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THE LUMINESCENCE SPECTRA OF DIAMOND

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1. INTRODUCTION

THE luminescence of diamond has been the subject of numerous investigations in the past and these have principally dealt with two types of emission spectra commonly met with, one lying in the blue and the other in the yellow-green regions of the spectrum. P. G. N. Nayar[1] made a detailed study of the former while the latter was first extensively studied by Miss Anna Mani.[2] The latter author investigated both the emission and absorption spectra of several fluorescent diamonds at room temperature and at 80° K. The principal features in the spectra of the blue luminescent diamonds are that at 80° K., a line at λ 4152 A.U. appears in emission as well as in absorption, accompanied by a set of bands arising out of the combination of the electronic frequency with the lattice vibrational modes of the crystal. These bands appear in emission on the longer wavelength side, while in absorption they lie on the shorter side. In the case of diamonds exhibiting a greenish-yellow luminescence, a sharp line at λ 5034 A.U. appears, accompanied by vibrational bands. Apart from these, Miss Mani reported the occurrence of numerous sharp electronic lines in the fluorescence spectrum of diamonds. Recently, Dyer and Mathews[3] have studied fluorescence spectra of several diamonds at liquid-air temperature, and report in addition to the above-mentioned two emissions, an electronic line at λ 6100 A.U. and a band system associated with it. They have also investigated luminescence spectra of irradiated and heat-treated diamonds. Gomon[4] reports studies on diamonds of Russian origin.

Several years ago, a set of uncut diamonds of South African origin were acquired by Professor Sir C. V. Raman and added to his impressive collection of nearly five hundred diamonds. Some of these newly acquired diamonds exhibited unusual types of fluorescence when exposed to near ultra-violet radiation. The spectra of these were recorded at room temperature, as far back as 1951 by the present writer and was reproduced in an article by Sir C. V. Raman in *Current Science*.[5] These, however, did not reveal any noteworthy features, except broad lines and unresolved bands superposed on a continuum. The recent acquisition of a liquid-air plant by this Institute enabled a study of the spectra of these diamonds to be made at liquid-air temperature. A number of other diamonds from the collection were also re-examined. These studies have revealed several interesting facts and some new features in addition to those briefly set out in the preceding paragraph. Three hitherto unrecognised strong electronic emission lines with associated band systems have been observed during the present investigation, namely, those located at λ 4958, λ 5106·38 and λ 5786. Numerous other electronic lines have also been recorded. The important question of the origin of luminescence in diamond will be discussed later in the light of the knowledge accumulated during recent years on the structure and physical properties of this fascinating substance.

2. MATERIALS AND METHODS

In all, spectra of over twenty diamonds were recorded both at room temperature (300° K.) and at 80° K. Eight uncut diamonds of South African origin declared as industrial quality were studied. They all belong to the strongly luminescing class. Many of these are free from any body colour and are clear crystal fragments, while a few are found to possess a light yellow body colour. Four of the specimens were beautiful octahedral crystals of South African origin, exhibiting blue luminescence of varying intensity. Another set of four well-crystallised diamonds, having curved edges, were from the State of Panna in Central India. These exhibited either a weak blue or greenish-blue luminescence. A batch consisting of four diamonds were cut gems exhibiting intense luminescence, the colours being respectively blue, green, bluish-green and bluish-white. In Table I are listed the diamonds which have been studied for the first time. The colour of luminescence and the principal emission lines observed in them are also given in Table I.

A Hanovia high-pressure quartz mercury arc was used for the excitation of fluorescence. The radiation after passing through a Wood's glass filter which cut off all wavelengths higher than 4046 A.U. was focussed on the diamond under investigation. The 3650 group of lines were the principal source for the excitation of fluorescence. For low temperature studies, the diamond was embedded in Wood's alloy filled in a small cavity formed in a copper block which was soldered to one end of a brass tube, one inch in diameter and about twelve inches in length. This arrangement had a pyrex glass envelope, the space between which was evacuated with a two-stage

TABLE I

No.	Shape	Body colour	Colour of luminescence	Observed emission systems
D 1	Irregular	No body colour	Orange	5786·27, 5898·88
D 2	,,	,,	Lemen yellow	4152 v.w., 5034 s.
D 3	,,	,,	Golden yellow	5034 v., 5018
D 4	,,	,,	Yellowish-white	4152 s., 5034 s., 5106 s.
D 5	,,	,,	Violetish-white	4152 s., b., 5034 s., 5106
D 6	,,	,,	Bright blue	4152 s., v.b., split into two
D 7	,,	,,	Whitish	4152 s., b., 5034 s.
D 60	Cut diamond	Colourless	Bluish-green	4152 s., b., 4958 v.s., 5031·5 s.
D 54	Cut diamond gem	,,	Bright blue	4152 s., b., split into two
D 52	,,	Greenish	Bright green	4152 v.s., v.b., split, 4958 v.s., v.b., 5034 self-reversed
D 178	Cut diamond	Colourless	Bluish-white	4152 v.s., v.b., 5034 v.w.

s., strong; v.s., very strong; v.w., very weak; b., broad; v.b., very broad.

rotary pump. A joint at the top was secured by flanges on the brass and glass tubes. The flanges had ground flat surfaces and DC 4 silicon grease was used between the two flanges to obtain a vacuum-tight seal. With this arrangement and maintaining a vacuum of 0·1 mm. of mercury, each liquid-air filling lasted for about 30 minutes. The glass envelope had flat windows at appropriate places for the ultra-violet radiations to enter and for the fluorescent radiations to come out. The latter was focussed on to the slit of a two-prism Huet spectrograph having an aperture of F 4·7. Spectra of strongly luminescent diamonds could be recorded intensely with this arrangement in about an hour's time, using Ilford H.P.S. plates. It took three to four hours to record weakly fluorescent diamonds. The H.P.S. plates, although possessing high speed, are poor in contrast and resolution. Photographing the spectra either with Ilford special-rapid or Process-Panchromatic plates was found to be highly satisfactory and rewarding, as the plates then revealed far more detail, although these plates demanded a four or even five-fold increase of exposure time.

3. EXPERIMENTAL RESULTS

The majority of diamonds exhibit a blue luminescence, the intensity however being highly variable. A green or yellowish-green luminescence is also met with not infrequently. A golden yellow or orange luminescence is somewhat rarer and especially the latter. One diamond in our collection shows an orange luminescence. A sensible increase in the intensity of luminescence is noticeable when diamonds are cooled down to 80° K. Another fact of observation worthy of mention is that the luminescence of diamonds which exhibit a white colour at room temperature turn distinctively yellowish when the diamond is cooled. Eight typical spectra recorded at 80° K. are reproduced in Fig. 1. A critical study of these reveals that five electronic emission lines occurring at λ 4152, λ 4963, λ 5034, and λ 5786 are prominent features. These are accompanied by vibrational bands and the colour of luminescence is largely dependent on which of the above principal emission line is the strongest. Accordingly, the blue luminescent diamonds show the λ 4152 emission line very strongly, the green ones the λ 4963 line, the greenish-yellow variety the λ 5034 or the λ 5106 line, while in golden yellow and orange luminescent diamonds the λ 5786 comes out with great intensity. In diamonds exhibiting an almost white, yellowish-white or bluish-white luminescence, both the 4152 and 5034 lines appear in equal strength. Some diamonds show exclusively one of these lines only.

λ 4152 *Emission*.—A great many diamonds exhibit this line in varying degrees of sharpness and intensity. In strong blue luminescent diamonds, the line is very intense and very broad and appears as a doublet with a dark line in the centre. This character is observable, if studies are made with thick crystals and arises due to self-reversal of the λ 4152 emission. In Fig. 1 (*f*) which is the spectrum of D 54, this feature can be clearly seen. In Figs. 1 (*a*) and 1 (*b*) which are spectra of D 4 and D 60 respectively, this line has come out with a fair degree of sharpness. It was thought that a non-birefringent diamond, exhibiting a weak blue luminescence might give a very sharp λ 4152 line. D 56 which is a natural octahedral cleavage plate showing no birefringence and of weakly blue luminescent class was chosen. The spectrum however showed that the λ 4152 line is no more sharper than that observable in the two above-mentioned diamonds.

λ 4958, 5034 and 5106·38 *Emissions*.—In bluish-green and green luminescent diamonds the λ 4963 line comes out strongly. The luminescence spectra of D 60 and D 52 which exhibit respectively a bluish-green and green luminescence are reproduced in Figs. 1 (*b*) and 1 (*e*). In the latter diamond, λ 4958 is the strongest and is very broad and diffuse even at 80° K. Diffuse bands also occur on the longer wavelength side. This line which comes out strongly in the three examples is also accompanied by a sharp line at λ 5031·16. In D 60 this line is of comparable intensity and therefore a band system associated with this electronic frequency also comes out and is overlapping the bands excited by λ 4963. In Fig. 2 (*c*) an enlarged spectrum of D 60 is reproduced. The spectrum of D 4 is also reproduced for purposes of comparison.

The 5034 and 5106 emission lines occur invariably together. The former is always found to be more intense than the other and is the strongest line in greenish-yellow diamonds. With diamonds in which these emissions appear along with the 4152 radiation in more or less equal strength, the colour of luminescence is almost whitish. In Figs. 1 (*a*), 1 (*c*) and 1 (*g*), the spectra of such diamonds are reproduced. Of these, the spectrum of D 4 exhibits numerous sharp electronic lines apart from the sharp λ 4152, λ 5034 and λ 5106 lines which dominate the spectrum. Figure 2 (*b*) is an enlarged photograph of the luminescence spectrum of this diamond. In Fig. 2 (*a*), a highly enlarged photograph of the λ 4152 emission line and the band system associated with it is reproduced. In Fig. 4, a microphotometer record of this portion of the spectrum appears. Figure 5 reproduces the microphotometer record of the λ 5034 and λ 5106 emissions and associated bands. In Fig. 3, the microphotometer record of the entire region between 4152 and 5200 A.U. of the spectrum of D 4 is reproduced. Some of the sharp electronic frequencies falling between λ 4152 and λ 5034 can be seen clearly in the record. A unique feature of this diamond is the occurrence of a sharp electronic line at λ 4403, next to the sharp edge of the band system. In Fig. 1 (*d*) which is the spectra of a lemon yellow luminescent diamond (D 2), numerous sharp electronic lines appear, but they are not so clear in the print.

The width of the lines is found to be variable and it can be said that it usually follows the general intensity of luminescence. The more the intensity of fluorescence, the broader are the lines.

λ 5786 *Emission.*—One of the diamonds in our collection has a projecting tip which exhibits an orange luminescence. The spectrum of this recorded at 80° K. is reproduced in Fig. 1 (*h*). The wavelength of the line corresponds to λ 5786·27 and this is accompanied by a set of bands on the longer wavelength side. In the spectrum of this diamond may be found other sharp electronic lines. The main body exhibits a faint blue luminescence and therefore the λ 4152 line is also recorded in the spectra of this diamond.

A comparison of the spectra of several diamonds recorded at room temperature and at 80° K. reveals that in general the electronic lines in all cases get sharpened and the bands appear better resolved on cooling. Such an effect is highly pronounced for lines occurring at wavelengths greater than 4400 A.U. In spectra recorded at room temperature, the line character of the electronic frequencies is hardly visible. Except the 4152 emission which appears as a very broad line shifted slightly towards longer wavelength, the line character of the electronic frequencies is hardly noticeable. The longer the wavelength at which the electronic lines occur, the more pronounced is the effect of temperature on the width of the line.

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In Table II are listed all the electronic frequencies observed. The more intense among these which are followed by a band system are italicised.

TABLE II

Diamond number and colour of luminescence		Electronic lines Wavelength in A.U.
D 4	Yellowish-white	*4152·59*, 4403·03, 4577·2, 4597·3, 4789·86, 4850·74, 4860·95, 4876·82, 4889·84, 4967·0, 5018·1, 5027·1, *5034·02*, *5106·38*
D 60	Bluish-green	*4152·59*, 4906·86, *4958·55*, 4981·03, *5031·16*, 5042·5, 5374·50, 5749·29, 5806·53
D 2	Lemon yellow	4152·49, 4402·08, 4615·98, 4494·29, 4635·54, 4737·61, 4790·21, 4889·25, *5034·81*, 5106·24
D 3	Golden yellow	4152·57, *5034·55*, 5106·69, 5179·87, 5232·23, 5245·57, 5786·27
D 1	Orange	5034·22, 5107·48, 5704·54, 5733·38, 5762·80, *5786·27*, 5822·65

The frequency shifts measured in wave-numbers of the bands are given separately in Table III.

TABLE III

Mode No.	Degeneracy	Frequency shift (evaluated)	Frequency shift observed in the luminescence spectrum
I	3	1332	1331·91
II	8	1250	1246·23
III	6	1239	..
IV	4	1149	1155·69
V and VI	3+3	1088	1090·8 1064·6
VII	4	1008	1007·09
VIII	6	740	750·0
IX	8	621	..

With D 4, the bands have resolved very well and the microphotometer record reproduced shows the peaks much more prominently and convincingly than those published earlier. The frequency shifts in wave-numbers are noted in the figure. The frequency shifts represent the vibration frequencies of the diamond lattice and much has been written about them in the earlier publications.

A detailed theoretical analysis of the vibration spectrum of the diamond lattice, based on Raman's theory of crystal dynamics, leads to the evaluation of frequencies of the diamond structure[6] and accordingly eight frequencies should be observable. Of these the principal mode of vibration with the frequency shift 1332 cm.$^{-1}$ appears in the first order Raman spectrum. The rest of the frequencies do not appear in the first order Raman spectrum, but appear as octaves and combinations in the second order Raman spectrum of diamond. However, in the luminescence spectrum, the electronic frequency combines with these frequencies and gives rise to the vibration spectrum.

The positions of the peaks correspond to the frequency shifts worked out and in Table III are given the evaluated frequencies and those obtained from a measurement of the shifts of the vibration frequencies observable in the luminescence spectrum. The latter represent oscillations of the diamond lattice with discrete frequencies, lending full support to the correctness of crystal dynamics developed by Prof. Raman. In Figs. 2, 3 and 4, the lattice spectrum can be clearly seen and the respective frequency shifts are inserted in the figures.

The author wishes to express his sincere thanks to Professor Sir C. V. Raman, F.R.S., N.L., for the continued interest he showed and the constant encouragement he gave during the course of this investigation.

SUMMARY

The communication reports the results of study of the luminescence spectra of diamonds recorded at liquid-air temperature (80° K.). Apart from the two well-known electronic frequencies at λ 4152 and λ 5034 and the associated band systems, the present study has revealed the existence of three new electronic emissions centred at λ 4958, λ 5106 and λ 5786 which come out with great intensity along with the vibrational bands excited by them. Numerous sharp electronic lines also appear in the spectrum of some of the diamonds.

Greatly improved records of the vibration spectrum associated with the λ 4152 emission have been obtained and the vibration frequencies deduced from them agree closely with the frequencies evaluated on the basis of Raman's theory of lattice dynamics. The investigation reveals that the λ 4152 emission, λ 4958, λ 5034 and λ 5786 emissions can exist independently and the colour of luminescence is dependent on which of these emissions is the principal feature of a particular diamond. In diamonds exhibiting a white luminescence λ 4152 and λ 5034 emissions appear in equal strength. The effect of temperature on the sharpening of the electronic frequencies is found to be more for emissions occurring at greater wavelengths.

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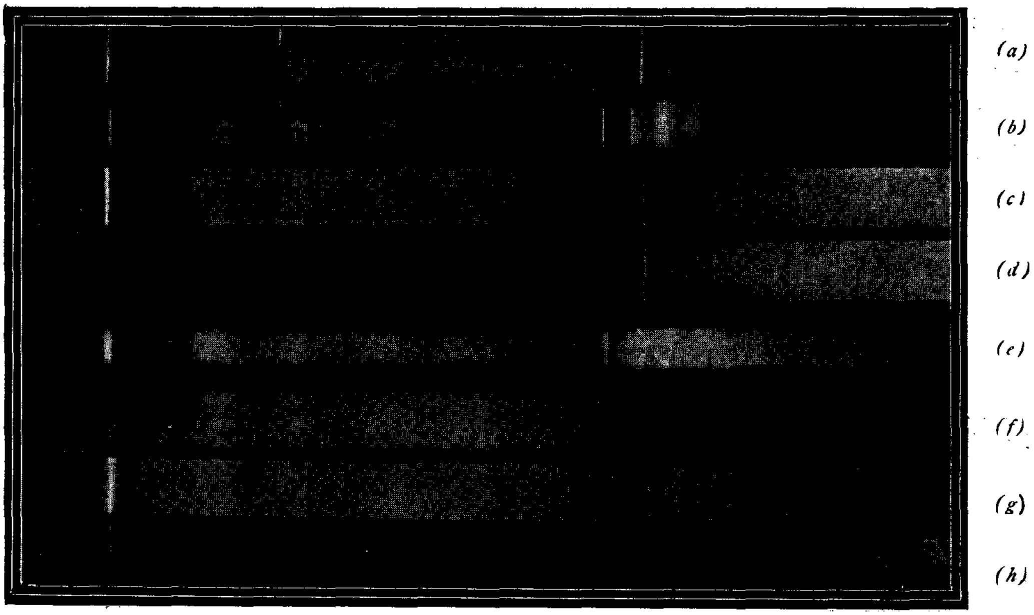

FIG. 1. Luminescence Spectra of Diamonds Recorded at 80° K.

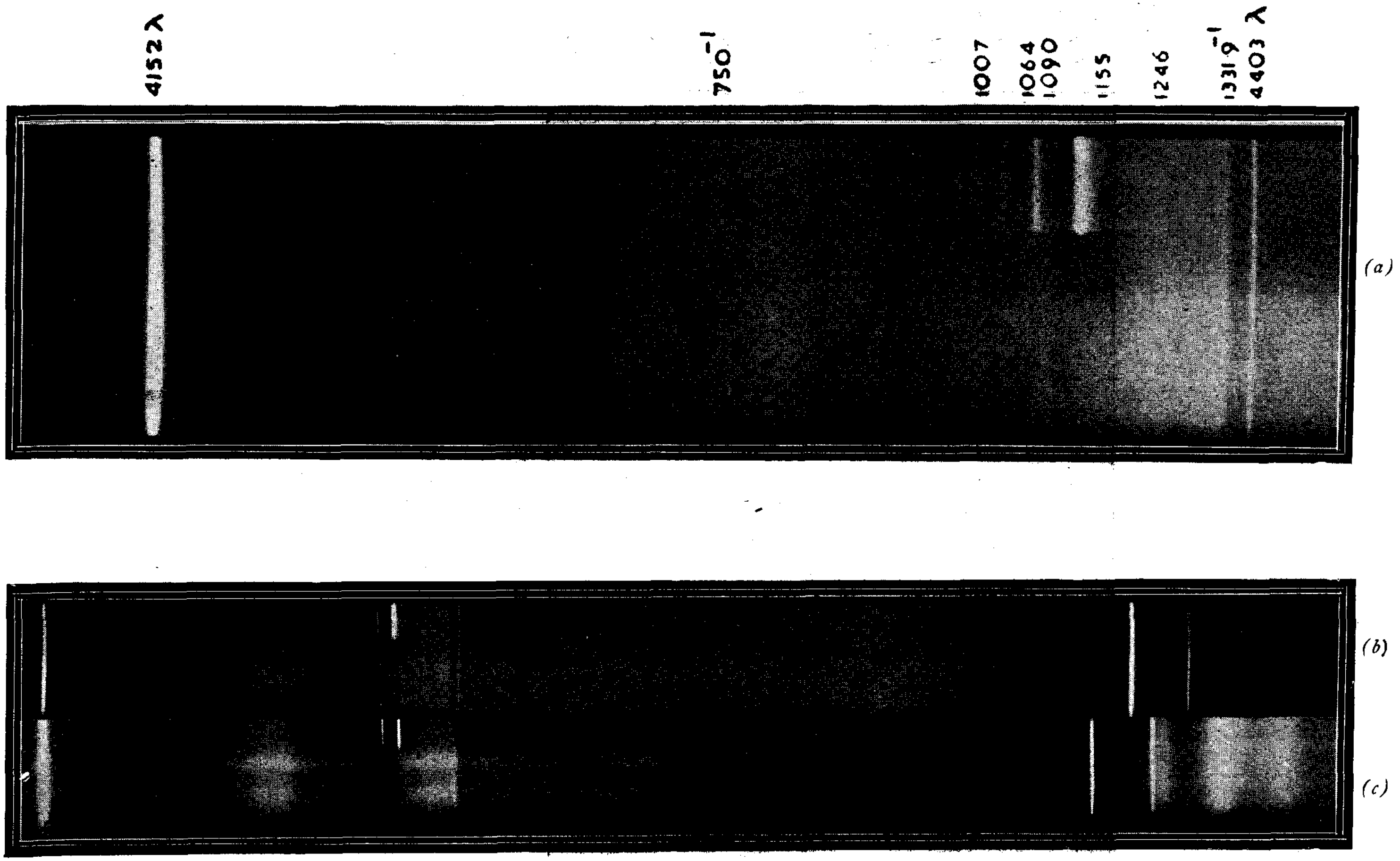

FIG. 2. (*a*) Enlargement of a portion of Fig. 1 (*a*); (*b*) Enlargement of Fig. 1 (*a*); (*c*) Enlargement of Fig. 1 (*b*).

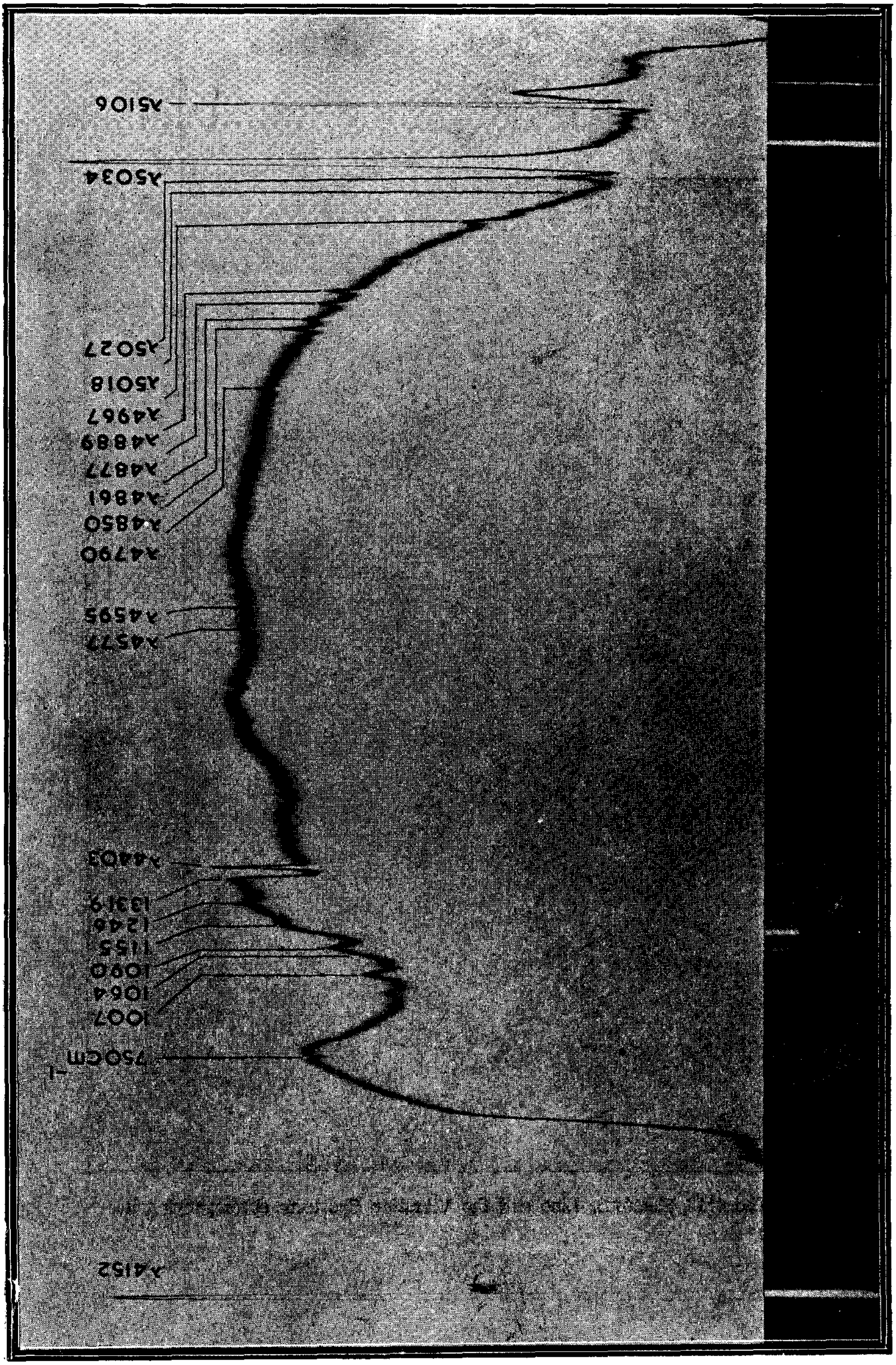

FIG. 3. The Luminescence Spectrum of Diamond and its Microphotometer Record.

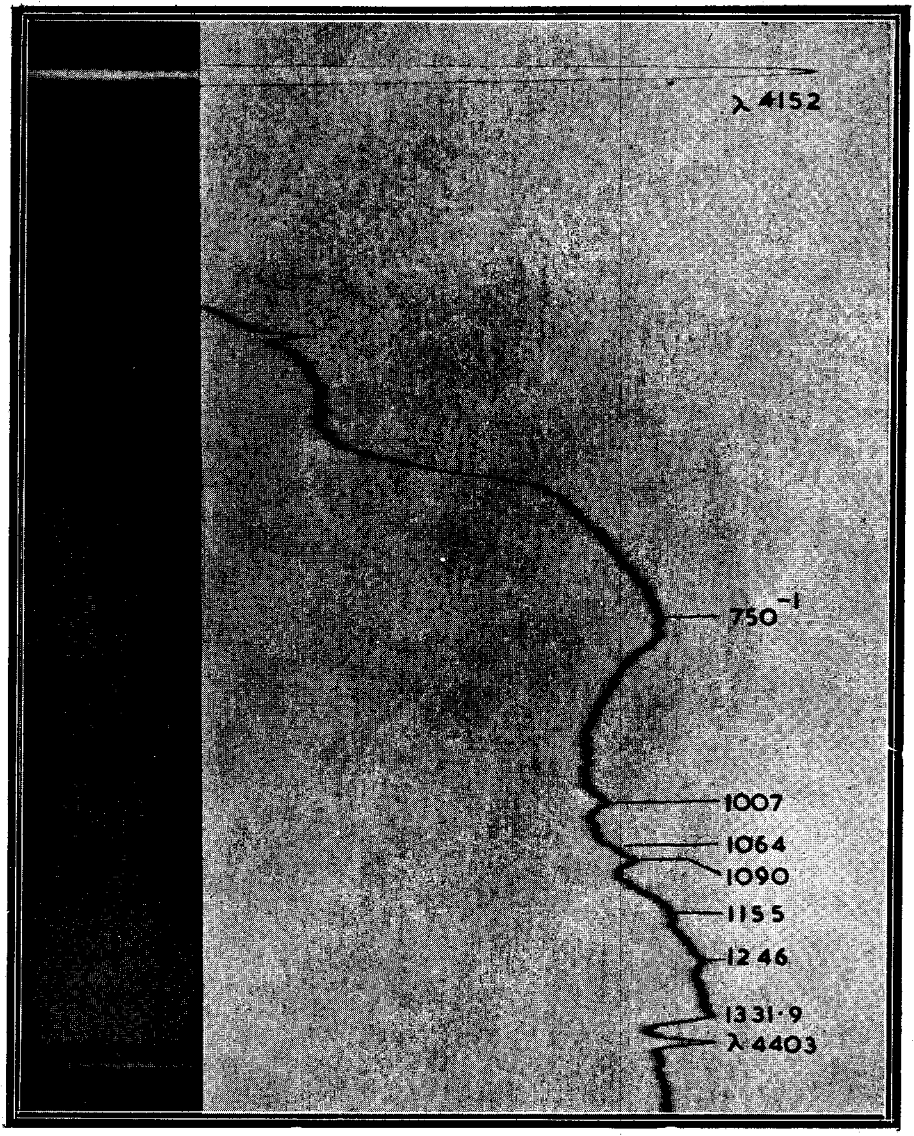

FIG. 4. The 4152 Electronic Line and the Vibration Spectrum accompanying it.

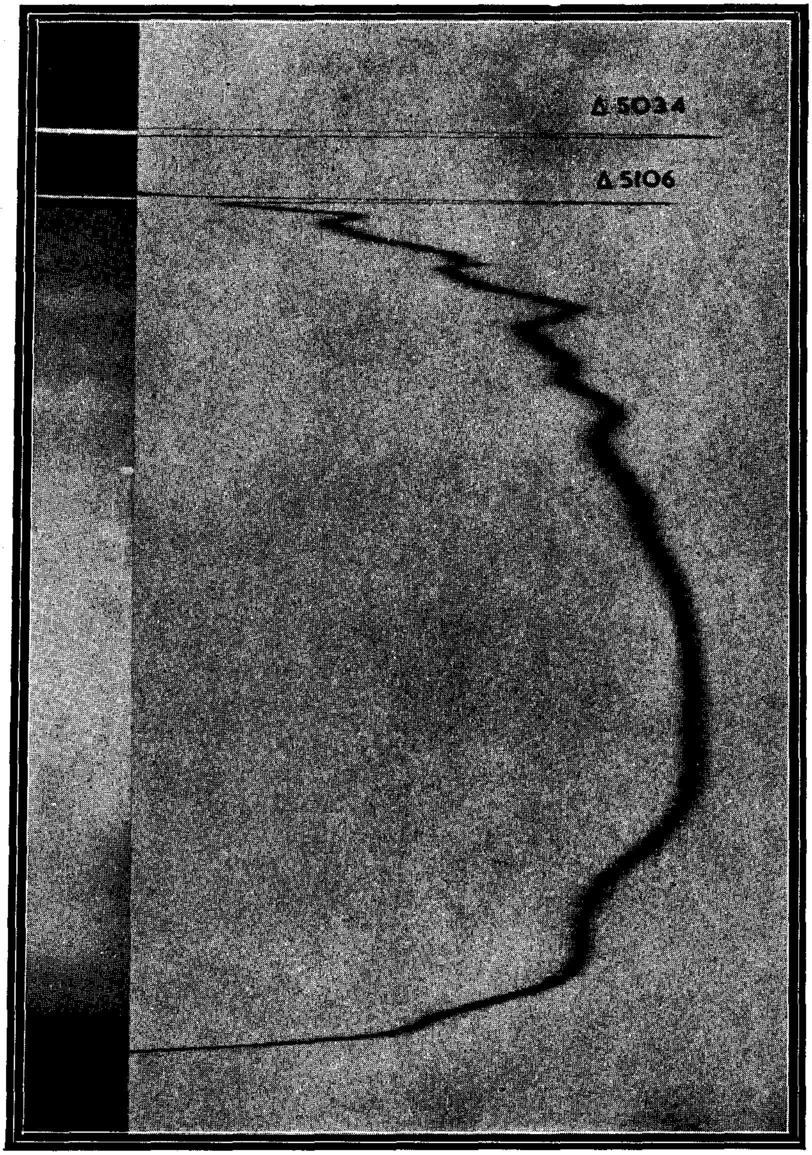

FIG. 5. The 5034 and 5106 Electronic Lines and the Vibration Spectrum accompanying them.