter inverted.

FIG. 6. (*a*) and (*b*). The 4152 and 5032 systems in emission for diamonds D1 and D3 respectively.

FIG. 7. (*a*), (*b*), (*c*) and (*d*). Emission spectra of four diamonds, showing variations in the appearance of the 4152 line, and its effect on the associated lattice spectrum. In Fig. 7 (*a*) the 4152 has disappeared by self-reversal, while in Fig. 7 (*c*), it has been much weakened.

FIG. 8. (*a*), (*b*), (*c*), (*d*) and (*e*). Sequence showing progressive change in the relative intensities of the 4152 and 5032 systems. Notice also the changes in the appearance of the 4152 line.

FIG. 9. Sequence showing the appearance of the 4152 system in absorption and its increased intensity with increasing intensity of luminescence. Note also the increased width of the 4152 line in the sequence. D227 is non-fluorescent and shows no lines.

FIG. 10. Sequence showing the 5032 system in absorption and its increasing intensity wtih intensity of luminescence.

FIG. 12. The complete fluorescence and absorption spectra of diamond in the visible with wave-length scale, to illustrate the general relationship between fluorescence and absorption.

FIG. 13. Microphotometer tracings of the 4152 line for six diamonds of increasing intensities of luminescence, illustrating the corresponding variations in the structure of the line.

FIG. 14. Microphotometer tracing of the 4152 system of D4 in fluorescence at liquid air temperature. The prominent electronic frequencies are indicated by their wavelengths in A.U. and the lattice lines by their frequency shifts in $cm.^{-1}$ from the 4152 line.

FIG. 15. Microphotometer tracing of the 5032 system of D15 in fluorescence at liquid air temperature. The electronic and lattice lines are indicated as in Fig. 14.

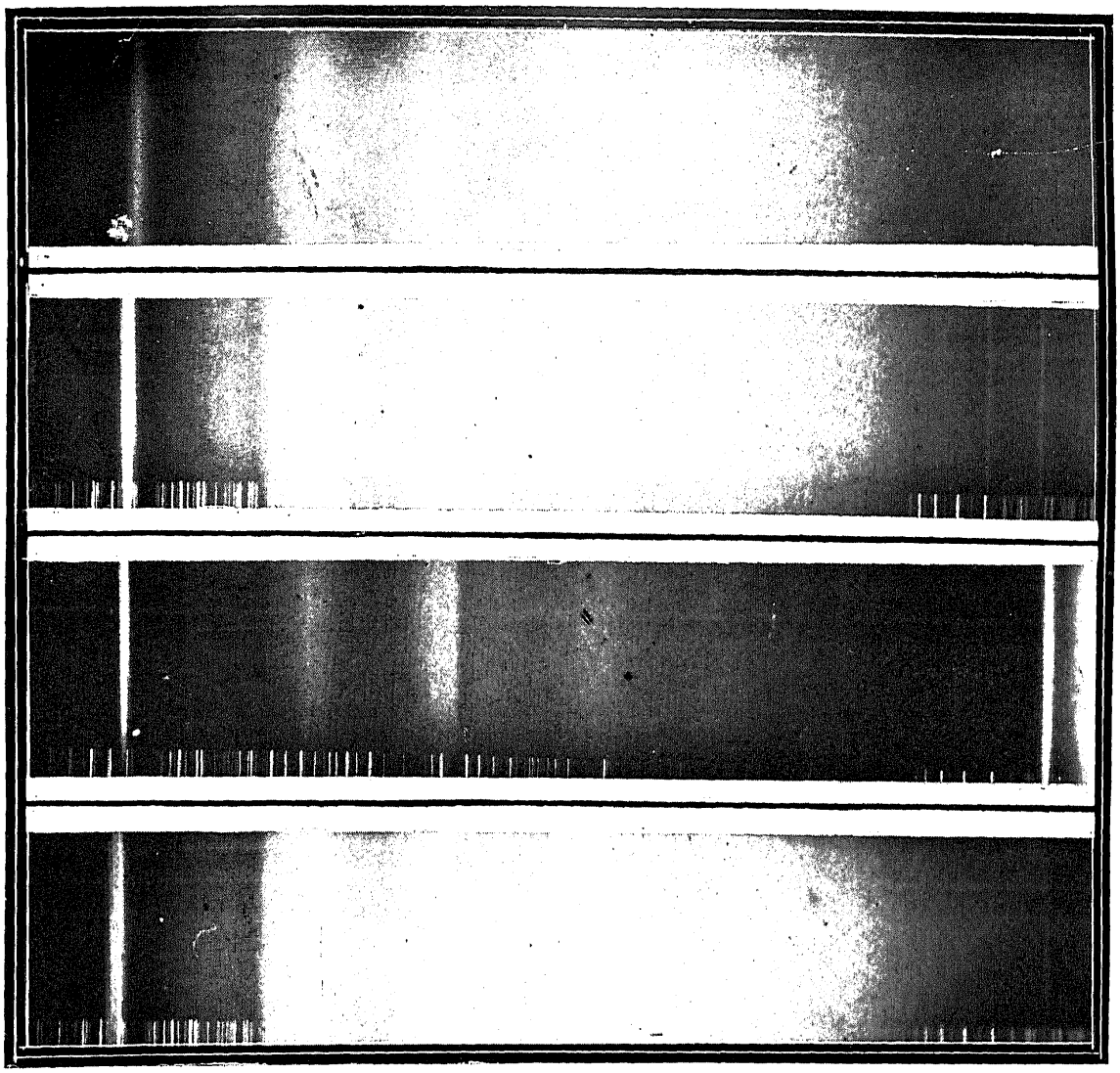
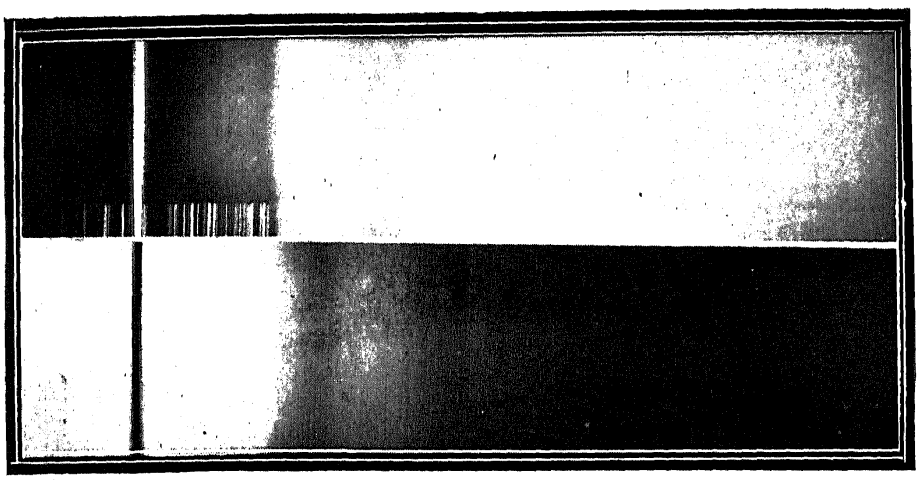


FIG. 1

$\lambda \rightarrow$



$\leftarrow \lambda$

FIG. 2

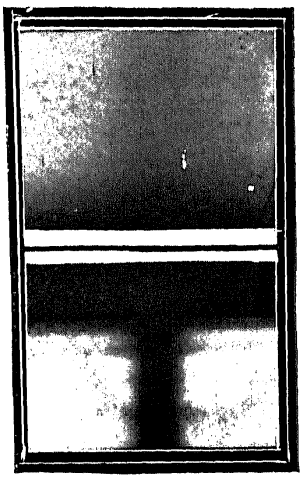


FIG. 3

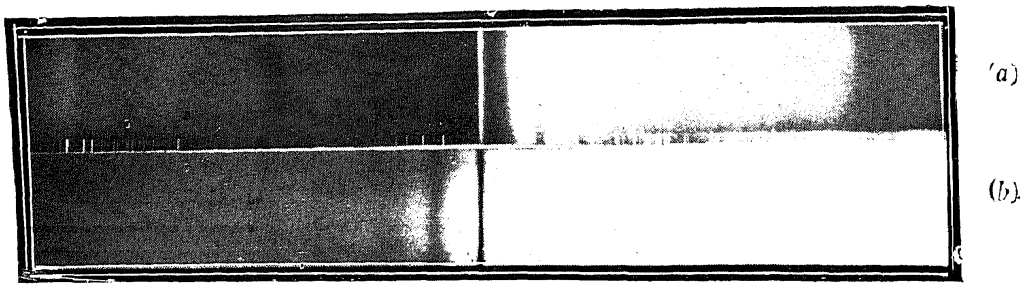


FIG. 4

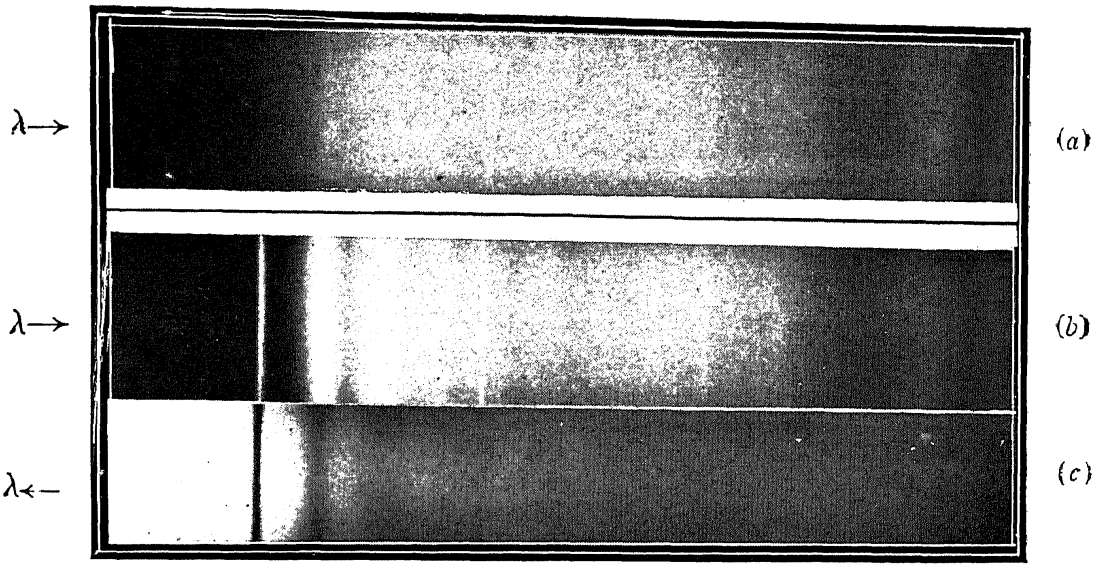


FIG. 5

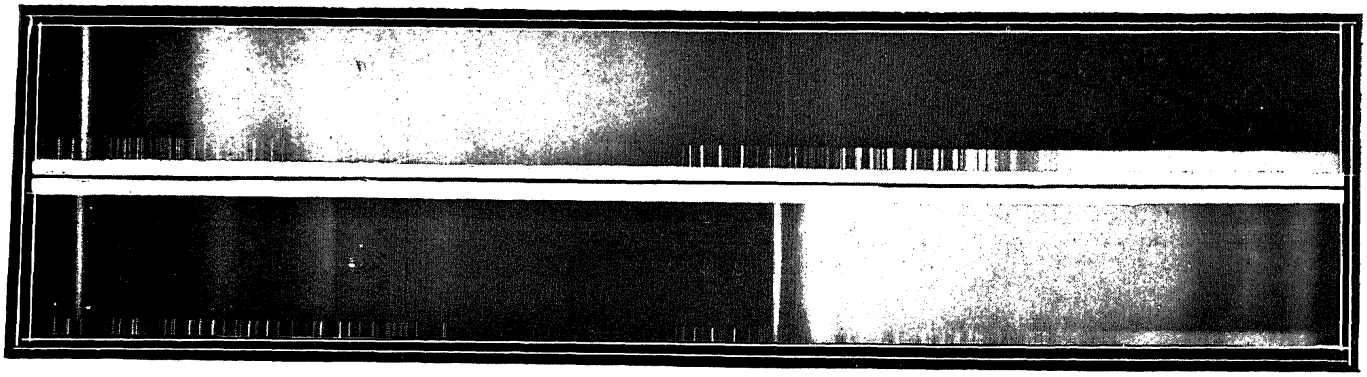


FIG. 6

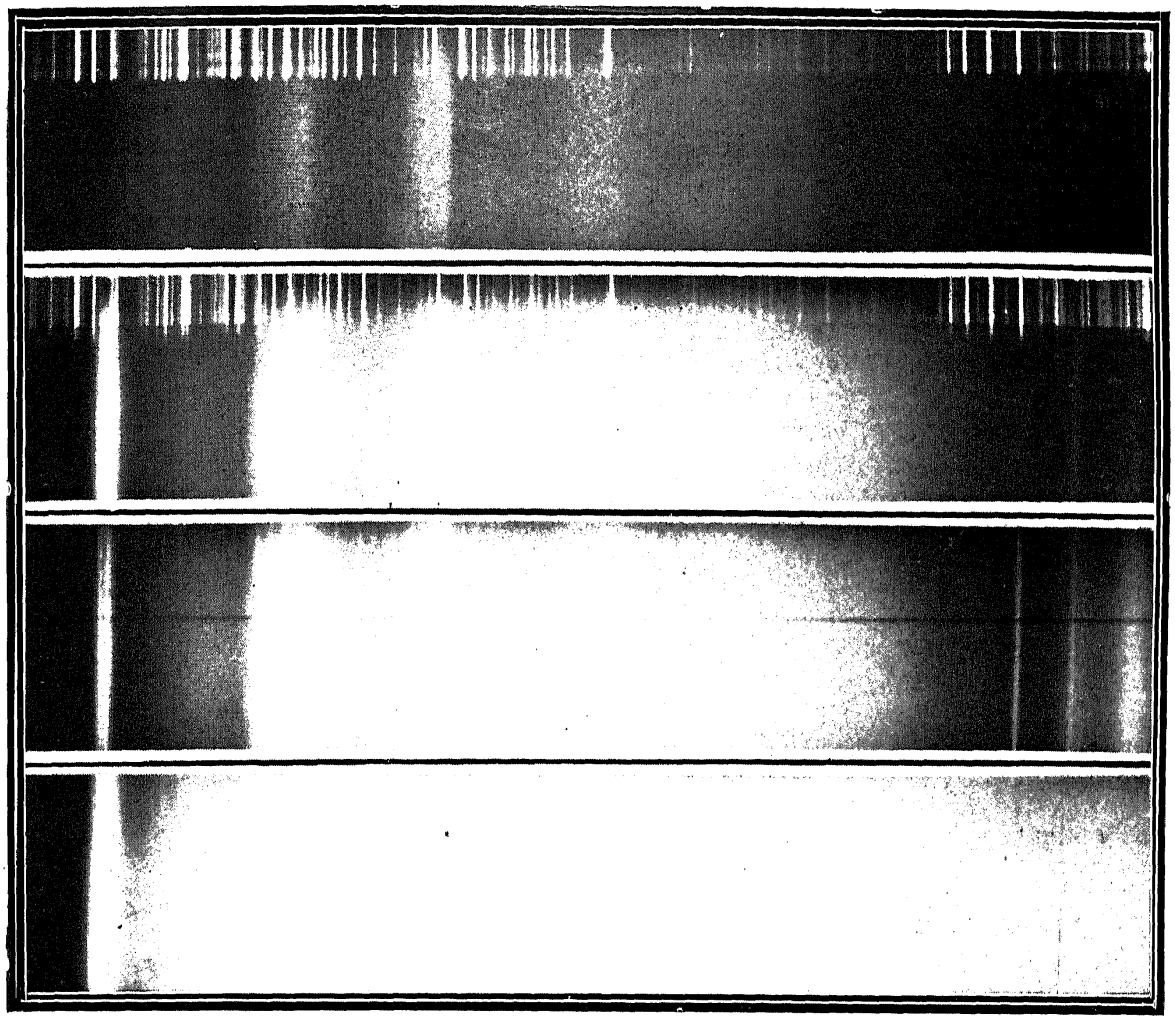


FIG. 7

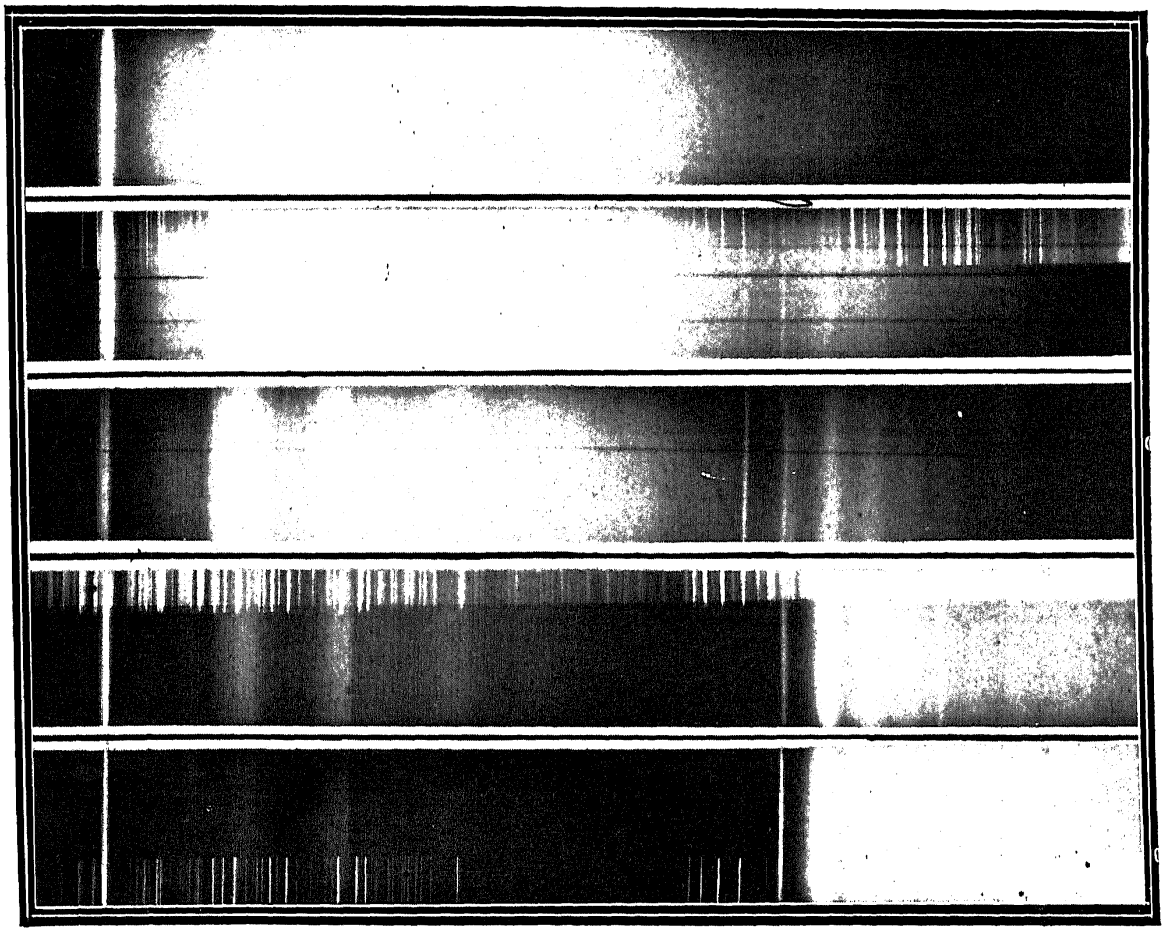


FIG. 8

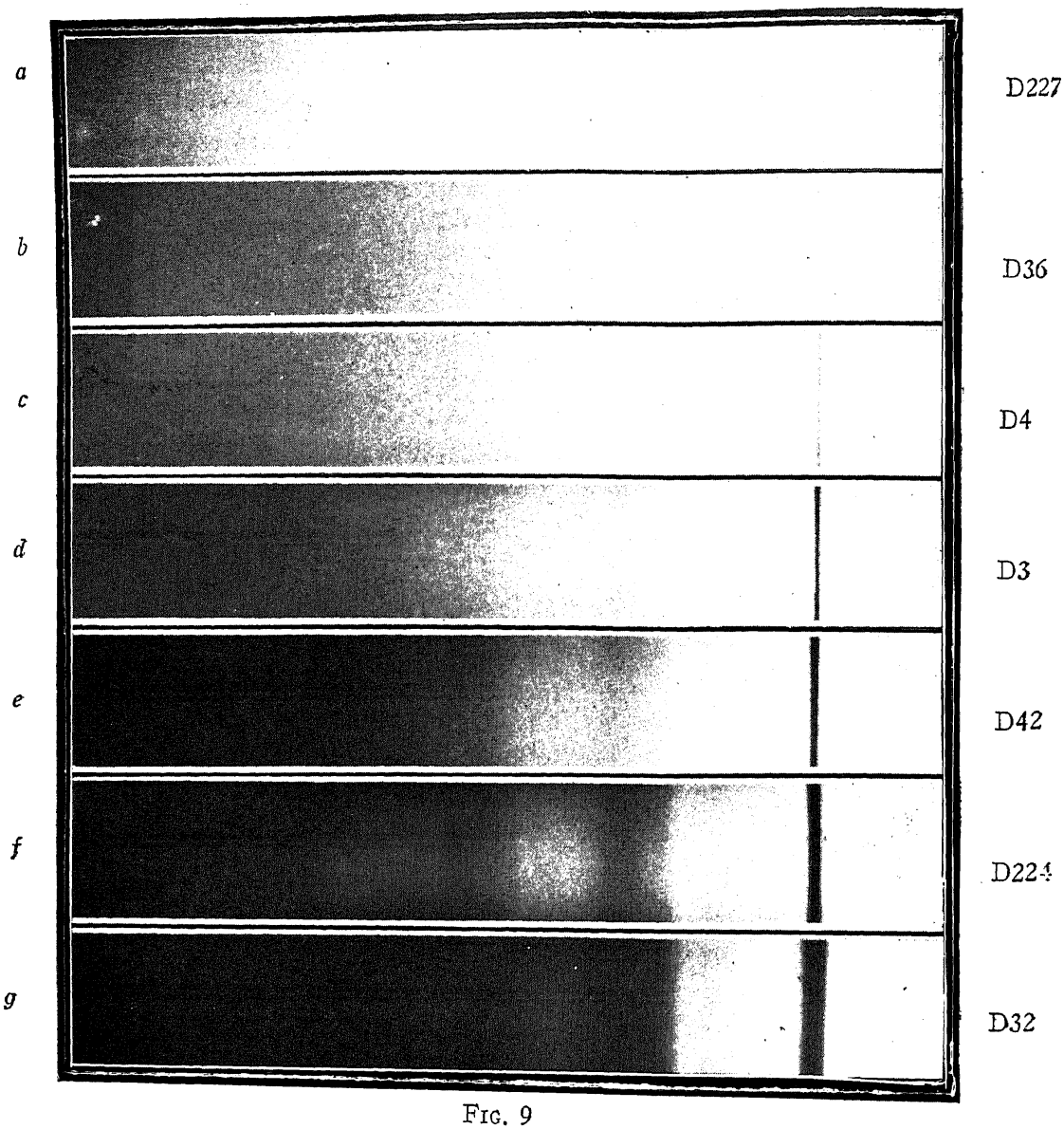
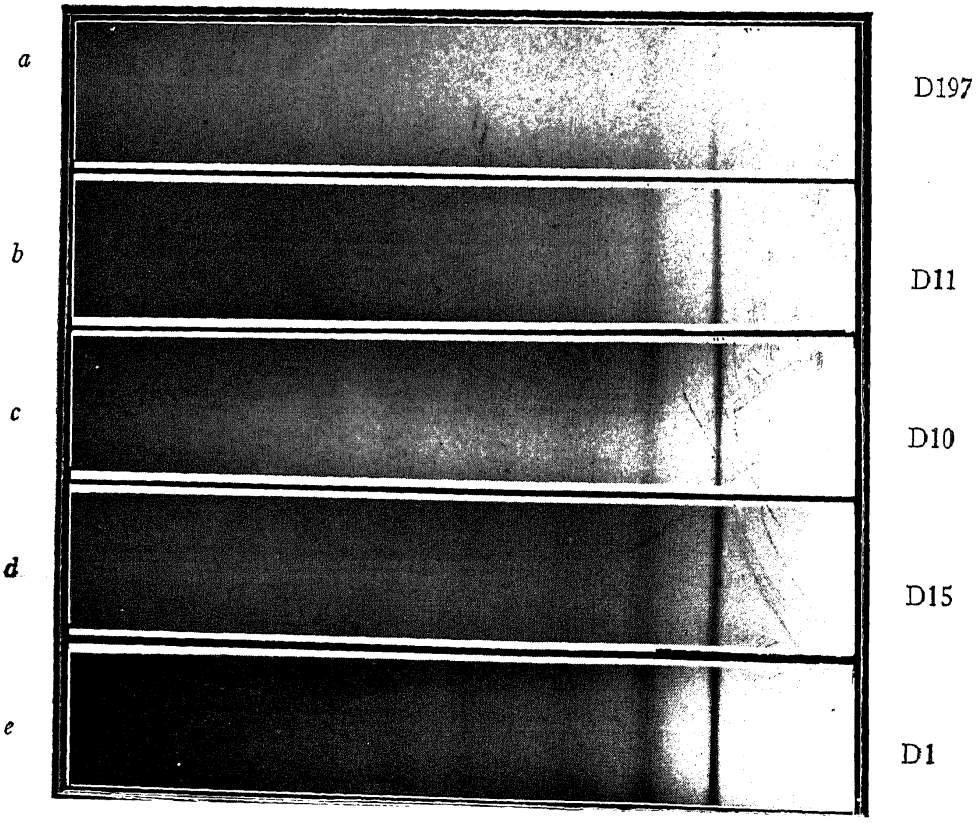


FIG. 9



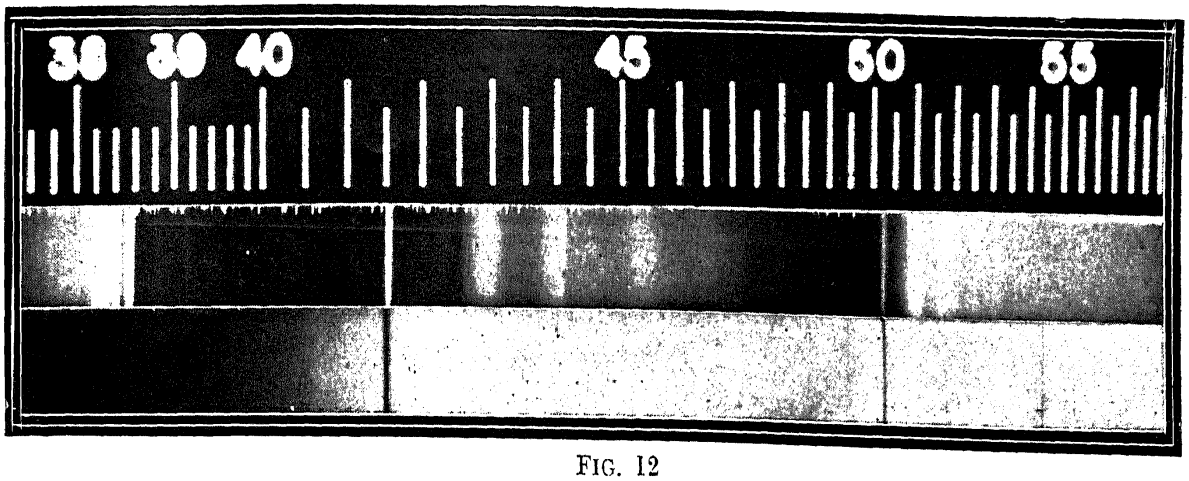
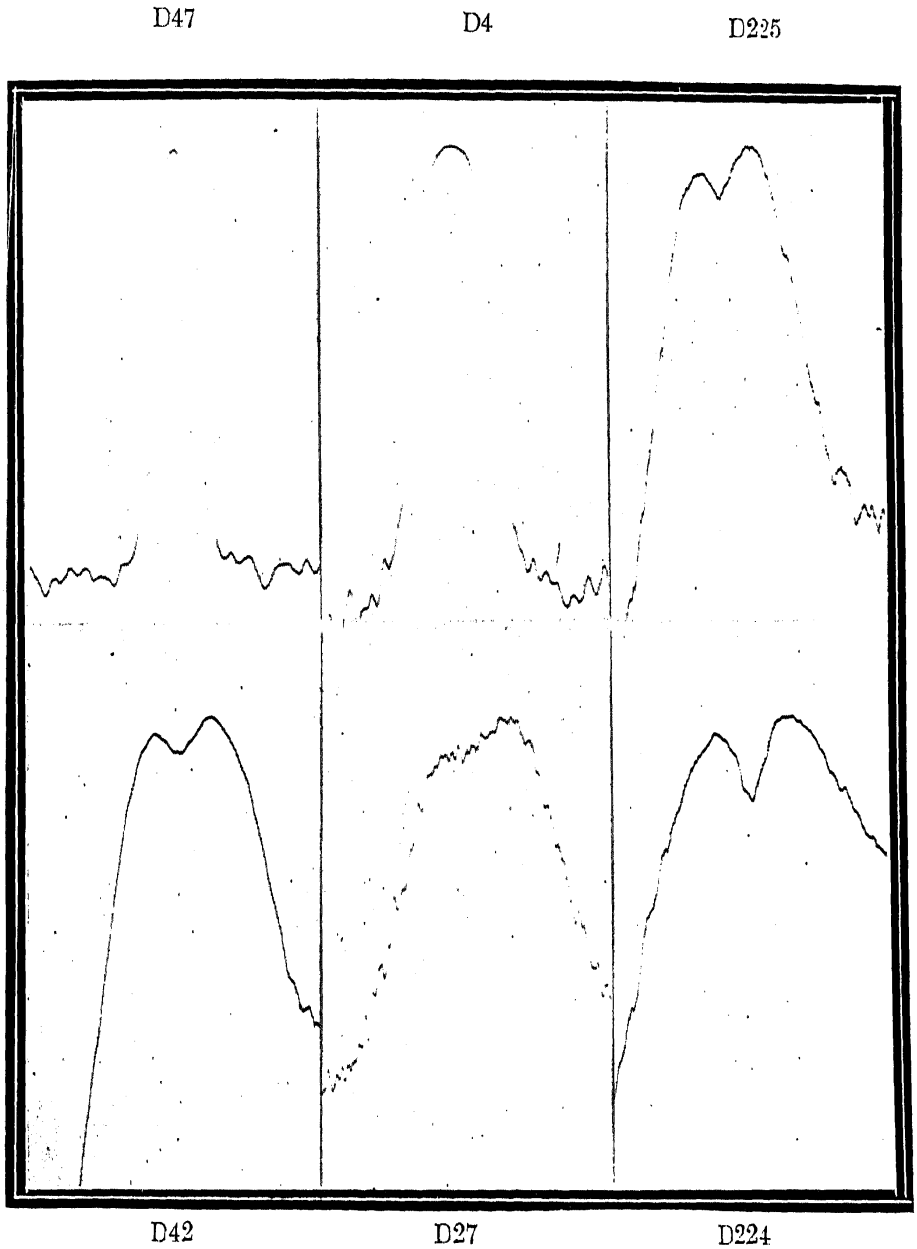


FIG. 12



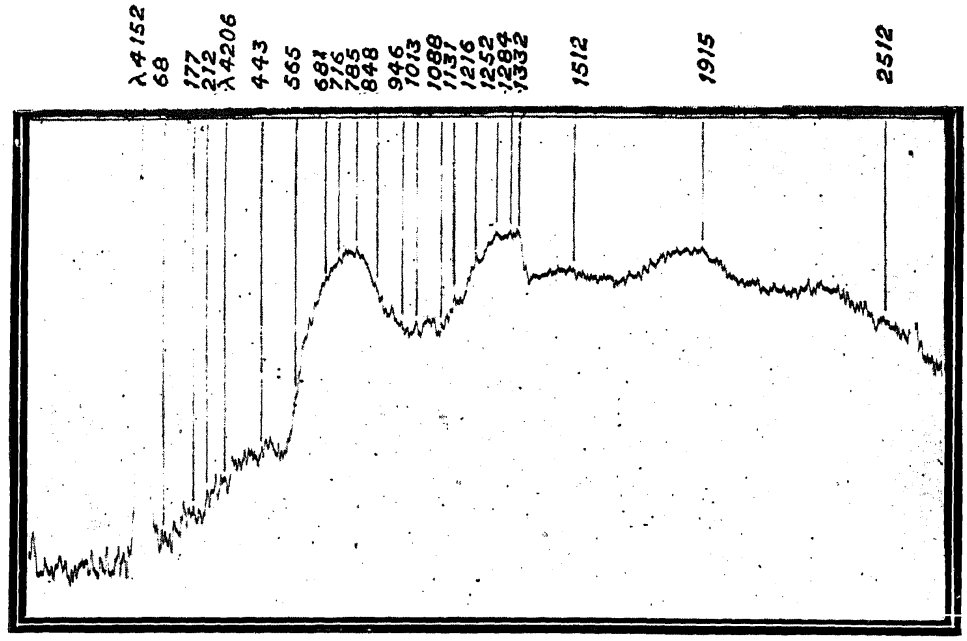

λ4152
68
177
212
λ4206
443
565
681
716
785
848
946
1013
1088
1131
1216
1252
1284
1332
1512
1915
2512

FIG. 14

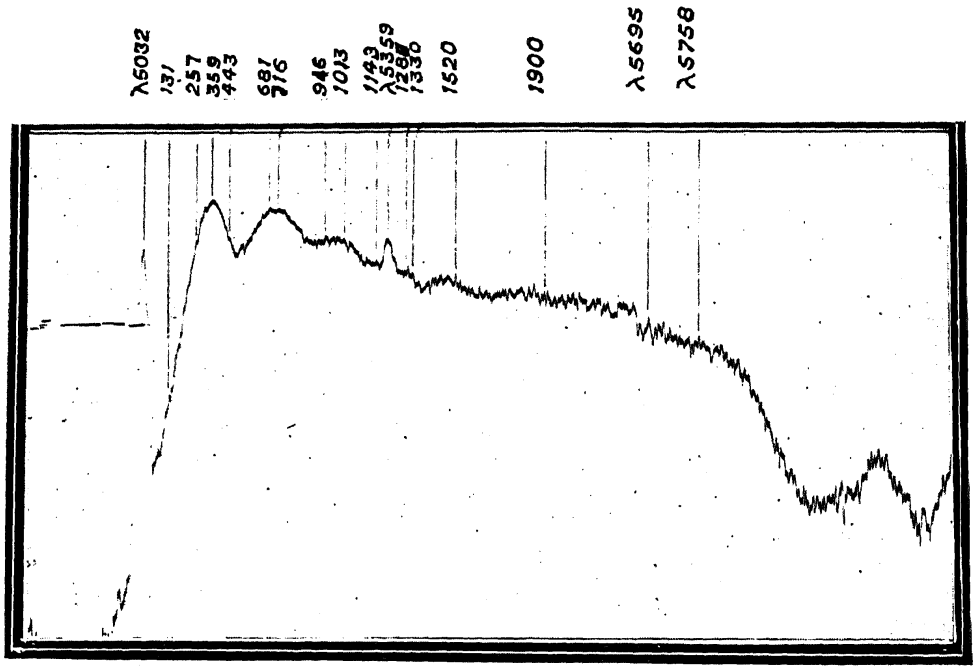

λ5032
131
257
359
443
681
716
946
1013
1123
λ1359
1396
1330
1520
1900
λ5695
λ5758

FIG. 15