STUDIES ON THE LUMINESCENCE OF DIAMOND

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STUDIES ON THE LUMINESCENCE OF DIAMOND

THESIS

presented to

THE UNIVERSITY OF MADRAS

for the

DEGREE OF DOCTOR OF SCIENCE

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CONTENTS

PREFACE

That some diamonds are luminescent has long been known, but owing to the belief that the phenomenon had its origin in impurities present in the specimens exhibiting it, interest in the subject had languished. Interest revived when in the year 1930 studies of the Raman effect in diamond drew attention to the spectrum of luminescence which simultaneously recorded itself on the plates. A fresh attack on the subject was commenced in the year 1941, when, at the instance of Sir C.V.Raman and with a dozen small specimens placed at his disposal, P.G.N.Nayar undertook a systematic comparative study of the spectrum of luminescence, absorption and scattering of light in diamonds. His main findings are recorded in the preface to his thesis for the Doctorate, a lengthy extract from the relevant portions of which is reproduced in Chapter I of the present thesis and need not therefore be repeated here. Dr.Nayar left this Institute in September 1942 and the present investigation was taken up at the point where he left it. Meanwhile, the collection of diamonds made by Sir C.V.Raman had been greatly extended in richness and variety, and the whole of this material containing over 300 specimens was placed at the disposal of the present writer for her work.

Chapter I of the thesis describes a study of the behaviour of 32 selected diamonds in respect of fluorescence and absorption in the visible region of the spectrum. Practically the whole of this work was done with the specimens held at the temperature of liquid air, a condition which, as was shown by Dr.Nayar, is essential for the luminescence and absorption spectra to exhibit themselves in all their characteristic detail. Chapter II describes a spectroscopic investigation of the nature of the geometric luminescence patterns observed visually in cleavage plates of diamond. Chapter III describes a confirmation and extension of the work of Chapter II with the plates held at liquid air temperature. Chapter IV describes an exploration of the behaviour of diamond in respect of luminescence when the same is excited by a comparatively narrow band of wavelengths in various parts of the visible spectrum. Chapter V describes a study of the state of polarisation of the Raman scattering and of the fluorescent emission in a perfect crystal of diamond in which accidental birefringence was practically absent. The details of each investigation and the results obtained are set out together with all necessary references to earlier work in each of the five chapters of the thesis. The main results are also summarised at the end of each chapter.

The following are the principal new contributions to knowledge set out in the present thesis:

(A) It has been shown that there are two conspicuously different kinds of luminescence in diamond, one based on an electronic emission at 4152 A.U. and its subsidiaries at longer wavelengths, and the second based on an electronic emission at 5032 A.U., also accompanied by subsidiary radiations at longer wave-lengths. The differences in the colour and intensity of the luminescence in different specimens of diamond arise from differences in the relative and absolute intensities of the two systems.

(B) It has been shown that accompanying the large variations in the relative and absolute intensities of the 4152 and 5032 radiations, there are corresponding differences in the absolute and relative intensity of the associated absorption spectra appearing at those wavelengths and extending towards higher frequencies.

(C) It has been observed that the system of subsidiary bands accompanying the 5032 line towards longer wavelengths in emission and towards shorter wavelengths in absorption is generally analogous to the corresponding system accompanying the 4152 radiation studied by Dr.Nayar, but exhibits some significant differences in detail.

(D) Besides, 4152 A.U. and 5032 A.U., eight other lines have been recorded which appear both in emission and absorption and are therefore clearly due to other electronic transitions. Four of these, viz. 4189, 4197, 4206 and 4959 A.U. are usually seen in diamonds exhibiting the 4152 system, while four others, viz. 4060, 4907, 5014 and 5359 A.U. generally accompany in the 5032 system. Twentysix other lines have also been noticed in different diamonds and in various parts of the spectrum between 3934 A.U. and 6358 A.U. It is believed that these also represent other electronic transitions.

(E) Remarkable variations in the fine structure of the 4152 line have been noticed in different diamonds. The self-reversal of this line in emission has also been noticed in some diamonds.

(F) It has been shown that the geometric patterns of luminescence observed in some diamonds have their origin in local variations of the intensity of the 4152 and 5032 systems, and that such diamonds exhibit absorption patterns in the visible spectrum analogous to their emission patterns.

(G) It has been observed that the intensity of excitation of the 4152 and 5032 systems fluctuates with the wavelength of the exciting radiation in a manner determined by the absorption coefficient of the latter.

(H) The Raman scattering and the blue luminescence of diamond have been found to exhibit apparently anomalous polarisation charatters.

A supplementary paper on the fluorescence, absorption and scattering of light in ruby is also submitted.

In conclusion, the author has great pleasure in acknowledging her indebtedness to Sir C.V. Raman for his helpful interest and encouragement.

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August 7, 1945.

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XIX, No. 5, Sec. A, 1944

THE FLUORESCENCE AND ABSORPTION SPECTRA OF DIAMOND IN THE VISIBLE REGION

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Received April 26, 1944
(Communicated by Sir C. V. Raman, KT., F.R.S., N.L.)

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."

* * * * * * *

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

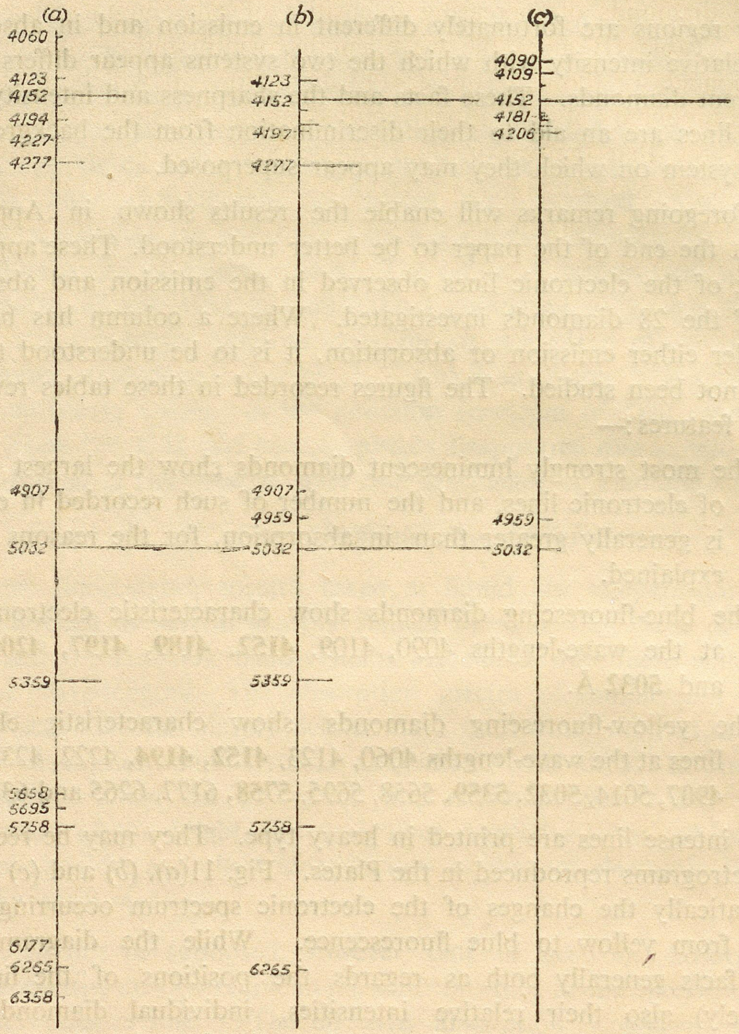

Fig.11

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		
	Wave-length in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency differences from 4152 in cm.$^{-1}$		Wave-length in A.U.	Frequency in cm.$^{-1}$	Frequency differences from 4152 in cm.$^{-1}$
I	4152	20	24077	..	Intense line	4152	24077	..
II	4158	$\frac{1}{2}$	24043	34	Sharp edge	..	..	..
	4164	$\frac{1}{2}$	24009	68	Discrete line	(4140)	24148	(71)
	4169	$\frac{1}{2}$	23980	97	Discrete line	(4135)	24177	100
III	4175	$\frac{1}{2}$	23945	132	Sharp limit	4130	24206	131
	4183	$\frac{1}{2}$	23900	177	Discrete line	(4123)	24247	(170)
	4189	$\frac{1}{2}$	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	$\frac{1}{2}$	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		
	Wave-length in A.U.	Inten-sity	Fre-quency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$		Wave-length in A.U.	Fre-quency 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 wave-lengths 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.

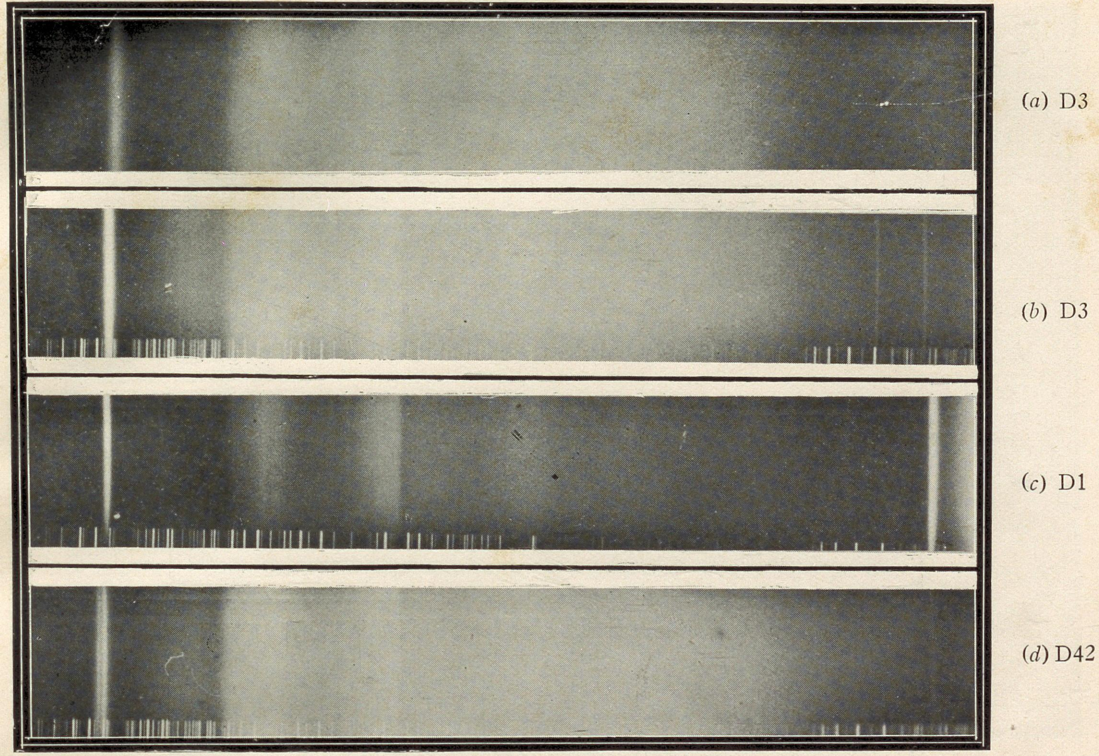


FIG. 1

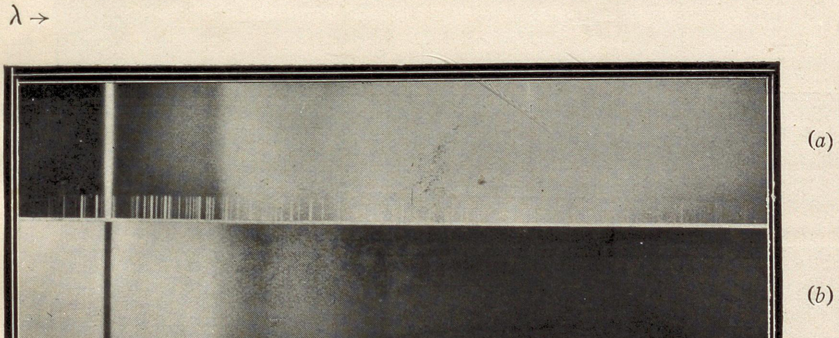


FIG. 2

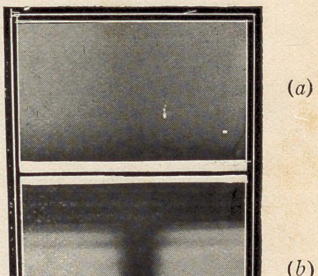


FIG. 3

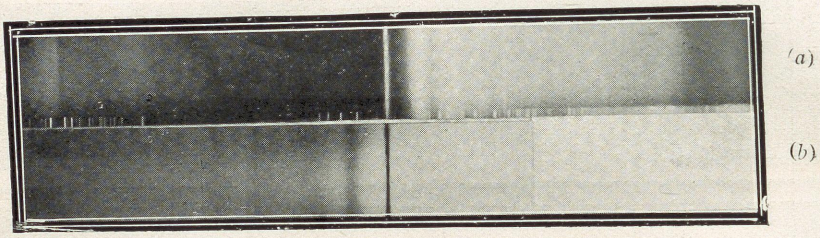


FIG. 4

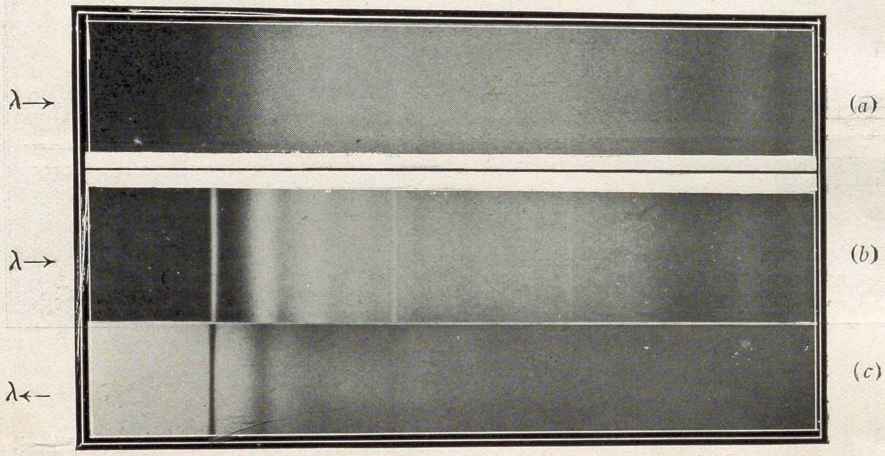


FIG. 5

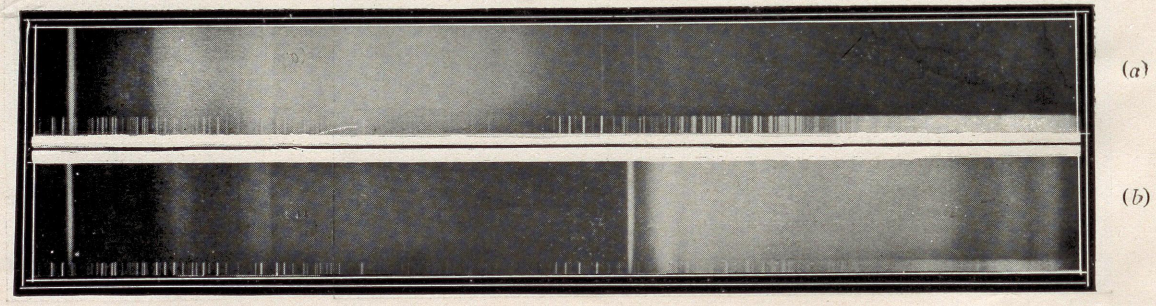


FIG. 6

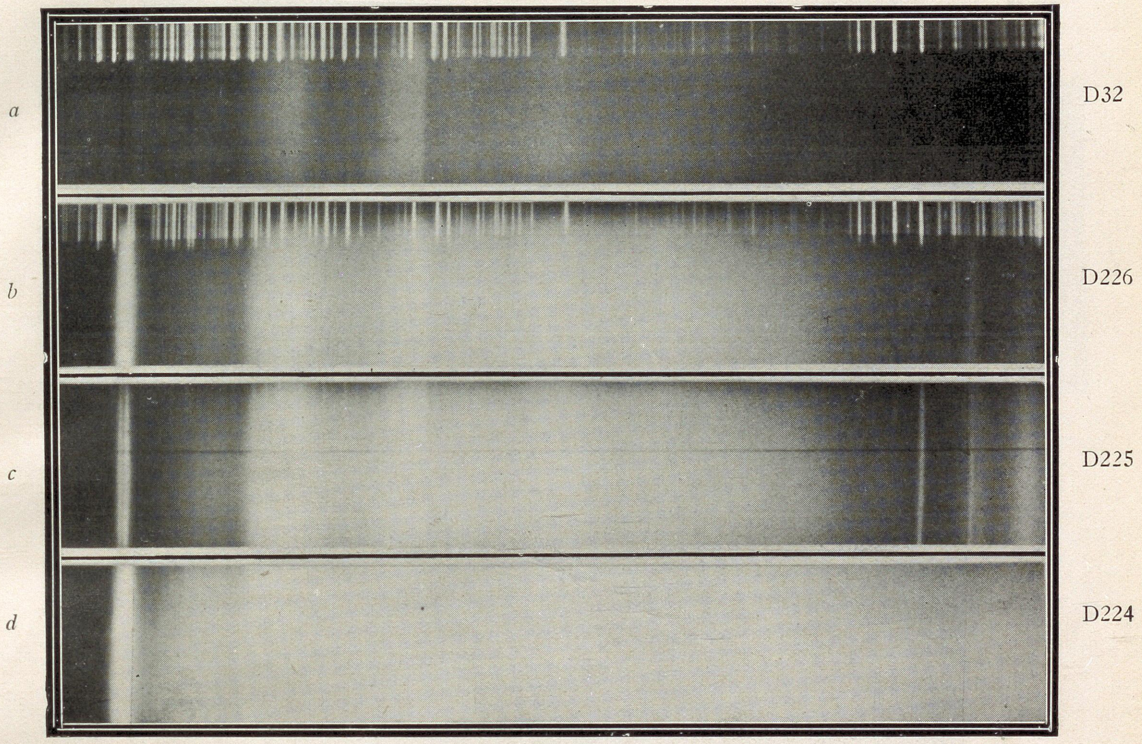


Fig. 7

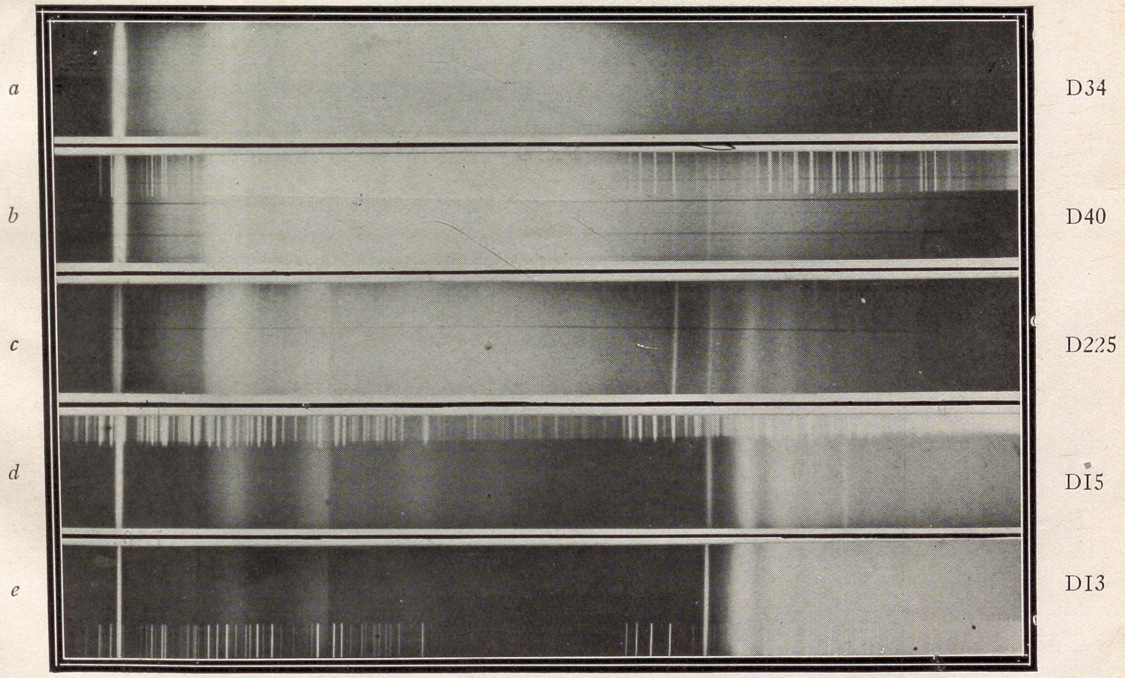


Fig. 8

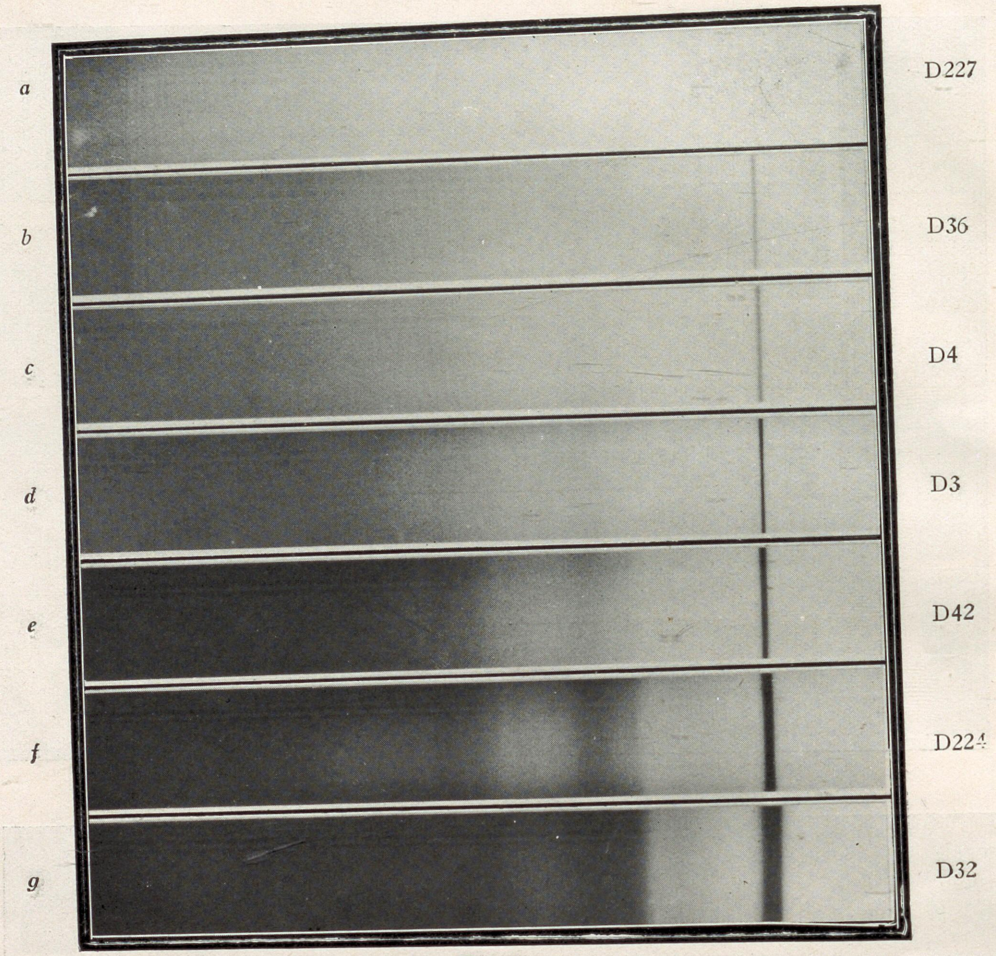


FIG. 9

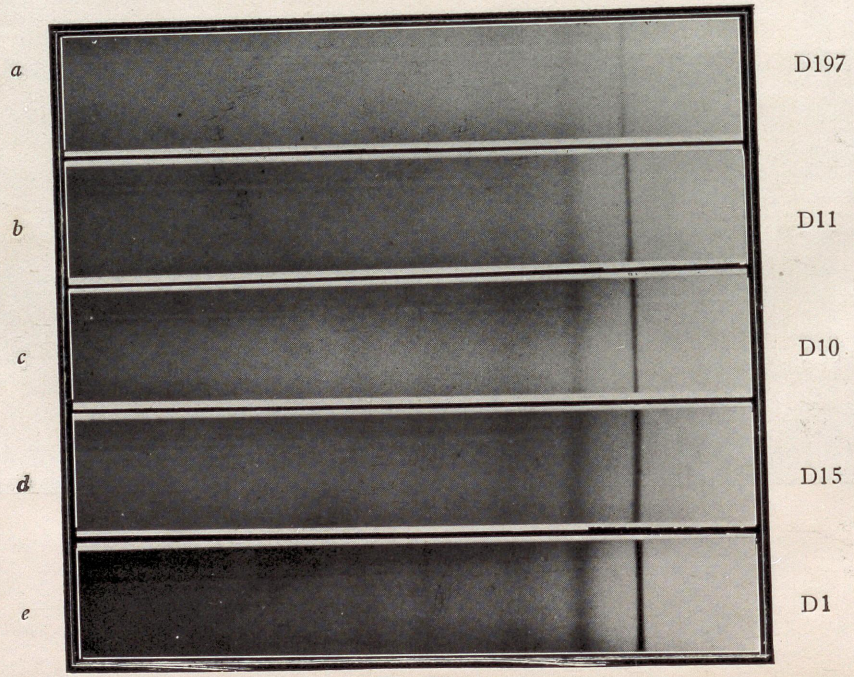


FIG. 10

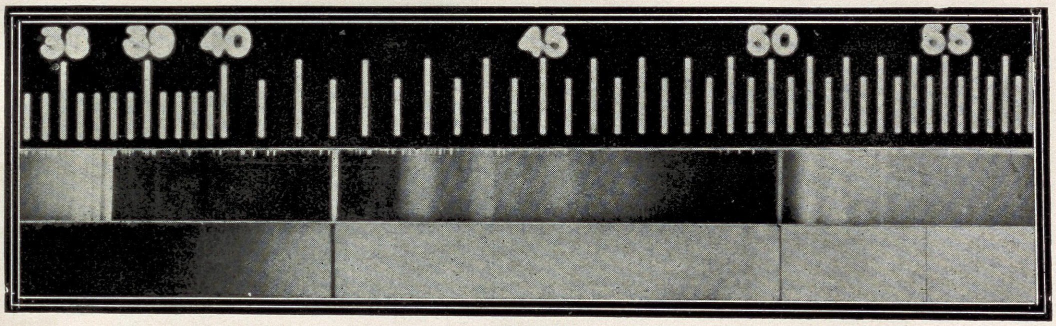
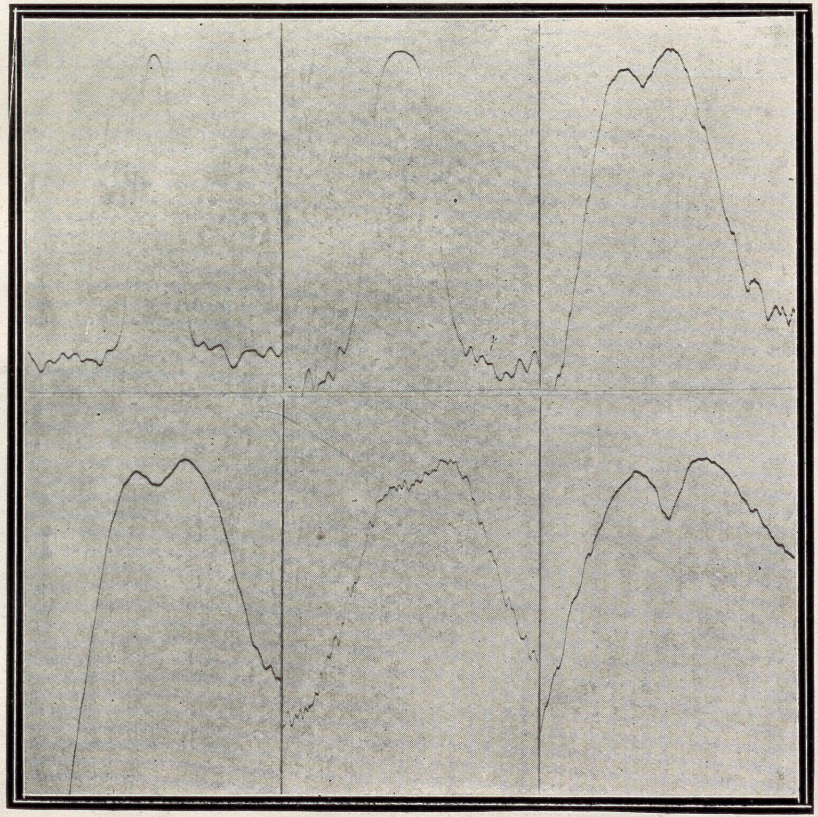


FIG. 12


D47 D4 D225

D42 D27 D224

FIG. 13

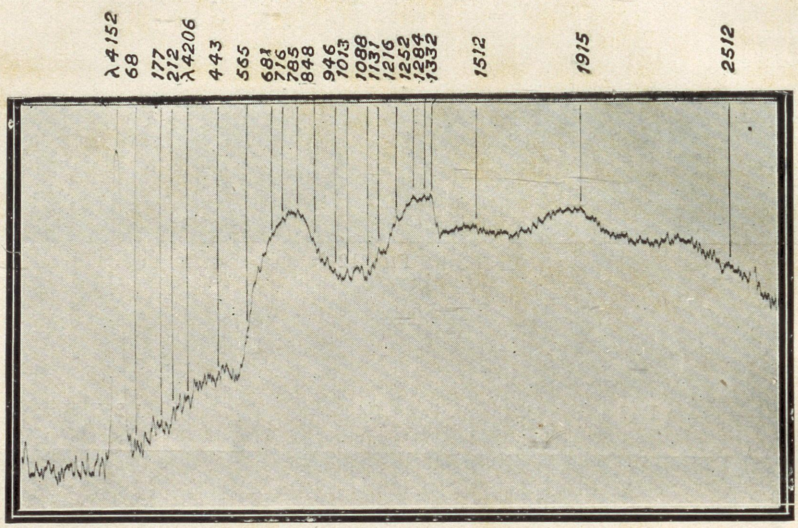

λ4152
68
177
212
λ4206
443
565
681
716
785
848
946
1013
1088
1131
1216
1252
1284
1332
1512
1915
2512

FIG. 14

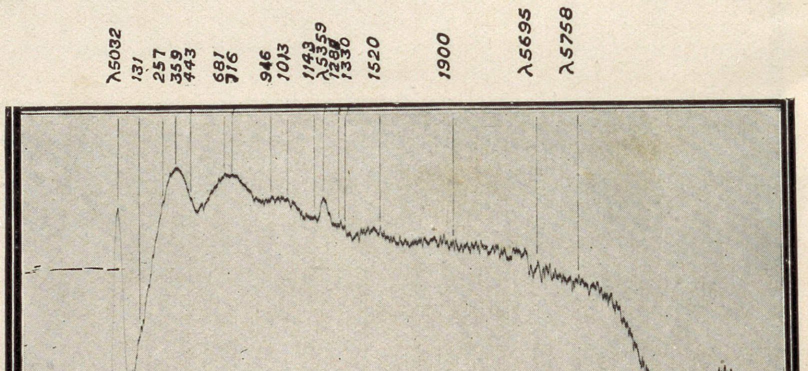

λ5032
131
257
359
443
681
716
946
1013
1143
λ5359
1288
1330
1520
1900
λ5695
λ5758

FIG. 15

Reprinted from " The Proceedings of the Indian Academy of Sciences ",
Vol. XX, No. 3, Sec. A, 1944

SPECTROSCOPIC STUDY OF LUMINESCENCE PATTERNS IN DIAMOND

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Received August 21, 1944
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

A previous communication to these *Proceedings* by the author (1944) contains a detailed report on the fluorescence and absorption spectra of thirty-two diamonds of widely different intensities and colours of luminescence. Numerous sharp electronic lines of varying intensities have been found in the visible region in the recorded spectra. The two most prominent of these are the lines at 4152 and 5032 A.U., and in combination with these two electronic lines, the vibration spectrum of the crystal lattice also appears towards longer wavelengths. The appearance of the 4152 electronic line and the associated lattice vibrations are characteristic of blue luminescence, while the 5032 system is similarly associated with the yellow luminescence. Whenever the 5032 system is recorded with any specimen, the 4152 system is an invariable accompaniment though its strength may be greater or smaller than that of the former system. The converse is not true, in other words the 4152 system may and indeed often does appear without a trace of the 5032 system being noticed.

The colour and intensity of luminescence may differ not only from diamond to diamond, but also in different parts of the same diamond. The luminescence patterns which arise in this way are often seen very conspicuously in polished cleavage plates of diamond. They have been described in detail by Sir C. V. Raman (1944), and their relationship to similar marked variations in other properties of the diamonds over their area have also been remarked on by him. Detailed studies of the luminescence patterns (Sunanda Bai, 1944), the patterns of transparency in the ultraviolet (Rendall, 1944), of the birefringence patterns (Raman and Rendall, 1944) and of the variations of X-ray reflection intensity (Ramachandran, 1944) have been published. The existence of parallel variations in such widely different physical properties indicates a common physical origin, *viz.*, a variation in the ultimate structure of the crystal, and it thus becomes of importance to make also a spectroscopic study of the luminescence patterns. In the previous investigation of the author, the fluorescent light from the diamond was condensed by means of a cylindrical lens on the slit of the spectrograph. This procedure prevents the spectra from different parts of the diamond being separately observed. If however, a cleavage plate is exposed and an image of it when excited to luminescence is thrown on the slit and moved over it in a series of exposures, the resulting spectra exhibit the variations in the nature and ntensity of the light emitted by the different parts of the diamond. The interest of such a study is that it enables us to understand the nature of the luminescence patterns more fully than is possible by simple visual observation and also to correlate the results with those obtained in the earlier spectroscopic investigation.

2. *Experimental Technique*

The diamonds employed were polished cleavage plates selected from Sir C. V. Raman's personal collection, to be representative of the various types of luminescence pattern wihch have been noticed. They have the new catalogue numbers N. C. 80 (D38), N. C. 82 (D235), N. C. 108 (D188), N. C. 110 (D190), N. C. 120 (D200) and N. C. 122 (D202), the numbering in the older catalogue being given within brackets. N. C. 80 was blue-fluorescent, N. C. 120 and N. C. 122 were yellow-luminescent, while N. C. 110, N. C. 108 and N. C. 82 exhibited both yellow and blue luminescence. Photographs of the luminescence patterns of all these specimens except N. C. 122 (202) are reproduced in the plates accompanying Sir C. V. Raman's paper quoted above.

The diamonds were mounted in metal blocks with suitable apertures for the entrance and emergence of light. Observation of the luminescence pattern was made normal to the area of the plate, the illuminating beam being obliquely incident. The source of light for exciting fluorescence was a carbon arc run at 220 volts with a current of 5 amperes. The light from the arc after passage through a water cell and a plate of Wood's glass which cuts off all visible radiation, was focussed on the diamond so as to illuminate the whole area uniformly. The image of the diamond was carefully focussed on the slit of the spectrograph by means of a high-quality Sonnar lens of 5 cm. focal length. By moving the lens, different parts of the image were made to pass over the slit. The whole area of the diamond could be scanned in this way, a series of fluorescence spectra being obtained for each specimen studied. Exposures of the order of two to four hours were sufficient to record each spectrum in the case of the strongly luminescent diamonds N. C. 80, N. C. 108, N. C. 110, N. C. 120 and N. C. 122, while twelve to fifteen hours were necessary to obtain a spectrum of N. C. 82 with satisfactory intensity. The spectra were photographed on Ilford H. P2 plates by means of a Hilger two-prism spectrograph. All observations were made at room temperature. It is hoped to take up studies at liquid air temperature later.

3. *Results*

(*a*) *Observations with diamond N. C.* 80 (D38).—N. C. 80 is a striking example of a diamond which exhibits geometrical patterns in blue luminescence and as visually observed, shows no trace of yellow luminescence. The pattern consists mainly of four pairs of intensely fluorescent bands inclined to each other at about 60°, interspersed by regions of non-luminescence. A series of four spectra were obtained for the diamond, the scanning slit traversing the plate so as to cut across both pairs of bands. Numerous bright streaks of varying intensities running throughout the length of the spectrum are present in every spectrogram, the pattern of streaks changing with the portion of the diamond scanned. Every bright streak is seen to correspond to a region of luminescence and the completely dark portions between them to regions of non-luminescence. From Fig. 1, Plate IV, where one of the spectra obtained is reproduced, it will be seen that the 4152 system is the prominent feature of the spectrum and that the 5032 system is completely absent. Sunanda Bai (1944) has shown that in N. C. 80 the non-luminescent regions transmit ultra-violet light up to 2400 A. U., whereas absorption commences at 3000 A. U. for the luminescent portions.

(*b*) *Observations with diamond N. C.* 82 (D235).—This is a predominantly blue-luminescent diamond which however, exhibits non-luminescent areas towards its two ends. The region of the plate which shows blue luminescence is also traversed diagonally by a series of faint yellow bands. Eight spectrograms were obtained, one of which is reproduced in Fig. 2. Four electronic lines at 4152, 5032, 5359 and 5895 A. U. are present in the spectrum and it will be noticed that the 4152 line and its subsidiary bands are more intense than the other three. The absolute and relative intensities of these four lines are different in the different spectrograms obtained, but in the same spectrogram, although the intensity of the lines vary along their length, their relative intensities remain constant, except where they are crossed by bright streaks.

The streaks exhibit a wide variation in intensity and many of them extend throughout the spectrum, while a number of streaks will be noticed to be present only in the blue, green, yellow or red regions. The ‘ blue ’ streaks belong to the 4152 system and appear with high intensity between 4100 and 5300 A. U. and extend weakly to 6500 A. U. The ‘ green ’ streaks similarly belong to the 5032 system and as is to be expected are present very weakly in the blue also. The ‘ yellow ’ and ‘ red ’ streaks are independent of the 4152 and 5032 systems and appear to commence from the electronic lines at 5359 and 5895 and extend up to 6500. It appears likely that the ‘ yellow ’ and ‘ red ’ streaks form two new independent systems, which may be called the 5359 and 5895 systems respectively. The line at 5895 deserves special mention. Crookes (1909) had reported a citron line in red-luminescent diamonds, having the wave-length of the sodium doublet and which he attributed to the presence of sodium in diamond. The line he observed was evidently the 5895 line which the present investigation shows to be a genuine electronic line of diamond that is probably responsible for the red luminescence.

Fig. 2 illustrates the different kinds of streaks obtained for N. C. 82 and shows that the majority of them lie in the 4152 system. The lower half of the spectrum corresponds to the region of the diamond which contains non-luminescent areas interspersed by luminescent patches. It will be noticed that a number of ‘ blue ’, ‘ green ’ and ‘ yellow ’ streaks are present in this region. The ‘ yellow ’ streaks in the upper portion of the spectrum testify to the existence of yellow luminescence bands visually observed to be present in this region.

(*c*) *Observations with diamond N. C.* 120 (D200).—As visually observed, this is purely yellow-luminescent showing no trace of blue fluorescence. The most prominent feature of its luminescence pattern is a set of four parallel bands. A series of six spectrograms were taken and one of these is shown reproduced in Fig. 3. Only the 4152 and 5032 systems appear in the spectrum, the 5032 system being more intense than the other. Numerous streaks traverse the spectra throughout the region of fluorescence, and though their intensities vary from point to point in the diamond, the relative intensities of the two systems are uniformly constant, every variation in the intensity of the 5032 system being repeated in the 4152 system.

(*d*) *Observations with diamond N. C.* 122 (D202).—Like N. C. 120 this is also yellow-luminescent; its whole area, however, is covered by a series of parallel yellow bands. Eight spectrograms were obtained with the diamond, one of which is reproduced in Fig. 4. The pattern of streaks is different in the different spectra obtained, but in the same spectrogram the 4152 and 5032 systems show identical variations in intensity. There is, however, one exception of a ‘ blue ’ streak where the 4152 system is more intense than the 5032.

(*e*) *Observations with diamond N. C.* 110 (D190).—N. C. 110 is a triangular shaped plate showing the mixed type of luminescence. The luminescence pattern consists of numerous wavy bands of blue and yellow near the apex of the triangle, the rest of the plate being fairly uniformly fluorescent. A series of ten spectrograms were taken, the plate being scanned from the apex to the base. Both the 4152 and the 5032 systems appear with comparable intensities. The spectra obtained in the region of uniform luminescence show little change in the relative intensities of the two systems, despite the many streaks that run through them. On the other hand, for spectra obtained near the apex, one of which is reproduced in Fig. 5, the structure and intensity of the ‘ blue ’ and ‘ green ’ streaks are seen to be quite different.

(*f*) *Observations with diamond N. C.* 108 (D188).—N. C. 108 is a typical example of a diamond exhibiting both blue and yellow luminescence and shows a very interesting pattern consisting of an intense blue spot surrounded by fainter blue and yellow hexagonal rings forming a figure similar to that of a spider web. A series of nine spectra were obtained, showing an amazing number and variety of streaks. No two of the spectra were found to be similar, in the intensities and the pattern of the ‘ blue ’, ‘ green ’, ‘ yellow ’ and ‘ red ’ streaks obtained. The four prominent electronic lines are those at 4152, 5032, 5359 and 5895, with which are associated the four kinds of streaks mentioned above. The 4152 and 5032 systems have comparable intensities. In many cases the streaks extend throughout the spectrum with approximately constant intensity. More interesting however, are the streaks present only in one or other of the four systems and whose intensities are completely independent of each other. In Fig. 6 is reproduced one of the spectra obtained.

4. *Significance of the Results*

It is now well established that the subsidiary bands observed in the 4152 and 5032 systems arise from combinations of the lattice vibrations with the electronic lines at 4152 and 5032 A.U. Hence, the intensities of the subsidiary bands should vary with that of the principal electronic lines. The spectroscopic study of the luminescence pattern shows this to be clearly the case. A close parallelism exists between the intensities of the 4152 line and the bands associated with it at longer wave-lengths, the variations which appear in the former being also clearly seen in the latter. A similar relationship is observed to exist between the 5032 line and the subsidiary bands associated with it.

The variations observed in the relative intensities of the 4152 and 5032 systems are also noteworthy. It is noticed that in blue-luminescent diamonds the 4152 system is present alone, the subsidiary bands of this system itself extending to 6500 A.U. In yellow-luminescent diamonds on the other hand, both the systems are present, the 5032 system being the prominent feature in the spectrum. The intensities of the two systems in any one diamond always bear a constant ratio to each other, every variation in the 5032 system appearing in the 4152 system also. In diamonds which, as visually observed, show both blue and yellow luminescence, the two systems appear with comparable intensities. But the relative and absolute intensities of the two systems vary not only from diamond to diamond, but in the same diamond from one region to the other. Among the numerous bright and faint streaks that cross the spectra, it is observed that some are present in both the systems and some in either the 4152 or 5032 systems while in the case of the third kind of streaks, neither their structure nor their intensities are similar in the two systems. In fact, fine streaks or dark regions in the 4152 system in many cases correspond to broad streaks in the 5032 system.

The facts observed are comprised in the statement that diamond may be either non-luminescent, blue-luminescent or yellow luminescent, and that in diamonds exhibiting luminescence patterns the different kinds of behaviour may manifest themselves simultaneously in different parts of the same specimen lying in close juxtaposition. The differences in behaviour are evidently associated with differences in the ultimate structure of the diamond. It is particularly interesting that yellow luminescence usually appears in thin layers exhibiting a stratification of intensity. Besides the 4152 and 5032 systems, we have also to consider two other and apparently independent kinds of luminescence appearing in the yellow and red regions of the spectrum respectively. They consist of the electronic lines at 5359 and 5895 and the subsidiary bands associated with them at longer wavelengths. The exact origin of these systems and their correlation with the 4152 and 5032 systems is a problem that demands further investigation.

In conclusion, the author wishes to express her respectful thanks to Professor Sir C. V. Raman for his interest and constant encouragement in the work.

5. *Summary*

A spectroscopic study has been made of the local variations in intensity and colour of the fluorescent radiation from six cleavage plates of diamond exhibiting blue, yellow and mixed types of luminescence. It is found that a close correlation exists between the variations exhibited in the intensities of the electronic lines at 4152 and 5032 and of their subsidiary bands, and also between the two systems themselves. The 4152 system is present alone in blue-luminescent diamonds, while both systems appear in diamonds of the yellow-luminescent and mixed types. In the former, the 4152 system occurs weakly and a close correspondence is found to

exist between the intensities of the two systems. In the latter, the 4152 and 5032 systems appear with comparable intensities no correlation between them being observed except in a few cases. There is also evidence of the existence of two other systems of luminescent bands, associated with the electronic lines at 5359 and 5895 A.U. respectively.

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Ramachandran, G. N.	.. *Ibid.*, 1944, **19**, 280.
Rendall, G. R.	.. *Ibid.*, 1944, **19**, 293.
Sunanda Bai, K.	.. *Ibid.*, 1944, **19**, 274.

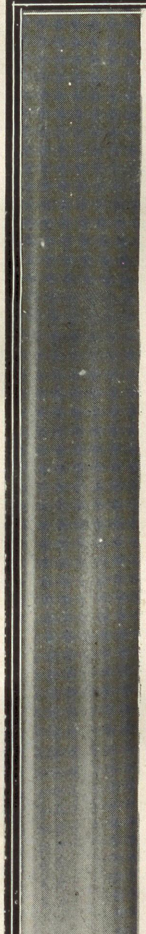

Fig. 1
N.C. 80

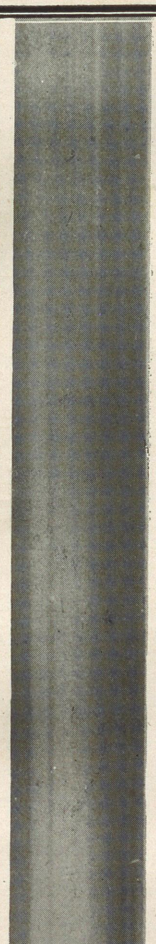

Fig. 2
N.C. 82

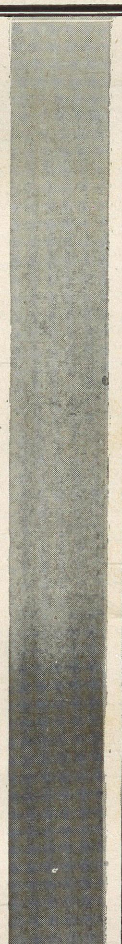

Fig. 3
N.C. 120

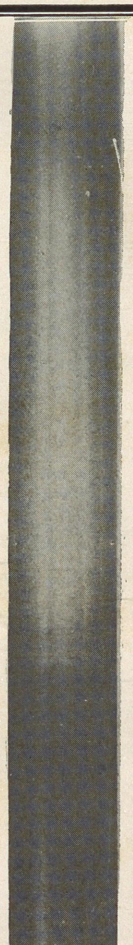

Fig. 4
N.C. 122

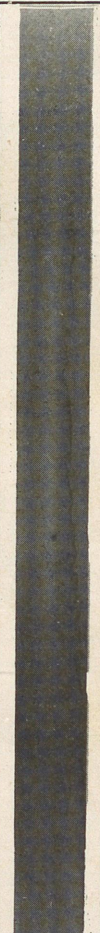

Fig. 5
N.C. 110

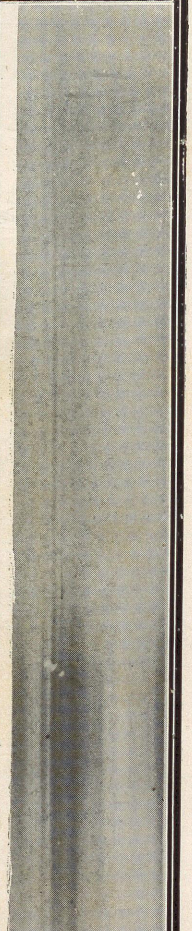

Fig. 6
N.C. 108

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XX, No. 6. Sec. A, 1944

FLUORESCENCE AND ABSORPTION PATTERNS IN DIAMOND AT LOW TEMPERATURES

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Received October 30, 1944
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

In an earlier investigation by the author (1944) reported in these *Proceedings*, the luminescence patterns exhibited by six cleavage plates of diamond at room temperature were studied spectroscopically. In other words, by focussing the entire image of the fluorescent diamond on the slit of the spectrograph and by moving the lens so that different regions of the diamond were successively scanned by the slit, the variations in the colour and intensity of the luminescence spectra over the area of the plate were investigated. In the present work this has been extended to an investigation of the patterns at liquid air temperature. Making use of the greater intensity and sharpness of the spectra at low temperatures, the same technique has also been employed to study the absorption spectra of a number of diamonds, although this arrangement limits the length of the available absorbing column to the thickness of the cleavage plates, which is of the order of 1 mm. or less. The spectra obtained exhibit variations in the intensity of the 4152 and 5032 systems similar to those in luminescence, giving rise to absorption patterns identical with the patterns observed in fluorescence. This is of course, to be expected from the very close correlation that exists between the spectra in fluorescence and absorption. An experimental demonstration of their existence is however, worthy of record. The low temperature investigation is also of interest in throwing light on the degree of correlation between the intensities of the principal electronic lines and those of the fainter ones which are too weak or diffuse to be observed at room temperature.

2. *Materials and Methods*

The diamonds employed were polished cleavage plates selected from Sir C. V. Raman's personal collection and had the catalogue numbers N.C. 80 (D38), N.C. 79 (D34), N.C. 100 (D180), N.C. 107 (D187), N.C. 106 (D186), N.C. 108 (D188), N.C. 110 (D190), N.C. 114 (D194), N.C. 120 (D200) and N.C. 122 (D202), the old catalogue numbers being given within brackets.

Of these, N.C. 79, N.C. 80, N.C. 100 and N.C. 107 were predominantly blue luminescent, N.C. 120 and N.C. 122 were yellow luminescent while the rest exhibited both blue and yellow luminescence with comparable intensities. Photographs of the luminescence patterns of these ten diamonds are reproduced in the plates accompanying the paper by Sir C. V. Raman (1944) on " The Nature and Origin of Luminescence in Diamond ".

The arrangement for obtaining the fluorescence spectra was the same as that described in the previous paper, a demountable Dewar flask being used for the low temperature studies. The diamonds were mounted in copper holders which were screwed to the bottom of the inner brass tube of the Dewar flask holding liquid air. The vacuum between the inner brass tube and the outer pyrex tube was maintained by a Cenco Hyvac pump in good condition. A 100 W. tungsten lamp was used as the source of light in the absorption studies, the light from the lamp being so condensed on the diamond as to illuminate the plate uniformly. A number of spectra were obtained for each diamond, the absorption spectra for each region being recorded in a graded series of exposures. The fluorescence and absorption spectra were photographed on Ilford HP_3 and selochrome plates respectively, the instrument used being a Hilger two prism spectrograph of high light gathering power.

3. *Results*

(*a*) *Luminescence Patterns.*—Descriptions of the patterns exhibited by the five diamonds N.C. 80, N.C. 108, N.C. 110, N.C. 120 and N.C. 122, whose fluorescence spectra have been investigated in the present work are described in the previous paper. In Figs. 1, 2, 3 and 4, Plate VII, are reproduced representative spectra obtained for N.C. 80, N.C. 108, N.C. 110 and N.C. 120 respectively. They show the same essential features as those observed at room temperature, except for the appearance of the fainter electronic lines at 4123, 4194, 4197 and 4206 A.U., the splitting of the 4152 line and the greater intensity and sharpness of the entire spectrum.

In the spectra of every diamond studied, the prominent electronic lines are those at 4152 and 5032, the lines at 4123, 4194, 4197, 4206, 5359 and 5895 being weaker. Numerous bright and dark streaks cross the spectra, extending throughout the spectrum or in the blue and yellow regions alone and these correspond to variations in the intensity of the 4152 and 5032 lines. The variations in the intensity of the two systems are identical for N.C. 120 and N.C. 122 except for a few 'blue' streaks. For N.C. 108, N.C. 80 and N.C. 110 they are generally different, the streaks present in the two systems on the whole being independent of each other. In the intensely blue luminescent diamonds N.C. 80, N.C. 108 and N.C. 110, the

4152 line appears as a doublet. Variations in intensity of the two components are however, the same. The weaker electronic lines at 4123, 4194, 4197 and 4206 also exhibit changes in intensity, these being parallel to those of the principal electronic line at 4152 with which they are associated.

N.C. 80 shows certain new features not observed at room temperature. In the previous study the 5032 system had been reported to be absent for this diamond. The spectra taken at liquid air temperature however, show that in the regions of many of the faint and a few of the bright streaks the 5032 system is present with intensities comparable with that of the 4152 system. The failure to observe this at the room temperature is to be ascribed to its extreme diffuseness and faintness at that temperature. In many of the intense streaks in its fluorescence spectra, the 4152 system is present alone, in a few both the 4152 and 5032 systems are present while in the case of the dark streaks both the systems are absent. These three types of streaks correspond to the blue, yellow and non-luminescent types of diamond respectively.

(*b*) *The Absorption Patterns.*—Spectroscopic studies of the absorption patterns of all the ten diamonds have been carried out at both room temperature and at liquid air temperature. The spectra for four of these, *viz.*, N.C. 80, N.C. 108, N.C. 106 and N.C. 114 are reproduced in Figs. 5, 6, 7 and 8, Plate VII.

As may be expected, in diamonds N.C. 80, N.C. 79, N.C. 100 and N.C. 107 which are blue luminescent, the 4152 system is the prominent feature of the spectrum, the 5032 system being too weak to be recorded with the thicknesses employed. The 4152 line in every spectrum shows remarkable variations in its width and intensity and the spectrum towards shorter wave-lengths is crossed by numerous dark and bright streaks. It will be noted that the streaks in fluorescence lie towards longer wave-lengths and that while the bright and dark streaks in fluorescence correspond to luminescent and non-luminescent regions in the diamond respectively, the reverse is the case in absorption. The bright streaks in fluorescence correspond to the dark streaks in absorption and *vice-versa.* A very close parallelism is thus seen to exist between the patterns in fluorescence and absorption. In N.C. 80 the spectra in both fluorescence and absorption consist of alternately bright and dark streaks. In N.C. 100 the luminescence pattern consists of a central triangular patch of blue luminescence surrounded by regions of non-luminescence. In the absorption spectrum we find the 4152 line to be intense in the central region and weak or absent towards either edge. N.C. 79 and N.C. 107 consist of alternating regions of blue and non-luminescence and the absorption spectra show the existence of identical patterns in absorption. It should be noted however, that the complete 4152 system appears only in N.C. 80 and N.C. 79. In N.C. 100 and N.C. 107 which are less intensely luminescent and thinner, only the 4152 line is recorded.

In the typically yellow luminescent diamonds N.C. 120 and N.C. 122, only the 5032 system is present in absorption, the 4152 system being naturally too weak to be observed. The absorption spectra in both cases show the presence of numerous parallel streaks of varying brightness, corresponding in every detail to the pattern observed in fluorescence. The spectra however, were too faint to be reproduced successfully.

N.C. 106, N.C. 108, N.C. 110 and N.C. 114 being diamonds of the mixed type, show both 4152 and 5032 systems in absorption with comparable intensities. Only in N.C. 108 however, were conditions favourable enough to exhibit the changes in intensity of both systems simultaneously. In all the other three, the 4152 and 5032 lines are alone recorded, the subsidiary bands being too weak to be obtained with any observable intensity. The distribution of intensities in the two systems are different for all the four diamonds. In the absorption spectrum of N.C. 106 reproduced in Fig. 7, it will be noticed that the 4152 line is intense in only one half of the plate. This corresponds to a region of blue luminescence as visually observed, the rest being yellow luminescent. In the absorption spectrum of N.C. 114 reproduced in Fig. 8, the 5032 line appears with uniform intensity throughout its length while the 4152 line is strong only in half the spectrum. In other spectra obtained for the same diamond the 4152 and 5032 lines exhibit variations which are complementary in nature, *i.e.*, the 4152 is strong while the 5032 is weak and *vice-versa*. The striking similarity between the fluorescence and absorption pattern for N.C. 108 is illustrated in Figs. 2 and 6. The central " blue " streak, in both spectra is specially noteworthy and corresponds to a spot of intense blue luminescence visually observed to be present at the centre of the diamond plate. N.C. 110 also exhibits similar variations in intensity in both systems, but only towards that apex of the plate where both blue and yellow luminescence are simultaneously present.

4. *Significance of the Results*

The general results obtained may be summed up as follows:

(*a*) In blue luminescent diamonds the 4152 system is the predominant feature of the spectrum and variations in intensities of the weaker electronic lines at 4197 and 4206 and the subsidiary bands at longer wave-lengths are identical with those of the 4152 line.

(*b*) In yellow luminescent diamonds both the 4152 and 5032 systems are present the latter system being much more prominent than the former. Every variation in the intensity of the 5032 system is repeated with identical features in both the 4152 and 5359 systems and the weaker electronic lines at 4123 and 4194.

(*c*) In diamonds showing the mixed type of luminescence the 4152 and 5032 systems appear with comparable intensities. Their spectra are characterised by three varieties of streaks, *viz.*, those present in the 4152 system alone corresponding to blue luminescent regions in the diamond, those present in the 5032 system and weakly in the 4152 system corresponding to yellow luminescent regions and those present in both the 4152 and 5032 systems but with relative intensities varying over a wide range from one streak to another. The first two types of streaks correspond to blue and yellow luminescent structures of diamond existing in the same specimen independently of each other and in these the intensities of the subsidiary electronic lines and the lattice bands show variations similar to those of the principal electronic lines. The third type of streaks may arise from either the intermingling of the blue and yellow luminescent structures in varying proportions or from the overlapping of the spectra from different layers of the diamond due to the finite thickness of the cleavage plates used. No correlation can of course, be obtained between the intensities of the different systems for these streaks.

(*d*) The absorption spectra show that corresponding to the different types of patterns of luminescence, the plates exhibit variations in transparency over their area, forming absorption patterns identical with the former in the distribution of both colour and intensity. The 4152 and 5032 lines in absorption show remarkable variations in its width and intensity not only in the same spectrum but in different spectra obtained for different regions of the plate. A close parallelism exists between these and the variations in intensity of the subsidiary bands appearing at shorter wavelengths. A comparison of the absorption and fluorescence spectra show that the intimate correlation between the intensities of luminescence and absorption holds good not only for different diamonds but for individual areas of the same diamond.

In conclusion the author wishes to express her grateful thanks to Professor Sir C. V. Raman for his guidance throughout the course of this investigation.

5. *Summary*

The paper reports a spectroscopic study of the luminescence and absorption patterns shown by ten cleavage plates of diamond at liquid air temperature. A close correlation is shown to exist in blue luminescent diamonds between the variations in intensity of the principal electronic line at 4152 and those of the fainter lines at 4197 and 4206 and the subsidiary bands at longer wavelengths, and in yellow luminescent diamonds between the intensities of the 4152, 5032 and 5359 systems and the lines at 4123 and 4194. The spectra of diamonds of the mixed type possess features characteristic of both the blue and yellow luminescent types. It is shown that in absorption the same intensity relations hold good in the different types of diamond. The variations in intensity and colour of the absorption spectra are thus identical with those in the fluorescence spectra and give rise to absorption patterns in the visible corresponding to the patterns in luminescence.

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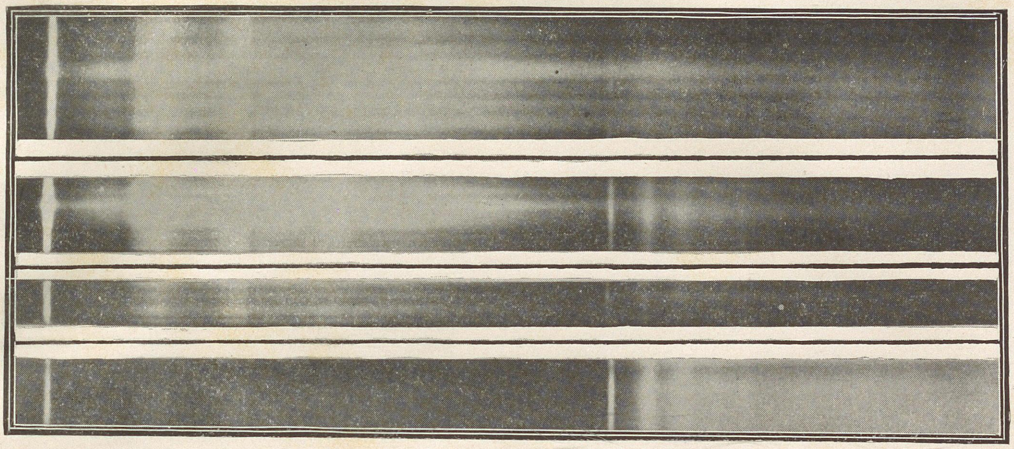

Fig. 1
N.C. 80

Fig. 2
N.C. 108

Fig. 3
N.C. 110

Fig. 4
N.C. 120

Patterns of Luminescence at Low Temperatures

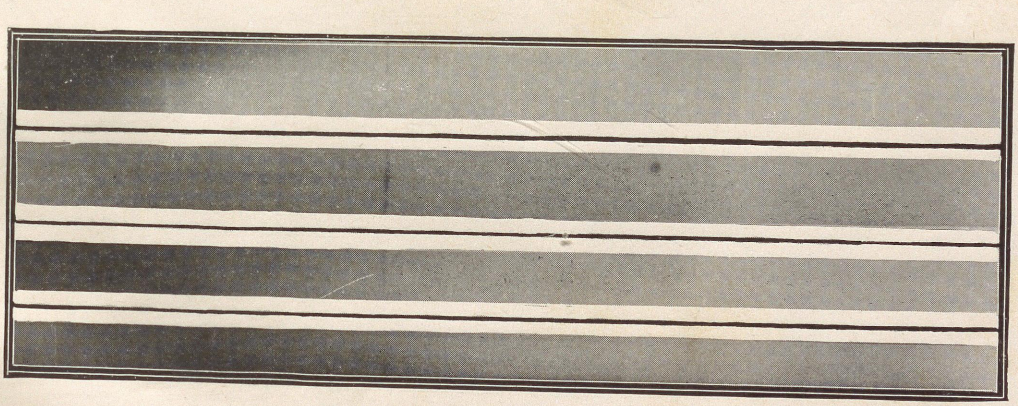

Fig. 5
N.C. 80

Fig. 6
N.C. 108

Fig. 7
N.C. 106

Fig. 8
N.C. 114

Patterns of Absorption at Low Temperatures

Reprinted from " The Proceedings of the Indian Academy of Sciences ",
Vol. XXI, No. 6, Sec. A, 1945

EXCITATION CURVES OF LUMINESCENCE IN DIAMOND

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Received June 5, 1945
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

It is well known that fluorescence in any substance is excited only when the exciting radiation is of shorter wavelength than the fluorescent emission. That this is true for blue fluorescent diamonds exhibiting the 4152 system of bands was shown by Nayar (1941). The most interesting result obtained by him was that the principal electronic frequency at 4152 A.U. exhibits a true resonance effect, the whole system of principal and subsidiary bands brightening up and then disappearing as the wavelength of excitation was made equal to and then greater than 4152. He pointed out, however, that the 4152 system does not strictly obey Stokes' law but persists though with relatively small intensity for excitation by wavelengths greater than 4152.

The discovery of the 5032 system of bands associated with yellow luminescence in diamond raised the question whether the principal electronic frequency at 5032 A.U. exhibits a resonance effect similar to that of 4152. Results of recent investigations by the author (1944) on the fluorescence and absorption spectra of numerous diamonds further indicated the necessity of a detailed study of the excitation curves for the two types of luminescence and of the effect of different excitation wavelengths on the relative intensities of the two systems. The present paper reports the results of such an investigation on the fluorescence spectra of typically blue and yellow luminescent diamonds, a monochromator being used to give beams of light of wavelength varying from 3700 A.U. to 6500 A.U.

2. Experimental Technique

The source of white light used was a special 100 Watt tungsten lamp in which the whole luminosity was concentrated in a short straight filament. When over-run at 20% more than the specified voltage it gave very satisfactory intensity for the entire visible region. A Hilger Constant Deviation Spectrograph served as the monochromator. The white light was spread by the constant deviation prism into a spectrum and thrown on a screen provided with a variable slit. The required wavelength of monochromatic light could be obtained by turning the drum head of the wavelength scale. The width of the monochromator slit was about half a millimetre, giving beams 20 to 60 A.U. broad in the blue and 70 to 200 A.U. broad in the yellow regions of the spectrum.

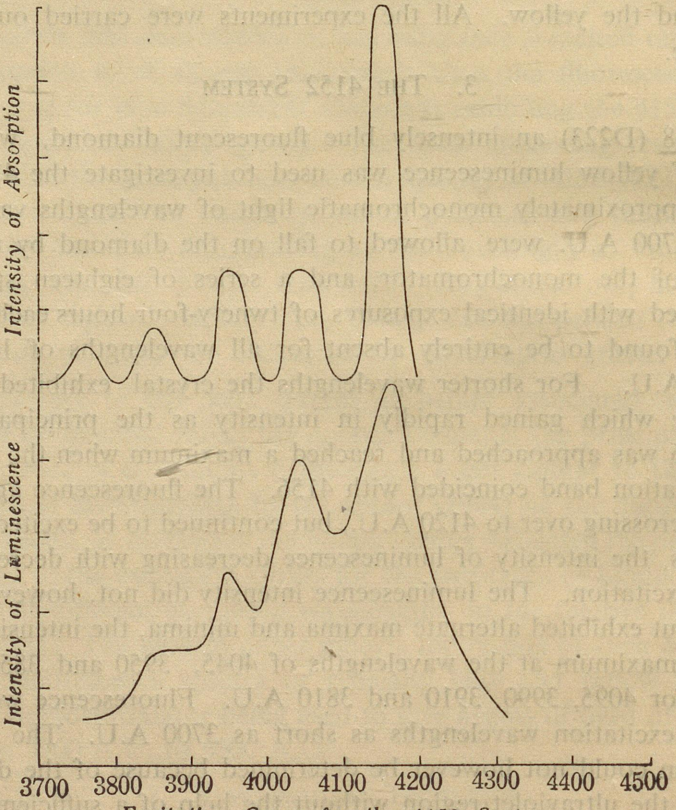
The image of the monochromator slit was condensed on the diamond by a short focus lens and the fluorescent light from the diamond focussed by a cylindrical lens on the slit of a Zeiss three prism spectrograph. The spectra were recorded on Ilford HP_3 plates using the short focus camera attachment, since this gave high light gathering power with sufficient dispersion in both the blue and the yellow. All the experiments were carried out at room temperature.

3. THE 4152 SYSTEM

N.C. 68 (D223) an intensely blue fluorescent diamond, which shows no trace of yellow luminescence was used to investigate the 4152 system. Beams of approximately monochromatic light of wavelengths varying from 6,500 to 3,700 A.U. were allowed to fall on the diamond by turning the drumhead of the monochromator, and a series of eighteen spectra were photographed with identical exposures of twnety-four hours each. Fluorescence was found to be entirely absent for all wavelengths of light longer than 4400 A.U. For shorter wavelengths the crystal exhibited very weak fluorescence which gained rapidly in intensity as the principal electronic line at 4156 was approached and reached a maximum when the wavelength of the excitation band coincided with 4156. The fluorescence again became weaker on crossing over to 4120 A.U., but continued to be excited for shorter wavelengths, the intensity of luminescence decreasing with decreasing wavelength of excitation. The luminescence intensity did not, however, diminish gradually but exhibited alternate maxima and minima, the intensity of excitation being maximum at the wavelengths of 4045, 3950 and 3850 A.U. and minimum for 4095, 3990, 3910 and 3810 A.U. Fluorescence was found to persist for excitation wavelengths as short as 3700 A.U. The lower limit of excitation could not however be determined because of the difficulties of working in the ultraviolet region without the help of a sufficiently powerful monochromator.

The effect of different excitation wavelengths on the intensity of the 4152 system is illustrated in Fig. 1, Plate XX, where twelve of the series of spectra obtained for N.C. 68 are reproduced. The highly exposed bands represent the excitation wavelengths. These range continuously from 4340 to 3810 A.U., and their wavelengths are recorded beside each spectrum. The fluorescence spectrum, which may be easily recognised, consists of the principal electronic band at 4156 and the subsidiary bands and continuum which extend to 6500 A.U. The resonance effect at 4156, the intensity maxima at 4045, 3950 and 3850 and the minima at 4120, 4095, 3990, 3910 and 3810 are readily noticed.

The relative intensities of blue fluorescence for excitation wavelengths between 4415 and 3810 A.U. were measured microphotometrically and plotted against wavelength as abscissæ on an arbitrary scale of 20. The excitation curve thus obtained for the 4152 system is reproduced in Fig. 2, the upper curve representing the 4152 system in absorption at room temperature. It will be immediately noticed that the two curves exhibit remarkably similar features. The absorption spectrum consists of discrete bands with mean wavelengths at 4156, 4045, 3950, 3850 and 3760 A.U., absorption for intermediate wavelengths being absent. The excitation curve exhibits corresponding maxima and minima at these same wavelengths.



Excitation Curve for the 4152 System

FIG. 2

The intensity of fluorescence is maximum for 4156 and variations in luminescence intensity for shorter wavelengths closely follow those of the subsidiary absorption bands. The intensity of blue luminescence for a particular excitation wavelength is thus seen to be roughly proportional to the intensity of absorption at the same wavelength.

In spite of the general resemblance between the two curves a few notable differences are also present. Firstly, the intensity of fluorescence for excitation wavelengths of 4120, 4095, 3990, 3910 and 3810 is not as small as one would expect from the absorption spectrum. This probably is due to the finite width of the illuminating beam used and the diffuseness of the absorption bands themselves at room temperature. By using narrower excitation bands and cooling the crystal to liquid air temperature the excitation curve should exhibit sharper maxima and minima which conform more closely to the absorption curve with regard to both width and intensity. It is proposed to take up the study of the excitation curve at low temperatures later.

Secondly, the intensities of the successive maxima in the two curves are not the same. While the 4045 and 3950 bands in absorption are of equal intensity the fluorescence excitation by 3950 is much weaker than that at 4045. It should however be remembered that in giving identical exposures for the different wavelengths with reference to time, no allowance was made for the variable distribution of energy in the spectrum of the white light used. Though the spectrum of the incandescent lamp is perfectly continuous, its intensity shows a gradual decrease with diminishing wavelength. The intensity of an illuminating beam at 3950 would be much smaller than that at 4045. The rapid decrease in fluorescence intensity with decreasing wavelength might also arise from the smaller probability of excitation for wavelengths distant from 4152.

Finally, wavelengths longer than 4152 by as much as 200 A.U. are capable of exciting the diamond to luminescence. Small transgressions of Stokes' law are possible if the crystal lattice possesses energy of vibration at the time of excitation to a higher electronic state. A return transition from this level to a level lower than the original one is then possible resulting in the emission of a frequency higher than that of the exciting band. In solids the probability of this occurring is not high since the excited atoms are apt to transfer at least that part of the absorbed energy which is vibrational to neighbouring atoms in the form of heat motion before light emission takes place. A more likely cause of antistokes excitation is the transference of heat energy from the surrounding atoms to the fluorescing atoms during the time it stays in the excited state. As Nayar (1941) pointed out it might also arise from diamond phosphorescence. In any case, it would decrease rapidly in intensity in passing from 4152 to longer wavelengths and should disappear at low temperatures. The former is actually observed to be the case.

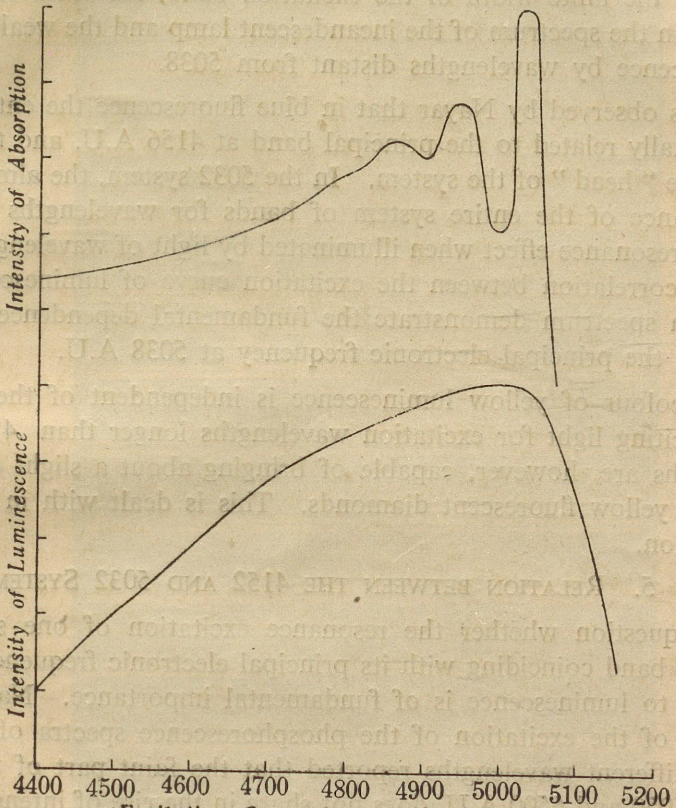
An interesting result worthy of note is that while variations in the wavelength of excitation cause remarkable changes in the intensity of fluorescence, they have no effect on the colour of the fluorescent light. In other words, the position of the maxima of the fluorescence spectra in blue luminescent diamonds is independent of the exciting wavelength.

The existence of resonance radiation for the 4152 band is illustrated in a different but more direct fashion in Fig. 3, Plate XX, where the fluorescence spectrum of N.C. 70 (D32) at liquid air temperature is reproduced. The crystal was held edgewise and the fluorescent light excited by ultraviolet radiation from a carbon arc, had to traverse the whole length of the crystal (11·5 mm.) before being caught by the lens. Only the principal band of the 4152 system undergoes absorption in the process. And as will be noticed in the spectrum only the centre or core of the 4152 band is re-absorbed. Wood (1934) has reported similar observations in the re-absorption of resonance radiation by sodium and mercury vapour.

4. THE 5032 SYSTEM

The intensely yellow luminescent diamond N.C. 41 (D13) was employed for the sudy of the 5032 system. A series of twenty-eight spectra was obtained for this crystal, the wavelengths of excitation ranging from 6500 to 3700 A.U. The fluorescence for wavelengths shorter than 4300 A.U. was so weak that longer exposures had to be given for these excitation wavelengths in order to record the spectra with any intensity. Eleven of the spectra obtained with identical exposures of twelve hours each and excitation wavelengths ranging, continuously from 6200 to 4480 A.U. are reproduced in Fig 4, Plate XXI. No trace of yellow luminescence was found to be present for excitation wavelengths above 5200 A.U. For shorter wavelengths the crystal exhibited feeble fluorescence which brightened up as the excitation band approached 5038 and reached a maximum of intensity when it coincided with the principal electronic line. The fluorescent intensity did not diminish for wavelengths immediately below 5038 the intensity of luminescence for 4940 remaining as high as at 5038. The fluorescence gradually weakened afte. 4800, but was found to persist for wavelengths as short as 3700 A.U.

The relative intensities of yellow luminescence for different excitation frequencies were determined microphotometrically and plotted against wavelength as abscissæ on an arbitrary scale of 20. The excitation curve for the 5032 system thus obtained is reproduced in Fig. 5, the upper curve corresponding to the absorption spectrum at room temperature. The two curves as will be noticed, show a general resemblance to each other. The intensities of fluorescence and absorption are a maximum for 5038 and this indicates the existence of a resonance effect for the principal electronic frequency at 5038 A.U. The resonance radiation is, however, not so marked as for 4152. This discrepancy might possibly disappear if the excitation curve for the 5032 system is studied at low temperatures using narrower excitation bands.



Excitation Curve for the 5032 System

FIG. 5

For wavelengths shorter than 5038, the two curves exhibit a gradual decrease in intensity with decreasing wavelengths and variations in the intensity of fluorescence are found to follow more or less closely variations in the intensity of absorption. The absence of any maxima or minima, the differences in intensity for succeeding wavelengths and the presence of antistokes excitation in the excitation curve are the observed discrepancies between the two curves, which as in the case of the 4152 system probably arise from the finite width of the excitation band, the variable distribution of energy in the spectrum of the incandescent lamp and the weaker excitation of fluorescence by wavelengths distant from 5038.

It was observed by Nayar that in blue fluorescence the entire system is fundamentally related to the principal band at 4156 A.U. and that the 4156 band is the " head " of the system. In the 5032 system, the almost complete disappearance of the entire system of bands for wavelengths longer than 5038, the resonance effect when illuminated by light of wavelength 5038 and the close correlation between the excitation curve of luminescence and the absorption spectrum demonstrate the fundamental dependence of the 5032 system on the principal electronic frequency at 5038 A.U.

The colour of yellow luminescence is independent of the wavelength of the exciting light for excitation wavelengths longer than 4152. Shorter wavelengths are, however, capable of bringing about a slight change in the colour of yellow fluorescent diamonds. This is dealt with in detail in the next section.

5. Relation between the 4152 and 5032 Systems

The question whether the resonance excitation of one system by an excitation band coinciding with its principal electronic frequency will induce the other to luminescence is of fundamental importance. Nayar (1941) in his study of the excitation of the phosphorescence spectra of diamond by light of different wavelengths reported that the faint part of the spectrum between 5050 and 6500 A.U. does not share in the rise of intensity which the blue region exhibits when the excitation bands have wavelengths equal to or less than 4152. The present investigation shows that this is a general result valid for all diamonds exhibiting the 4152 and 5032 systems in fluorescence and that the excitation of one system is entirely independent of the other. It must be mentioned that in blue luminescent diamonds like N.C. 68, the resonance excitation of the 4152 system will cause a corresponding increase in the intensity of the continuous part of the 4152 system from 4900 to 6500 and that this is entirely unrelated to the 5032 system.

Diamonds N.C. 41 (D13) and N.C. 43 (D15) were employed in the investigation of the effect of the resonance excitation of the 4152 system on the 5032 system. The reverse, *viz.*, the excitation of the 4152 system by the 5032 system is obviously impossible. Both systems are present in N.C. 41 and N.C. 43. In the former the 5032 system is the prominent feature of the spectrum, while in the latter both appear with comparable intensities.

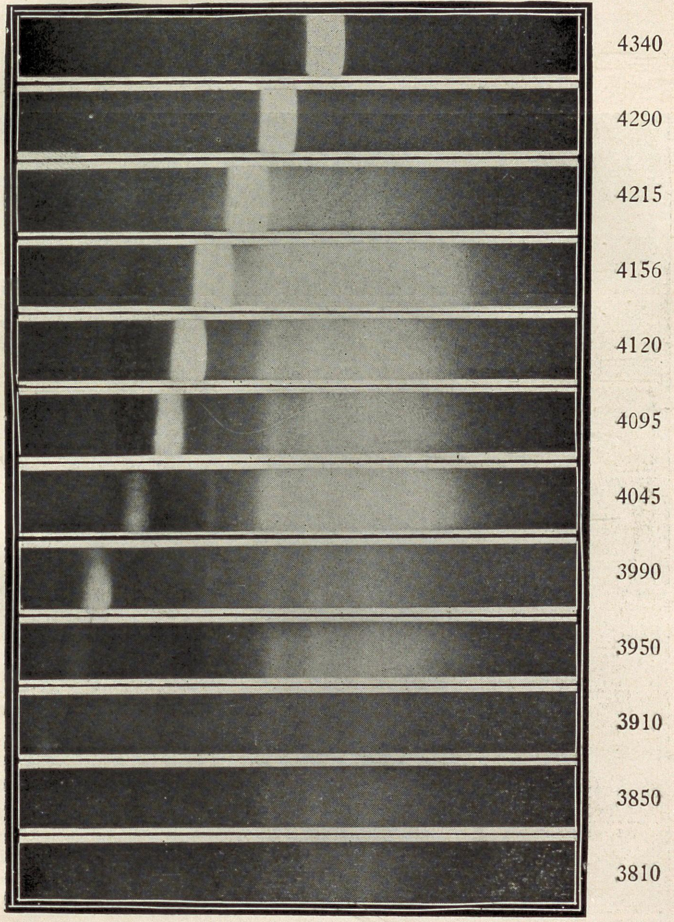


FIG. 1

The 4152 System

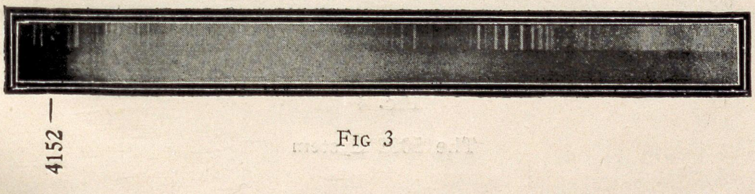


FIG 3

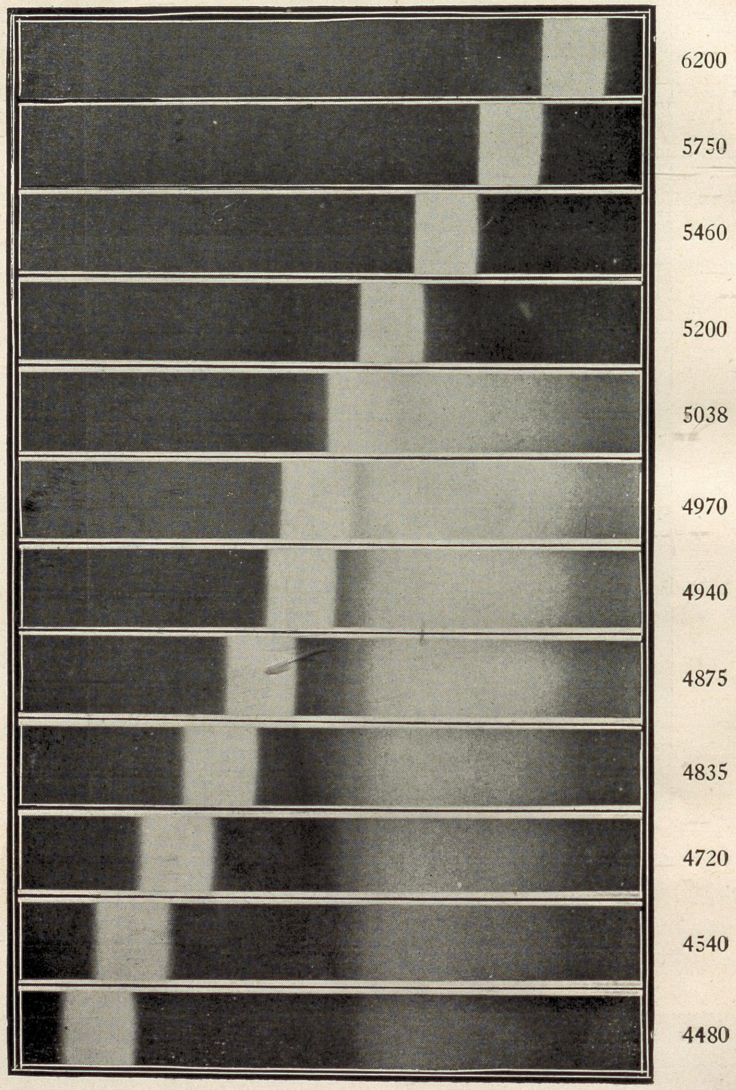


FIG. 4

The 5032 System

It was reported in the previous section that all wavelengths between 3700 and 5300 are capable of exciting the 5032 system to luminescence. On varying the excitation wavelength within this range, it was observed that the intensity of the 5032 system which decreases gradually with decreasing wavelength continued to do so independently of the excitation of the 4152 system by wavelengths equal to or less than 4152. A series of three spectra obtained for N.C. 41 with excitation wavelengths of 4250, 4150 and 4060 A.U. showed that while there was a large increase in intensity of the 4152 system for the two latter wavelengths, there was no corresponding increase in the 5032 system. For excitation wavelengths equal to and less than 4156 the two systems thus appear with comparable intensities. This naturally results in a change in luminescence colour and causes the predominantly yellow fluorescent diamonds N.C. 41 and N.C. 43 to appear bluish yellow. Similar variations in fluorescence colour should occur in every diamond exhibiting both systems in luminescence.

In conclusion, the author expresses her grateful thanks to Professor Sir C. V. Raman for his helpful interest and encouragement in this work.

6. SUMMARY

Using a monochromator, the effect of excitation by wavelengths varying from 3700 to 6500 A.U. on the fluorescence spectra of typical blue, yellow and blue-yellow luminescent diamonds has been studied. Excitation curves for the 4152 and 5032 systems have been obtained and they reveal the existence of resonance effects for the principal electronic lines at 4152 and 5032 and a close correlation between the intensity of fluorescence excited by a particular wavelength and the intensity of absorption at the same wavelength. Stokes' law is found generally to be valid but it is observed that both systems are capable of being weakly excited by wavelengths longer than the principal electronic frequencies. The two systems are excited independently of each other, the resonance excitation of the 4152 system having no observable effect on the 5032 system. The colour of fluorescence is independent of the exciting wavelength, except for excitation wavelengths equal to or less than 4152 in the case of yellow fluorescent diamonds which then appear bluish-yellow.

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Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XX, No. 3, Sec. A, 1944

POLARISATION OF RAMAN SCATTERING AND OF FLUORESCENCE IN DIAMOND

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Received July 31, 1944
Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.

1. *Introduction*

It is well known that the principal vibration of the diamond lattice in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other manifests itself in the Raman spectrum as a sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ at room temperature. Observations of the state of polarisation of this line were made by Ramaswamy (1930) who reported it to be strongly polarised. Bhagavantam (1930) in the course of his study of the Raman effect in several diamonds however, observed the line to exhibit only imperfect polarisation. This difference between the two observers is not surprising in view of the numerous disturbing factors capable of influencing the experimentally recorded result. More recently, Nayar (1942) made a re-determination of the depolarisation ratio, using a small octahedral crystal and immersing it in benzene to reduce the disturbances arising from the refractions and internal reflections at the surfaces of the crystal. He found that when the incident light was unpolarised, the two components of the scattered beam were of equal intensity, giving a value of 1·0 for the depolarisation factor. This, as he pointed out, differs from the theoretical value of 2 predicted by Saxena (1940) on the basis of Placzek's theory for triply degenerate vibrations in cubic crystals. In view of these conflicting results reported by different observers and their divergence from the theoretical values, it was considered desirable to obtain more accurate polarisation data, taking the precautions necessary to eliminate the factors giving rise to errors, *viz.*, birefringence in the diamond, refractions at the surfaces of entry and emergence, internal reflections and finally the convergence error present in all depolarisation measurements. The first three of these were avoided by choosing for the investigation from Sir C. V. Raman's personal collection a diamond (N.C. 4) which had a symmetric and approximately octahedral form and smooth lustrous faces and was free from any internal flaws or inclusions. The diamond was also free from any noticeable birefringence. This was tested by passing a beam of polarised light through the crystal and determining the state of polarisation of the emergent beam. The disturbing effects of surface reflections and refractions were minimised by immersing the diamond in a high refractive index liquid, while convergence errors were reduced by using a small-aperture short-focus lens for condensing the light into the crystal. A careful study of the polarisation characters of the Raman line as well as of the fluorescense bands of diamond has been made in the present investigation, using incident unpolarised as well as polarised light for excitation.

2. *Experimental Technique*

The diamond was kept immersed in α-bromonaphthalene contained in a small Wood's tube just large enough to hold the crystal. The tube was provided with optically plane windows and was blackened throughout except for stops for the entrance and emergence of light, which besides cutting off parasitic light, served to confine the incident and scattered beam to mutually perpendicular directions. Light from a mercury pointolite arc was condensed by a small-aperture lens at the centre of the crystal through one of its octahedral faces, the scattered light being observed through another octahedral face approximately normal to the former. The scattered light was focussed on the slit of the spectrograph by a lens of small aperture. The convergence error in this arrangement was only 1%, the maximum semi-convergence angle being about 11°. A large aperture Ahrens Nicol interposed in the path of the incident light served as the polariser. A sodium nitrite filter isolated the 4358 radiation for exciting the Raman line effectively cutting off light of shorter wave-lengths which excite fluorescence, while during polarisation measurements of the fluorescence bands the filter was dispensed with. A quartz double-image prism of the Wollaston type properly oriented and placed just before the slit of the spectrograph split the beam into vertical and horizontal components. The spectra were photographed on Ilford Selochrome plates, the instrument used being a Hilger two-prism spectrograph having a dispersion of 28 A.U./mm. in the 4358 A.U. region.

3. *Polarisation Measurements of the Raman Line*

As usual in polarisation studies, three mutually perpendicular directions OX, OY and OZ in the crystal were chosen as reference axes; the direction of the incident beam was designated as along OX, the direction of the scattered beam as along OY while OZ was the direction mutually perpendicular to both. Since diamond is isotropic, it was possible to obtain only three different spectrograms of scattered light; *viz.*, with

(*a*) incident light unpolarised,

(*b*) incident light polarised with electric vector along OY,

(*c*) incident light polarised with electric vector along OZ.

Quantitative measurements of the depolarisation values for these three cases were made and are given in Table I along with the theoretical values predicted by Saxena for the triply degenerate vibrations in the cubic class.

TABLE I

$$\rho = \frac{E_x^2}{E_z^2}$$

Direction of the Incident Electric vector	Depolarisation	
	Experimental	Theoretical
Along OY	1·5	1
Along OZ	0·6	∞
Unpolarised Light	1·0	2

The depolarisation factor ρ was determined as usual by microphotometering the plates and obtaining the densities of the lines for the horizontal and vertical components. A set of intensity marks were obtained on the same photographic plate by the method of varying slit-widths, using as the source of illumination a small tungsten filament lamp fed from a battery at constant voltage. From the density-log intensity curve thus obtained for the wave-length of the Raman line, the intensity ratios of the horizontal to the vertical component were calculated. The ratios obtained in this way involve errors due to the spectrograph caused by oblique refraction and reflection at the prism surfaces which strengthen the horizontal component. This error, which is characteristic of the instrument used, was determined by allowing light from a tungsten lamp after it had passed through a double-image prism to fall on the slit of the spectrograph and photographing the spectra for a series of exposures. The ratio of the intensities of the vertical and horizontal components was determined microphotometrically as described above. This gave a value of 0·71 for the spectrographic correction. The values in Table I are corrected for the instrument error.

4. *Theoretical Derivation of the Polarisation Characteristics of the Raman Line*

Tables of selection rules for the different types of oscillations in crystals belonging to the seven classes of symmetry have been given by Placzek (1934, 1938). On the basis of these, Saxena (1940) has calculated the polarisation ratios and the total intensities of Raman lines in terms of the tensor components in the transverse and longitudinal scattering. He has shown that Raman lines in crystals may be considered as due to the deformations of the optical polarisability ellipsoid of the solid produced by the internal oscillations and that the deformations can be expressed in terms of the six components of the change of polarisability tensor. The equation for the deformed ellipsoid is given by

$$(A+\epsilon_{xx})\,x^2+(B+\epsilon_{yy})\,y^2+(C+\epsilon_{zz})\,z^2+\epsilon_{xy}\cdot xy+\epsilon_{xy}\cdot yz+\epsilon_{xz}\cdot xz=1$$

where A, B and C are the lengths of the principal axes of the polarisability ellipsoid and $\epsilon_{ii}=(\epsilon_{xx},\ \epsilon_{yy},\ \epsilon_{zz})$ $\epsilon_{ik}=(\epsilon_{xy},\ \epsilon_{yz},\ \epsilon_{zx})$ are the six components of the change of polarisability tensor. It is possible to evaluate these tensor components by illuminating the crystal along a fixed direction, say OX, and observing the scattered light along OY, and calculating the induced moments in the scattered radiation. The components of the scattered radiation lie along the x and z directions and the induced moments in these directions are given by

$$\Delta M_x=\epsilon_{xx}\cdot E_x+\epsilon_{xy}\cdot E_y+\epsilon_{xz}\cdot E_z$$

$$\Delta M_z=\epsilon_{zx}\cdot E_x+\epsilon_{zy}\cdot E_y+\epsilon_{zz}\cdot E_z$$

Since the depolarisation ratio ρ is given by

$$\rho=\frac{(\Delta M_x)^2}{(\Delta M_z)^2}$$

it will be seen that for an incident electric vector along OY

$$\rho_{OY}=\frac{(\epsilon_{xy})^2}{(\epsilon_{yz})^2}$$

and for an incident electric vector along OZ

$$\rho_{OZ}=\frac{(\epsilon_{xz})^2}{(\epsilon_{zz})^2}$$

while for incident unpolarised light

$$\rho_{unp.}=\frac{(\epsilon_{xy})^2+(\epsilon_{xz})^2}{(\epsilon_{yz})^2+(\epsilon_{zz})^2}.$$

The principal vibration of the diamond lattice falls under the triply degenerate class for which the selection rules given by Placzek are

$$\epsilon_{xx}=\epsilon_{yy}=\epsilon_{zz}=0$$

$$\epsilon_{xz}=\epsilon_{yz}=\epsilon_{xy}\neq 0$$

Thus we find that $\rho_{OY}=1$, $\rho_{OZ}=\infty$ and $\rho_{unp.}=2$.

It will be seen from Table I that while the results for incident unpolarised light agree with those obtained by Nayar (in spite of the small error introduced in his results by the crystal birefringence), they agree in no case with the theoretical values obtained on the basis of the selection rules given by Placzek. This discrepancy between the theoretical and the experimental values indicates the necessity for a reconsideration of the theoretical ideas, on the basis of which the selection rules have been derived.

5. *Polarisation of the Fluorescence Bands of Diamond*

Table II gives the values for the depolarisation ratio ρ for the fluorescence bands of the 4152 system for the 3 cases mentioned above, corrected for the instrumental error.

TABLE II

$$\rho = \frac{E_x^2}{E_z^2}$$

Incident light unpolarised	1·0
Incident light polarised with electric vector along OY	0·8
Incident light polarised with electric vector along OZ	0·2

Ramaswamy had previously observed that with incident unpolarised light the fluorescence bands were depolarised. It will be observed from the table that the two components of the fluorescent beam are of equal intensity for incident unpolarised light, while the bands appear partially polarised with the incident electric vector along OY and strongly polarised with the incident electric vector along OZ. No obvious difference was noticed in the polarisation characters of the main band at 4156 A.U. and the subsidiary bands at longer wave-lengths.

In conclusion, the auther wishes to express her grateful thanks to Professor Sir C. V. Raman for his helpful interest and encouragement in this work.

6. *Summary*

The depolarisation values for the principal Raman line in diamond have been determined using a natural crystal and taking the necessary precautions to eliminate errors due to the birefringence of diamond and to refractions and internal reflections in the crystal. The results obtained for the three different cases, *viz.*, with the incident light unpolarised and polarised with the electric vector along the OY and OZ axes, are found to differ notably from the theoretical values predicted by Saxena on the basis of the selection rules given by Placzek.

The polarisation of the fluorescence bands of the 4152 system has also been studied. It is found that with incident unpolarised light the bands appear depolarised while they appear polarised in the other two cases.

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Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XV, No. 1, Sec. A, 1942

FLUORESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN RUBY

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Received January 14, 1942
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

The fluorescence and the pleochroism exhibited by ruby have been the subject of detailed investigations at the hands of many investigators, notably du Fay (1724), Boisbaudran (1887), Crookes (1887, 1889), Miethe (1907), Becquerel (1907, 1910, 1911), Mendenhall and Wood (1915) and Gibson (1916). They have been studied with especial thoroughness by du Bois and Elias (1908) and by Deutschbein (1932, 1934). Reference may also be made to recent papers by Venkateswaran (1935) and Thosar (1938). The fluorescence spectrum consists at room temperatures of two sharp and intense lines at 6927 and 6942 A.U. respectively, accompanied by other bands of varying width and intensity. At ordinary temperatures, these appear at wavelengths longer and shorter than the principal doublet. But at liquid air temperatures the bands towards the shorter wavelength disappear completely from the fluorescence spectrum. At such temperatures, there is no correspondence between the fluorescence and absorption bands except in regard to the principal doublet and certain fainter companion lines which appear on the longer wavelength side of the same. In other words, the Stokes Law is strictly obeyed, only longer wavelength bands appearing in fluorescence and the shorter wavelength bands in absorption.

Despite the numerous investigations mentioned above, the fluorescence spectrum of ruby has not as yet been fully elucidated. The two principal lines are usually regarded as due to electronic transitions in the triply ionized chromium atoms present as an impurity in the crystal. This explanation leaves it obscure why the principal lines do not agree in position and intensity when the nature of the ground material is varied. The fainter components accompanying the principal doublet have been ascribed by Deutschbein to an intra-molecular Stark effect. Why, if this be the case, the companions appear only on the longer wavelength side is unexplained. Further, the diffuse bands have been attributed to the superposition of the molecular or crystal lattice vibrations on the electronic transitions. This view, however, is unsupported by any independent data regarding the lattice spectrum of the crystal except in regard to one frequency nearly at 415 cm.$^{-1}$, which has been identified in the Raman spectrum of alumina, and agrees tolerably with the frequency shift of the 7138 band in fluorescence.

That the chromium activator forms an integral part of the crystal lattice of the ground material *viz.*, aluminium oxide, is indicated by the fact that the principal lines in emission and absorption are partially polarised (Pringsheim, 1928). Previous investigations on the polarised absorption and polarised excitation of fluorescence are however, confined to the principal doublet. A fuller study of the polarisation characters of the fluorescence and absorption bands as well as the Raman spectrum of the crystal has been carried out and is described in the present paper. The work was undertaken in order to elucidate the origin and nature of the principal, subsidiary and diffuse bands exhibited by ruby, as well as the nature of the arrangement of the Cr^{+++} ions in the ground lattice.

2. *The Lattice Spectrum of Alumina*

The Raman spectrum of alumina has been previously studied by Hibben (1932) who reported four weak lines having frequency shifts of 536, 728, 931 and 1191 cm.$^{-1}$, and by Deutschbein (1932) who could observe only one Raman line at 415 cm.$^{-1}$ Two large crystals of transparent synthetic alumina of dimensions $3{\cdot}5 \times 2 \times 1{\cdot}5$ cms. and $4 \times 2 \times 2$ cms. respectively were used in the present investigation. A two prism glass spectrograph supplied by Adam Hilger, having a dispersion of 28 Å/mm. in the 4358 A.U. region was employed for photographing the spectra. The crystal was immersed in a liquid of nearly the same refractive index, *viz.*, α-bromonaphthalene, to minimise parasitic illumination and diminish the strong continuum due to fluorescence. The spectrum recorded, however, was very weak even after two days of continuous exposure. Two Raman lines having frequency of 412 and 376 cm.$^{-1}$ have been recorded with fair intensity on the plates. The line at 412 cm.$^{-1}$ is stronger than the other. It may, however, be remarked that there are indications of the presence of a few more faint lines in the spectrum. But due to the superposition of the strong continuum, they cannot be listed with certainty.

Coblentz (1908) has reported three maxima in selective reflection for alumina at $11\,\mu$, $11{\cdot}8\,\mu$ and $13{\cdot}5\,\mu$ corresponding to frequency shifts of 909, 847 and 741 cm.$^{-1}$ and it will be seen that they do not coincide with either of the observed Raman lines.

3. *The Absorption Spectrum of Ruby*

The absorption spectrum of the sample of ruby used for the study of fluorescence was obtained using a tungsten filament lamp as the source of continuous radiation. The crystal was placed with its optic axis perpendicular to the direction of observation so that light traverses the crystal in a direction perpendicular to the optic axis, and the ordinary and extraordinary spectra were recorded.

The absorption spectrum in the red consists of a doublet with three bands on the Stokes and six on the anti-Stokes side. The spectrum is reproduced in Fig. 5, and the relative intensities of the different bands in both spectra are given in Table I. It will be seen from a comparison of Tables I and II that the absorption bands correspond closely with those appearing in emission. In the extraordinary spectrum, with the electric vector vibrating along the optic axis, all bands except 6595 and 6693 are very weak. These results are in agreement with those of du Bois and Elias (1908). Three bands in the blue, ascribed by Deutschbein to $^4F \rightarrow {}^2H$ transitions of Cr^{+++}, are also given in Table I, along with their intensities in the two spectra, and reproduced in Fig. 6. The results show that two of these bands *viz.*, 4686 and 4768 A.U. are opposite in behaviour to those in the red region, the intensity of the extraordinary ray for them being greater than the ordinary. The strong

TABLE I

The Absorption Spectrum of Ruby

No.	Wave-length	Wave-numbers	Intensities of bands	
			Ordinary	Extraordinary
1	6581	15191	..	..
2	6595	15158	6	5
3	6649	15036	..	..
4	6693	14937	5	2
5	6758	14793	2	0
6	6822	14654	2	0
7	6927	14431	9	2
8	6942	14400	10	1
9	6996	14290	1	0
10	7016	14249	1	0
11	7049	14182	1	0
12	4686	21334	2	6
13	4753	21033	5	1
14	4768	20967	3	5

polarisation of these bands had been visually observed by du Bois and Elias.

4. *The Fluorescence Spectrum of Ruby*

For the observations of the photo-luminescence of ruby, a piece of synthetic ruby, 9 × 7 × 5 mms. cut with its longest edge parallel to the optic axis was employed. The axis was fixed by observing the extinction directions between crossed polaroids and confirmed by viewing it in convergent light between crossed nicols, after cutting it. Light from a pyrex mercury arc was focussed on the crystal by a long-focus lens and the fluorescence spectrum photographed with a Fuess glass spectrograph having a dispersion of nearly 100 Å/mm. in the 6900 A.U. region. The fluorescent light emitted transversely to the incident beam was focussed on the slit of the spectrograph. In experiments with polarised light, a properly oriented nicol was placed between the crystal and the incident beam and a double-image prism was inserted in the path of the fluorescent light. Ilford H.P.2 plates having an H and D number of 2500, and Ilford infra-red plates with H and D 100, sensitized with ammonia were used in photographing the spectra. Wavelengths of the bands were ascertained by measurements with a cross-slide micrometer in comparison with neon lines as standard.

Table II gives the wavelengths and intensities of the bands obtained along with those given by Deutschbein and Venkateswaran. Besides the twenty-four bands observed by Deutschbein, three new bands with centres approximately at 7539, 7544 and 7772 A.U. have been recorded. Further the 7138 band shows a definite doublet structure with components at 7129 and 7147 A.U. respectively. Because of the insensitiveness of the infra-red plates used to the 6000–6900 A.U. region, the bands 6495 and 6430 observed by Venkateswaran could not be obtained. The author's values show fairly good agreement with the rest, considering the low dispersion of the instrument used. It should, however, be remarked that the bands on the Stokes side appear to be sharper in the ruby used in the present investigation than those recorded by Deutschbein. Their intensities as compared with the principal lines also show differences from those given by the latter. The complete fluorescence spectrum of ruby is reproduced in Fig. 1 in the accompanying Plate.

TABLE II

The Fluorescence Spectrum of Ruby

Author—25° C.		Deutschbein—20°			Venkateswaran—35°
Wave-length	Intensity	Wave-length	Intensity	Half-width in cm^{-1}	Wave-length
5900–6700	..	..	..	..	6100–6900
..	..	..	..	..	6430
..	..	..	..	..	6495
6581	1	6583	1	30	..
6595	2	6595	3	40	6592
6649	1	6647	1	50	6650
6693	4	6692	4	80	6690
6758	3	6762	3	70	6753
6802	3	..	..	..	6791
6817	3	6820	3	100	6814
6833	2	..	..	..	..
6927	9	6927	9	16	6927
6942	10	6942	10	19	6945
6978	1	6977	2	18	..
6985	2	6986	4	18	..
6996	2	6996	4	18	6992
7016	4	7017	6	18	7027
7049	6	7049	6	18	7059
7078	6	7072	2	60	7089
7129	7	..	..	..	7125
7147	7	7138	3	60	..
7188	6	7188	2	80	7164
..	..	..	..	..	7222
7275	5	7276	2	60	7266
7324	4	7323	2	60	..
7359	2	..	..	..	..
7440	1	7438	1	100	..
7520	2	7517	1	100	..
7544	2	..	..	..	..
7606	1	7603	1	40	..
7674	1	7675	2	40	..
7725	3	7723	3	100	..
7772	2	..	..	..	..
7924	2	7921	2	100	..

5. *Polarisation of the Fluorescence Bands*

Designating the three mutually perpendicular directions in pace as OX, OY and OZ, where OX is the direction of incidence, OY the direction of observation and OZ the vertical direction perpendicular to the other two, the crystal is set with its optic axis along any one of the three directions for studying the polarisation characters of the bands. For each of the three settings, three separate photographs were taken,

(1) with incident light unpolarised,

(2) with incident electric vector polarised with vibrations along OZ, and

(3) with incident electric vector polarised with vibrations along OY. The fluorescent light was analysed into vertical (OZ) and horizontal (OX) components by means of a double-image prism, and are marked V and H in the figures. The spectra obtained are illustrated in Figs. 2, 3, 4, 7, 8, 9, 10, 11 and 12 in the accompanying Plates.

(*a*) Figs. 2, 3 and 4 give the horizontal and vertical components for unpolarised incident light where the optic axis is respectively along OX, OY and OZ.

(*b*) Figs. 7 and 8 illustrate the spectra with the optic axis along OX and the incident light vector along OY and OZ respectively.

(*c*) Figs. 9 and 10 correspond to the same setting as for *b*, but with the optic axis along OZ.

(*d*) Figs. 11 and 12 correspond to the same setting as for *b*, but with the optic axis along OY.

The directions of the optical vibrations in the incident light and the fluorescent light are indicated, when along OX and OY, by arrows parallel to them and by circles with central dots when along OZ. The optic axis is indicated by a set of three lines parallel to OX and OY when along them and by a triangle with a central dot when along OZ. Taking 20 as the intensity of the strongest band in each plate, intensities of the strong bands have been visually estimated and are given in Table III.

It will be seen from all the figures, that the principal doublet and almost all the bands are very intense when the fluorescent light vector vibrates in the (0001) plane, perpendicular to the optic axis ; *i.e.* in general, the ordinary fluorescence spectrum is stronger than the extraordinary. Moreover, as may be seen from Figs. 7–12, both vertical and horizontal components appear brighter when the incident light vibrates perpendicular to the optic axis than when along it. This becomes intelligible when it is remarked that the absorption of light by ruby is also stronger for vibration-directions perpendicular to the optic axis. Figs. 2, 11 and 12 illustrate the fact that whatever the nature of polarisation of the incident light, with the crystal oriented with its optic axis along OY, both V and H components are equally intense for all the bands. This should be so, because for this particular orientation of the crystal, both components of the fluorescent light vibrate in the (0001) plane. However, the most remarkable fact is that with the incident light vector vibrating along

TABLE III

The Intensities of the Fluorescence Bands in Polarised Excitation

Direction of vibration of Incident Light	Orientation of the Optic Axis along	Components of Fluorescent Light along	Relative Intensities of the Components of the Flourescence Bands																
			6595	6693	6758	6822	6927	6942	7016	7049	7078	7129	7147	7188	7275	7324	7520	7725	7924
YZ Plane	OX	OX	2	1	2	2	12	10	4	4	4	7	8	5	7	4	3	3	2
		OZ	4	5	3	3	17	20	5	7	8	10	10	7	6	5	1	2	1
YZ Plane	OZ	OX	4	6	4	3	17	20	7	8	9	11	11	8	7	6	1	4	4
		OZ	2	2	2	2	12	10	6	5	5	8	8	5	6	4	4	3	1
OZ	OX	OX	1	1	2	2	12	10	4	4	4	8	7	4	6	2	2	1	1
		OZ	2	5	3	3	17	20	3	7	8	9	8	7	6	5	1	3	2
OZ	OZ	OX	3	5	3	3	17	20	3	7	8	9	8	7	6	5	1	3	2
		OZ	2	1	2	2	12	10	4	3	3	7	6	4	5	3	3	4	3
OY	OX	OX	1	1	2	2	12	10	5	4	4	8	8	5	6	5	3	2	2
		OZ	2	4	2	2	17	20	4	6	7	9	9	7	6	6	1	3	1
OY	OZ	OX	3	5	3	3	17	20	4	7	8	10	9	7	6	5	1	4	2
		OZ	2	1	2	2	10	8	4	4	4	7	6	4	5	3	3	3	3

the optic axis, it is the component in fluorescence perpendicular to the optic axis that appears stronger. This may be clearly seen from Fig. 10. In general, whether the incident light vector vibrates along or perpendicular to the optic axis, it is that component vibrating perpendicular to the optic axis that comes out more intensely.

6. *Discussion of Results*

A. The Lattice Spectrum of Alumina.—According to detailed X-ray analysis, the crystal structure of alumina (corundum) is similar to that of calcite, and the unit cell belongs to the space group D^6_{3d} of the holohedral class of the rhombohedral system, having three equal axes making an angle of 85° 42′ with each other. For the purpose of analysing the lattice spectrum of the crystal, we shall consider the fundamental unit cell containing four aluminium and six oxygen atoms. The character table for this is identical with that given by Bhagavantam and Venkatarayudu (1939), and indicates that the thirty degrees of freedom of the atoms are distributed among six representations, four of which are single and two doubly degenerate. Two vibrations of the totally symmetric class and five of the doubly degenerate types are active in the Raman effect, the same being inactive in the infra-red. Besides these seven, there are eleven modes of vibration, nine of which are active in the infra-red and two inactive in both the infra-red and the Raman spectra. Only three of the former have been observed in infra-red absorption.

One of the important facts emerging from the investigations of the Raman spectrum of alumina is its extreme feebleness in spite of the fact that a clear, transparent crystal of large size was available. It has been shown by several authors that the Raman lines connected with ionic bindings are generally of very low intensity. Therefore, the observed weakness of the spectrum of alumina rather suggests that the binding between Al and O atoms is more or less ionic in character.

The strongest of the Raman lines recorded, *viz.*, 412 cm.$^{-1}$ is presumbaly due to one of the two totally symmetric oscillations of the unit cell considered above in which the two aluminium and the three oxygen atoms situated around the cell corners, move towards or away from their common centre.

B. Electronic Transitions of Triply Ionized Chromium.—All chromium phosphors give emission lines in the red, indicating that the lines owe their origin to the chromium activator embedded in the ground lattice isomorphically. Deutschbein (1932) has shown that these characteristic lines of chromium undergo significant changes in wavelength and intensity, with different metallic oxides and silicates as the basic material. This is also evident from Venkateswaran's work (1935) on emerald (beryllium aluminium silicate) whose principal doublet coincides not with the 6927 and 6942 A.U. bands but with 6802 and 6822 A.U. bands of ruby. This suggests that the 'subsidiary' lines *viz.*, 6802, 6822, 6978, 6985, 6996, 7016 and 7049 together with the principal doublet of 6927 and 6942 A.U. in ruby, are due mainly to electronic transitions of the Cr^{+++} ion. The ground material has thus the effect of suppressing some of the electronic bands and enhancing some others. The principal doublet has been assigned to a transition $^4F \rightarrow {}^2G$ of a 3*d* electron of triply ionized chromium. Deutschbein assumes that the subsidiary bands arise from an intramolecular Stark effect. Candler (1937) has however, pointed out the difficulties inherent in the latter suggestion as it does not explain either the position or the differential intensities of the bands on either side of the doublet. Thosar (1938) has given reasons to believe that the 7016 and 7049 bands have frequencies that agree with the electronic transitions $^4P_{5/2} \rightarrow {}^4F_{5/2}$ and $^4P_{7/2} \rightarrow {}^4F_{7/2}$ of the Cr^{+++} ion respectively. The assignments of these bands to electronic transitions of Cr^{+++} ion is also supported by the observation that the floruescence and absorption bands in the region 6927-7049 overlap.

C. Vibrational Bands of Ruby.—The important role played by the lattice of the ground material in the fluorescence and absorption spectra of ruby becomes clear when we consider the origin of the bands which lie on either side of the electronic bands in ruby. The present investigation shows that at room temperature the Stokes bands are distinctly stronger than the corresponding anti-Stokes bands. The observation of some authors that the anti-Stokes bands are stronger, is obviously due to the insensitiveness of the plates used by them to the longer wave-length region. The relative intensities of the Stokes and anti-Stokes bands observed in the present investigation suggest that they arise from the superposition of the lattice vibrations of alumina on the electronic transitions. Deustchbein was the first to suggest that these bands might arise thus and he explained the band at 7138 A.U., as due to the Raman frequency of 412 $cm.^{-1}$ observed by him, being superposed on the electron jump. It has been shown earlier that there are altogether eighteen normal modes of vibration for the alumina lattice which may modulate the electronic transitions and give rise to fluorescence bands. On the basis of the two Raman frequencies at 412 and 376 $cm.^{-1}$ and the three infra-red frequencies at 909, 847 and 741 $cm.^{-1}$, eight fluorescence bands on the Stokes and anti-Stokes sides of the principal doublet may be satisfactorily accounted for. These assignments are given in Table IV. A perusal of Table IV and the accompanying Plates, shows that more or less perfect mirror

TABLE IV

Wave-length in A.U. at 25° C.	Wave-length in A.U. at −195° C.	Shift in cm.$^{-1}$ from 6934. R_1	Assignments from the Lattice spectrum in cm.$^{-1}$
6595	6586	761	741 — ν_3
..	6620	683	..
6649	6640	638	..
6693	6688	530	..
..	6707	488	..
6758	6744	407	412 — ν_2
6764	6757	378	376 — ν_1
6817	6807	268	..
7078	7067	273	..
7129	7120	377	376 — ν_1
7147	7140	416	412 — ν_2
7188	7178	491	..
..	7196	525	..
..	7260	648	..
7275	7279	683	..
7324	7318	757	741 — ν_3
	7346	809	847 — ν_4
	7404	915	909 — ν_5

image symmetry holds for the bands 6595, 6649, 6693, 6758 and 6817 on the anti-Stokes side and for 7324, 7275, 7188, 7138 and 7078 bands on the Stokes side. It is also possible that besides the principal doublet, the other electronic transitions give rise to vibrational bands in the fluorescence spectrum. This may possibly account for the slight departure from mirror image symmetry about the principal doublet, of the fluorescence and absorption bands observed at liquid air temperature. A more detailed experimental study of the lattice spectrum of alumina is desirable in order to give a complete explanation of the fluorescence and absorption bands exhibited by ruby.

D. Polarisation Characters.—Table I indicates that for all bands except 6595, 6693, 6927 and 6942 of ruby, absorption of light takes place almost exclusively in the ordinary spectrum *i.e.*, in the (0001) plane perpendicular to the optic axis of ruby. This absorption, however, has little effect on the emission spectrum, as may be inferred from Figs. 3, 4, 5, 6, 7 and 8 in which the fluorescence bands come out strongly when the electric vector vibrates perpendicular to the optic axis. Therefore, to a first approximation we are justified in ignoring the effect of absorption on the relative intensities of emission bands in polarised excitation. The principal doublet is strongly polarised, the degree of polarisation of 6942 band being higher than that of the 6927 band. Two other electronic bands *viz.*, 6822 and 7049 A.U. are also polarised to the same extent as the latter while the 7016 A.U. band is depolarised. The continuous spectrum is also polarised to the same extent and in the same sense as the principal doublet. These polarisation characters of the electronic bands support the suggestion that the Cr_2O_3 activator possesses a preferred orientation of distribution in the ground lattice. The origin of the polarisation of the electronic bands is not well understood. However, in the present investigation it is observed that the fluorescent vibrations appear stronger with the light vector vibrating normal to the optic axis than when along it, whatever be the nature of the polarisation of the incident light vector. This indicates that the phosphorescent centre in ruby is not a simple electric dipole.

From the values of intensities given in Table III, the vibrational bands have been divided into the following groups, and are listed in Table V.

(1) Bands whose polarisation is in the same sense, and equal to or greater than that of the principal doublet.

(2) Bands whose polarisation is opposite to that of R_1 and R_2 *i.e.*, when the vertical component of the latter is more intense than the horizontal component, the horizontal components of the bands are more intense than the vertical and *vice versa*.

TABLE V

Bands polarised in the same sense as R_1 and R_2	Bands polarised in the opposite sense to R_1 and R_2	Bands completely depolarised
I	II	III
6595 .... $-\nu_3$		
6693		6758 .... $-\nu_1$
7078		7129 .... $+\nu_1$
7147 .... $+\nu_2$		
7188		7275 ....
7324 .... $+\nu_3$		
	7520	
7725		
7924		

(3) Bands which are completely depolarised, *i.e.*, the vertical and horizontal components are nearly equal in all settings.

It will be seen from the above table that the Stokes and anti-Stokes components of the vibrational bands show more or less the same polarisation characters in polarised excitation. It may also be seen that the two components of the doublet at 7138 are polarised differently, the 7129 component being depolarised nearly to the same extent as the 6758 band on the anti-Stokes side, while the component at 7147 A.U., having a frequency shift of 412 cm.$^{-1}$ appears to be more highly polarised. It is obvious that the vibrations which appear polarised in light scattering should give rise to fluorescence bands which are highly polarised, especially as the principal doublet itself is polarised. This agrees with the assignment of the Raman line at 412 cm.$^{-1}$ to the symmetric oscillation. The bands which are completely depolarised and those whose polarisation characters are opposed to that of the principal doublet may be attributed to the degenerate vibrations of the crystal lattice.

In conclusion, the author wishes to express her grateful thanks to Sir C. V. Raman, F.R.S., N.L., for the continued interest he has shown throughout the course of this investigation. My sincere thanks are due to Dr. C. S. Venkateswaran for the valuable help rendered by him.

Summary

The paper deals with the results of a spectroscopic investigation of the fluorescence, absorption and scattering of light in ruby. The first order lattice spectrum of alumina is shown to possess eighteen normal modes of vibrations. Two Raman lines having frequency shifts of 376 and 412 cm.$^{-1}$ have been obtained with a single crystal of alumina. The fluorescence and absorption spectra of ruby have been recorded using specially sensitized infra-red plates to register the bands in the long wavelength region with good intensity. The polarisation characters of the bands have also been studied with reference to the direction of the optic axis of the crystal and the direction of polarisation of the incident beam. From a perusal of the results, the emission bands have been divided into two groups *viz.*, (1) electronic bands caused by transitions of the shielded electrons of Cr^{+++} ion, (2) vibrational bands arising from a modulation of the electronic transitions by the crystal lattice vibrations. The frequency shifts of eight of the vibrational bands from the principal doublets agree fairly well with one or the other of the observed Raman and infra-red frequencies of alumina. The polarisation characters of the bands on the Stokes sides are also in good agreement with those of the corresponding bands on the anti-Stokes side.

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Note.—After the paper had been written, a note by Thosar in the *Physical Review* for October 15, 1941, came to hand which deals with the same subject.

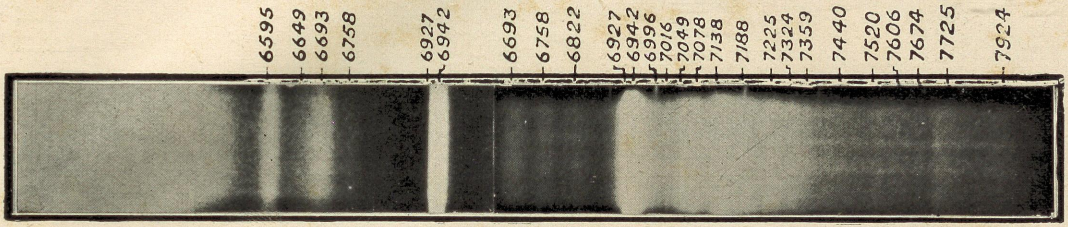

Fig.1

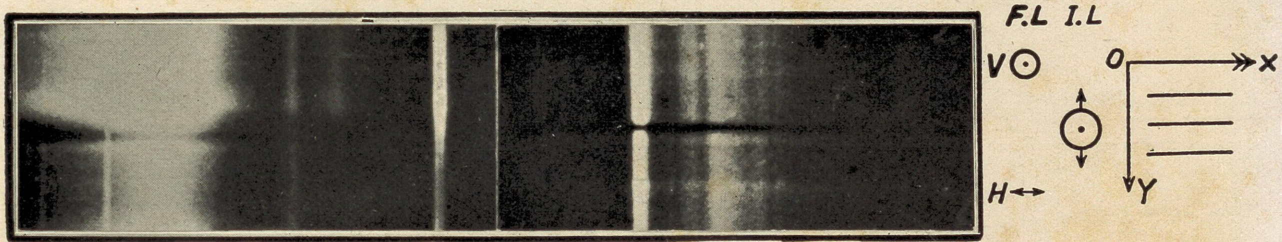

Fig.2

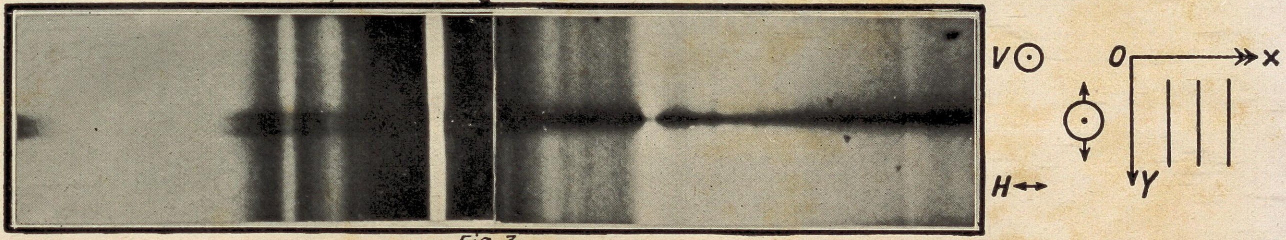

Fig.3

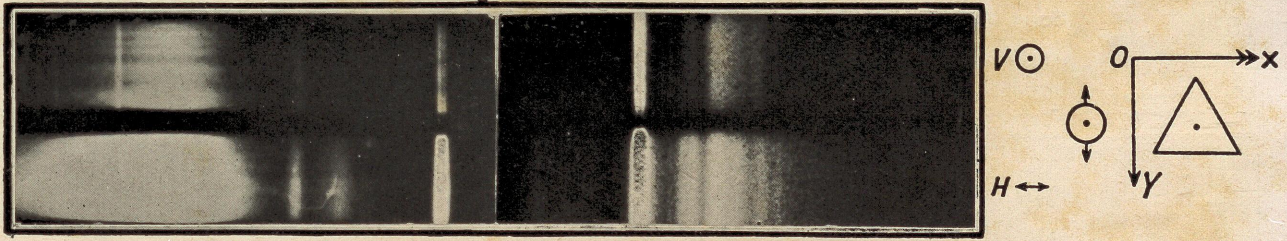

Fig.4

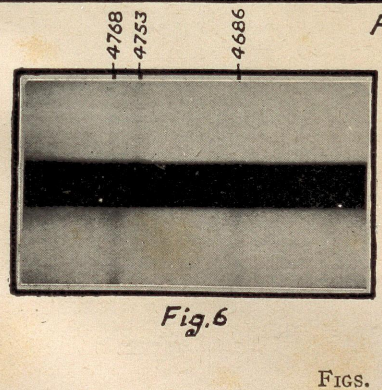

Fig.6

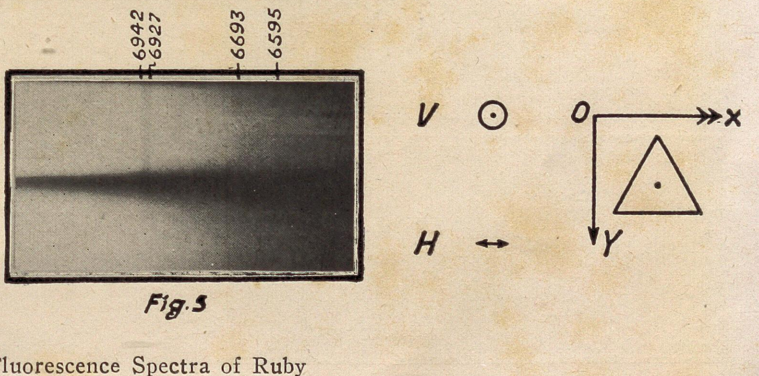

Fig.5

Figs. 1-4. Fluorescence Spectra of Ruby

Figs. 5-6. Absorption Spectra of Ruby

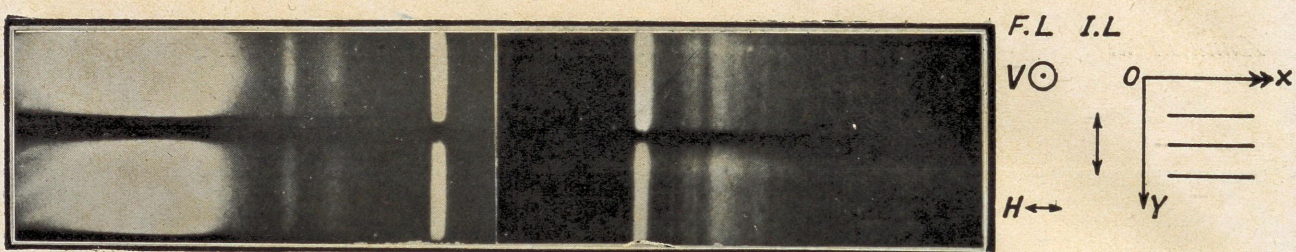

Fig. 7

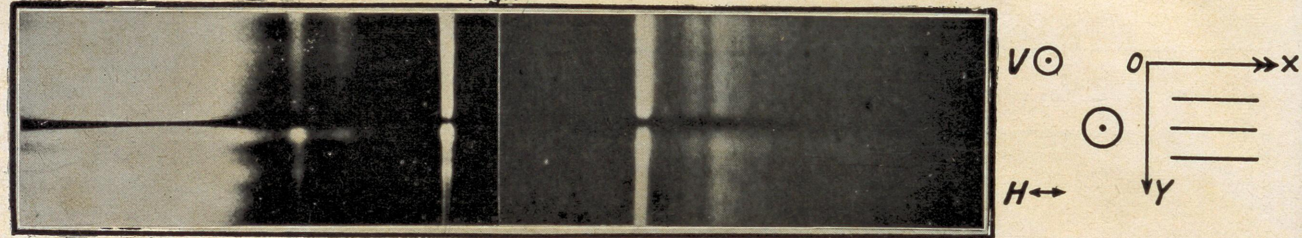

Fig. 8

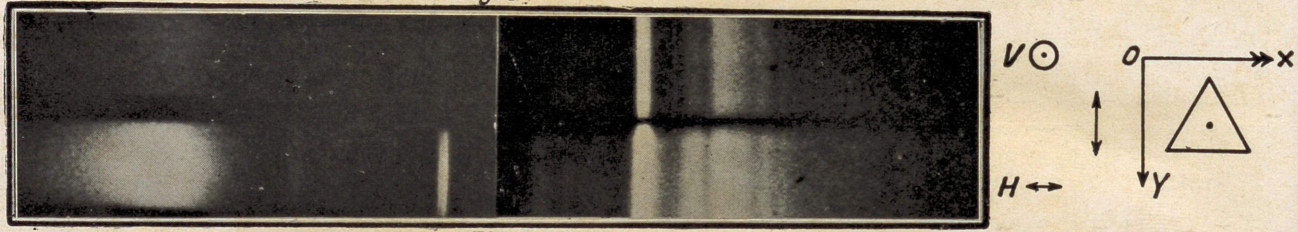

Fig. 9

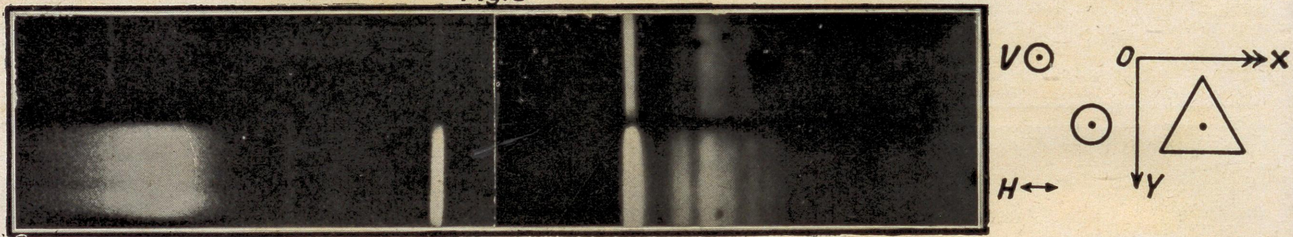

Fig. 10

Fig. 11

Fig. 12

Fluorescence Spectra of Ruby

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