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.

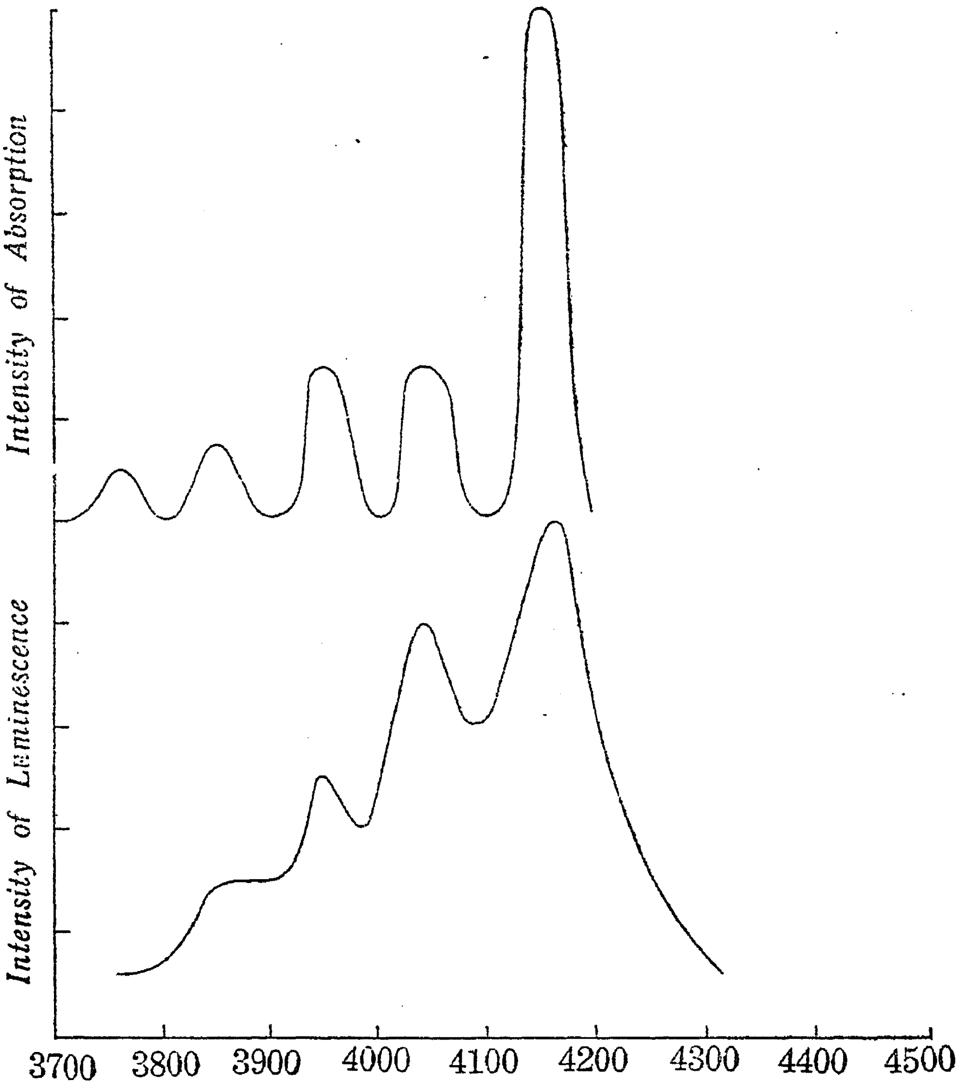
The image of the monochromator slit was condensed on the diamond by a short focus lens and the fluorescent light from the diamond focussed by a cylindrical lens on the slit of a Zeiss three prism spectrograph. The spectra were recorded on Ilford HP_3 plates using the short focus camera attachment, since 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,



Excitation Curve for the 4152 System

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.

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.

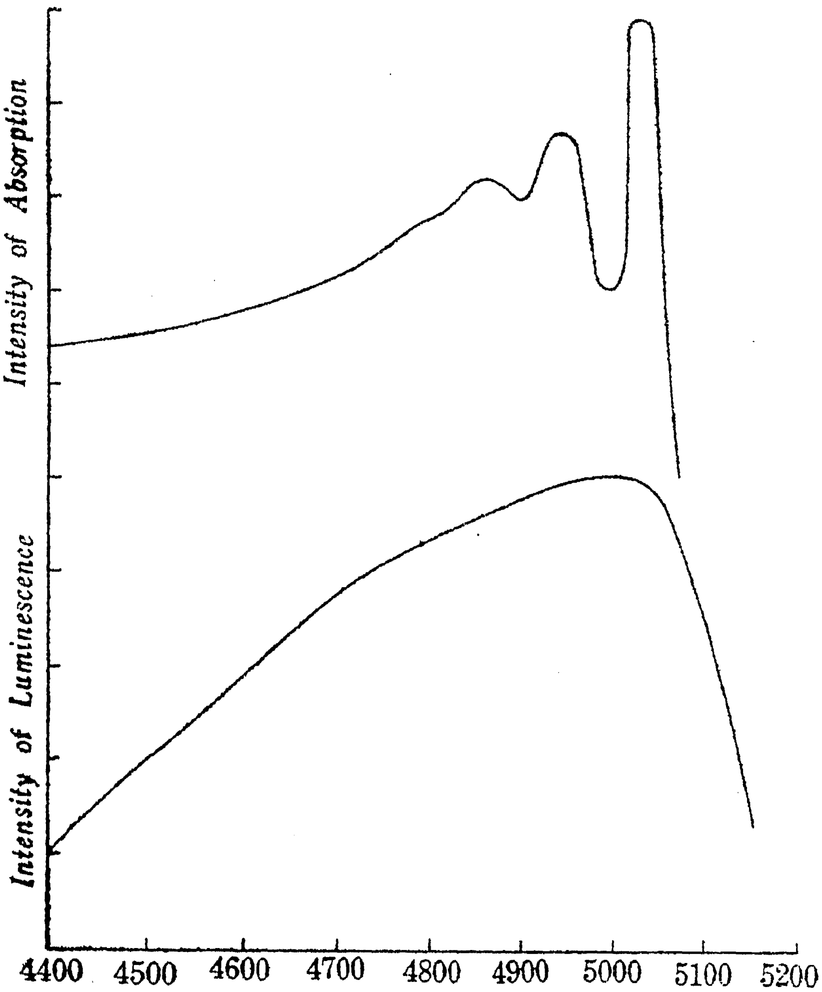
An interesting result worthy of note is that while variations in the wavelength of excitation cause remarkable changes in the intensity of fluorescence, they have no effect on the colour of the fluorescent light. In other words, the position of the maxima of the fluorescence spectra in blue luminescent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

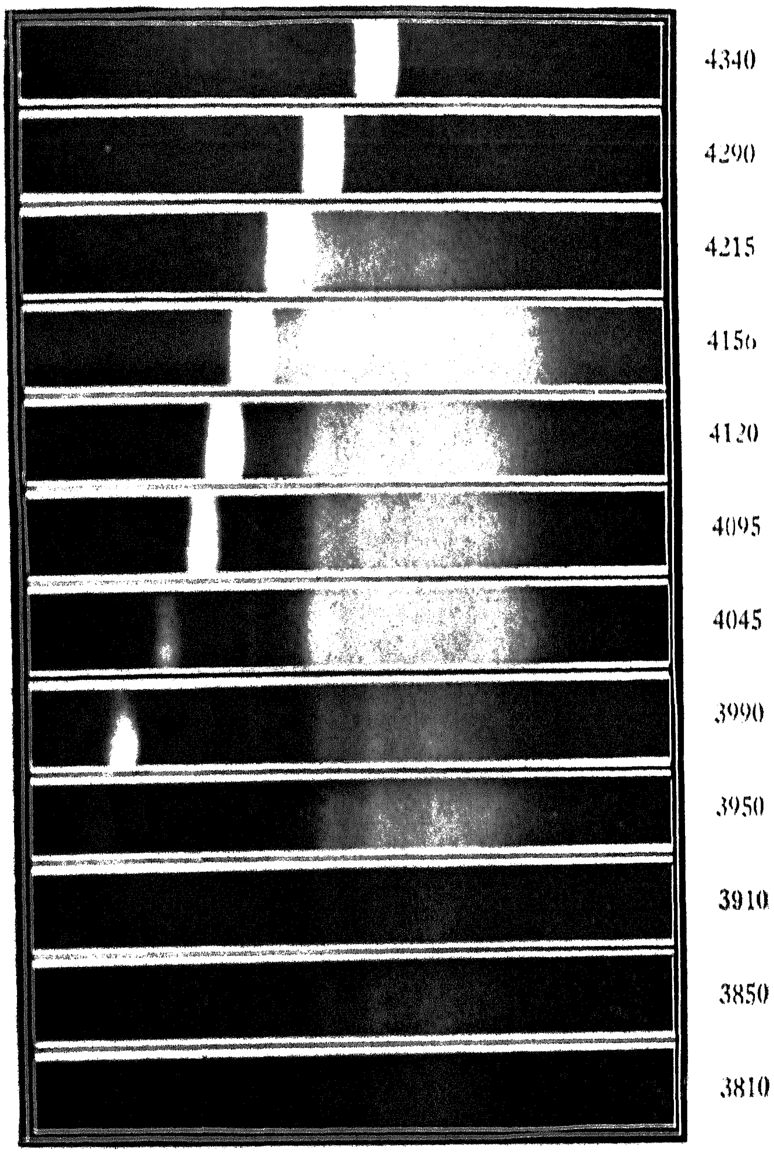


Fig. 1

The 4152 System

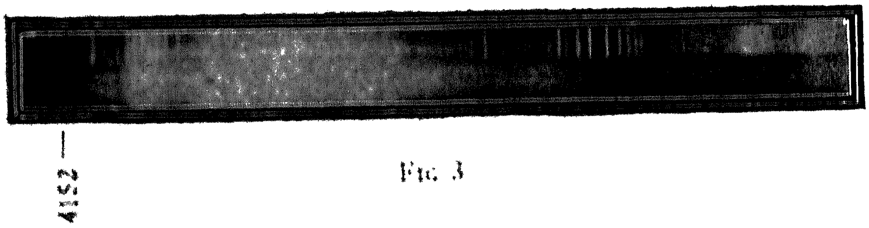


Fig. 3

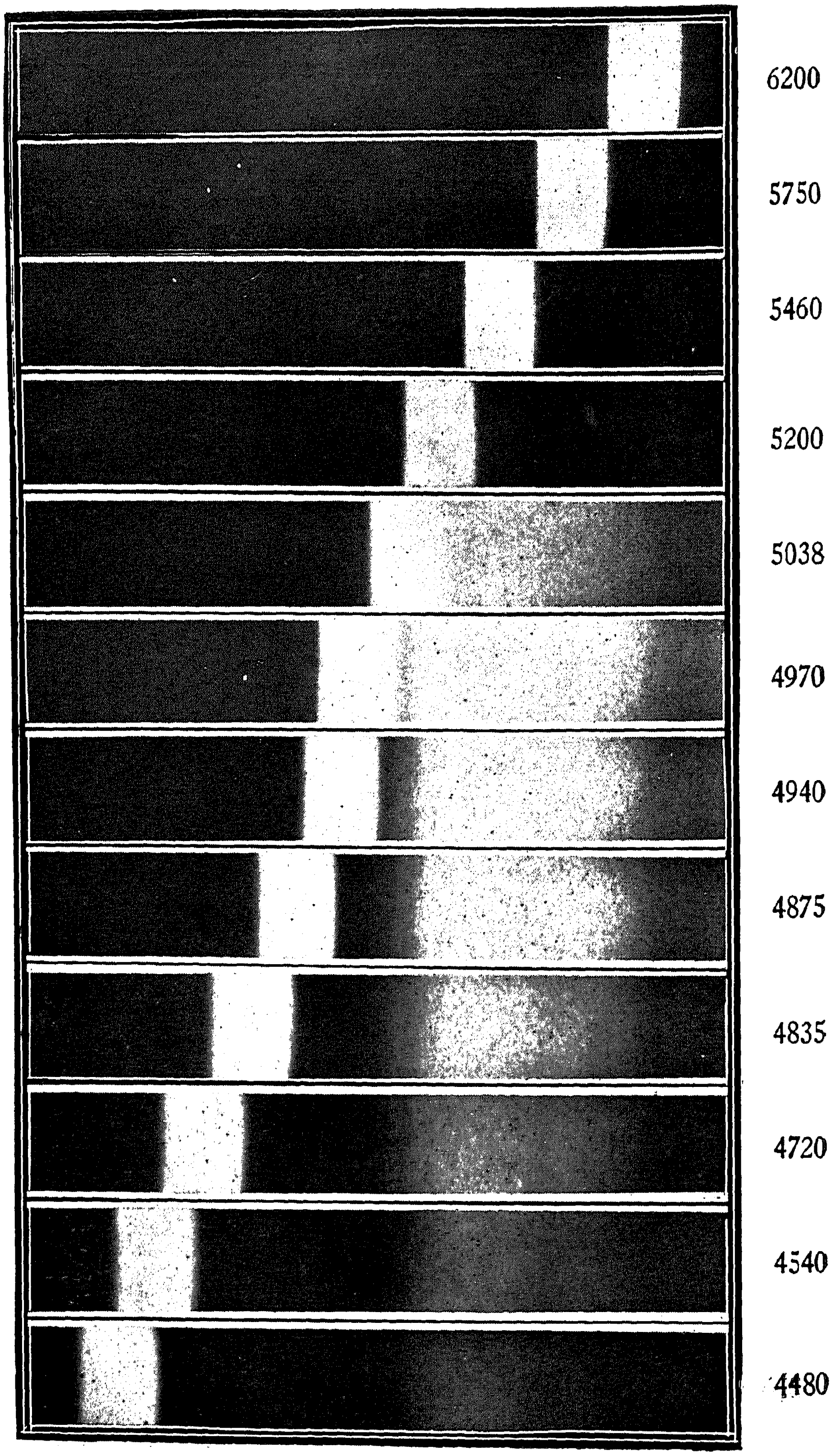


FIG. 4

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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