

LUMINESCENCE AS "FORBIDDEN" ELECTRONIC TRANSITIONS IN DIAMOND

BY G. N. RAMACHANDRAN AND V. CHANDRASEKHARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. INTRODUCTION

THE fluorescence spectrum of all diamonds at the room temperature exhibits an electronic line at 4156 \AA , which also occurs in absorption, accompanied by vibrational bands on the longer wavelength side of it (Nayar, 1941). When the diamond is cooled to liquid air temperatures, the electronic line becomes sharp and is resolved into a doublet with a mean wavelength of 4152 \AA . The separation of the doublet is variable, depending on the specimen, but is not less than 2 \AA or about 12 cm.^{-1} . A number of other electronic lines are also observed, of which one at 5032 \AA is also accompanied by subsidiary bands (Mani, 1944). This, however, is very weak in blue-luminescing diamonds. In this paper, we shall discuss the nature and origin of the doublet at 4152 \AA , which is present in the spectrum of all fluorescing diamonds.

The first question that arises in this connection is "What is the agent which gives rise to luminescence in diamond?" In the past, it has been generally supposed that some chemical impurity present in the diamond is responsible for the fluorescence. As has been, however, shown by Sir C. V. Raman (1944), there are good reasons for believing that this is not the case. Blue fluorescence is a very general and characteristic property of diamond irrespective of its source of origin and especially of the diamonds which are chemically the purest and physically the most perfect. Blue-fluorescing diamonds exhibit little or no birefringence, while the comparatively less common non-luminescent ones show a characteristic laminated structure accompanied by a strain pattern in the polariscope. The X-ray studies made by one of the authors (Ramachandran, 1944, 1946) indicate, in agreement with this, that the non-luminescent diamonds possess a high degree of mosaicity of structure, while the blue-fluorescent ones make a near approach to the ideal of crystal perfection. These considerations, as well as the close relationships observed between luminescence and other physical properties of diamond, make it highly improbable that it is due to extraneous impurities.

On the other hand, one is led to suppose that the electronic transition is really one occurring between levels belonging to the diamond structure itself. There are, however, considerations to show that the transition is ordinarily forbidden, but that it has become allowed under the conditions existing in the fluorescing diamonds. A study of the refractive index and dispersion of both ultraviolet opaque (fluorescing) and ultraviolet transparent (non-fluorescing) diamonds shows that these do not sensibly differ in the two cases (Martens, 1901; Peter, 1923) and that the variation of the refractive index with wavelength can be represented by a formula using two characteristic frequencies lying in the extreme ultraviolet, *viz.*, at 1750 and 1060 Å respectively (Peter, *loc. cit.*). The contribution of the electronic transition at 4152 Å to the dispersion of diamond is negligible, except probably in the close neighbourhood of this wavelength, where no measurements have been made. This means that the probability of the transition is small, which is equivalent to saying that it is ordinarily forbidden.

There are several cases known in which such forbidden transitions occur in crystals giving rise to both fluorescence and absorption. In ruby, for example, the principal lines in fluorescence and absorption have been attributed to transitions between different levels in the normal configuration $3d^3$ of Cr^{+++} (Deutschbein, 1932). As is to be expected, the wave-numbers do not coincide exactly with those deduced from the energy levels of Cr IV, but are quite close to them. Similarly, a large number of lines have been found in absorption in $\text{KCr}(\text{SO}_4)_2$ of which the sharpest and the most intense can be attributed to some of the forbidden transitions in Cr^{+++} (Spedding and Nutting, 1934). However, a study of the absorption spectra of a large number of chrome alums shows that the wave-numbers of the intense lines in the red vary appreciably with the compound concerned over a range of nearly 300 cm.^{-1} (Kraus and Nutting, 1941). Similar results have also been found with the salts of the rare earth elements. Ellis (1936) has given reasons to believe that the absorption lines observed in these are due to forbidden transitions taking place between low-lying levels belonging to the normal configuration of the atoms. Calculations of the term values of such levels for Tm^{+++} made by Bethe and Spedding (1937) show remarkable agreement with experimental values. These observations suggest that we might reasonably look for a similar transition to explain the fluorescence in the case of diamond also.

2. ELECTRONIC ENERGY LEVELS IN DIAMOND

In order to obtain an idea of the energy levels in diamond, it is useful to consider the case of the carbon atom and see if there are any levels in it,

transitions between which are ordinarily forbidden. The authors, however, do not wish to suggest that it is the carbon atom which gives rise to fluorescence in diamond. The energy levels in the carbon atom are only brought in as an analogy in order to obtain an idea of where to look for other forbidden transitions, if any.

The normal configuration $2s^2 2p^2$ of the carbon atom consists of 3 levels, viz., a group of three levels (3P_0 , 3P_1 , 3P_2) forming the ground state and two excited levels 1D_2 and 1S_0 . The term values of these levels with respect to the ground state of C II can be obtained from standard tables (Bacher and Goudsmit, 1932). In Fig. 1 (a) an energy level diagram is given with the term value of the 3P_0 state taken to be zero. The scheme of energy levels is identical with that in a number of other cases where forbidden transitions have been observed, e.g., that of N II, O III and Pb I and that of O I, except for the inversion of the triplet levels of the ground state 3P . On the analogy of these cases (Bowen, 1936; Mrozowski, 1944), the transitions which might be expected to occur in C I are shown in Fig. 1 (a). The lines $^3P_1-^1S_0$ and $^3P_2-^1S_0$ have been observed in Pb I by Mrozowski (*loc. cit.*). As will be seen from the diagram, these lines in the case of C I have wave-numbers 21632

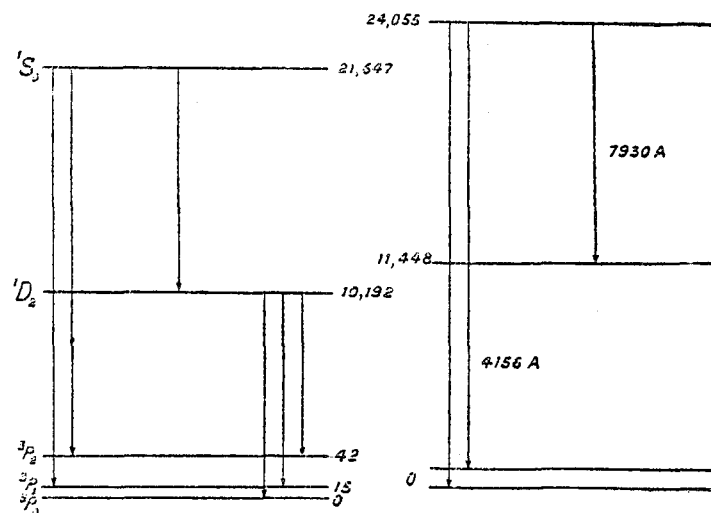


FIG. 1a. Energy levels in carbon atom

FIG. 1b. Energy levels in diamond

and 21605 respectively, thus forming a doublet with a separation of 27 wave-numbers. As already remarked, the 4152 Å line is also a doublet. One may therefore take the above transitions in carbon to correspond to the 4152 Å line (24077 cm.^{-1}) in diamond. It will be noticed that the wave-number of the diamond doublet is 1.114 times that in C I.

Following the analogy, one may expect an intermediate level in diamond corresponding to the 1D_2 level in C I. A rough idea of the term value of this level can be obtained if we assume that this also is shifted in the same ratio as the one corresponding to the 1S level in the carbon atom. The value comes out to be 11340 cm.^{-1} . Now, transitions from the 1D to the 3P level have been observed in auroral and nebular spectra in the case of N II, O III and O I and in the laboratory in O I and Pb I. Similarly, the transition 1D - 1S has been found to occur in all the cases, except Pb I where it lies in the infra-red. On the basis of these analogies, one may expect emission lines in diamond at about 7849 \AA and 8816 \AA . An attempt was therefore made to discover whether any such lines actually occur.

3. SEARCH FOR THE EMISSION LINES IN THE INFRA-RED

An intensely blue-luminescent diamond (N.C. 67) was used for the purpose and was excited by ultraviolet radiation between 3600 and 4050 \AA by using light from a carbon arc filtered through Wood's glass. The red and the infra-red rays transmitted by this glass were cut out by means of a filter of copper sulphate solution. In practice, a round-bottomed flask containing a 10% solution of copper sulphate was used to focus the carbon arc on the diamond. The fluorescence spectrum of the diamond was photographed with a Zeiss 3-prism spectroscope having an aperture of $f/2.3$. With this instrument, the 4152 spectrum could be obtained in 5 seconds, while it required nearly 3 hours to record the infra-red. The spectra were photographed on Kodak extra-rapid infra-red plates which were sensitive upto 8500 \AA . (See Plate XXI.)

Actually, it was found that there was a sharp emission line in the fluorescence at 7930 \AA . This is clearly shown in Fig. 2 (a) at the position indicated by the arrow. The line has also been obtained with another brilliantly blue-fluorescent diamond N.C. 68, whose spectrum is shown in Fig. 2 (b). It may be noticed that the line at 7930 \AA is actually sharper than the one at 4152 \AA indicated by the arrow in Fig. 2 (d). This is probably due to the very small dispersion of the spectrograph in the infra-red region. The wavelength of the observed line agrees fairly closely with the expected value of 7849 \AA . The other expected line was not recorded, being beyond the limit of sensitiveness of the photographic plate that was available.

It is of interest to examine whether the line at 7930 \AA arises from a transition from an upper level to an intermediate level, or whether it is an ordinary transition to the ground level, many examples of which are known. For example Mani (1944) has recorded a number of such electronic lines, occurring both in emission and absorption by diamond, of which those at

5032, 4959, 5359 come out strongly. Two tests can be done to decide the issue. If the transition were one ending in an intermediate level, then it should not occur in absorption and also it should not be emitted unless the exciting light has a wavelength smaller than 4152 Å. The first test, of course, is not very sensitive since it depends on a negative result and may be affected by the fact that a sufficiently long column has not been used for absorption. However, the experiment was tried and it was found that although the absorption line at 4152 Å came out quite clearly, no trace of any absorption could be found in the neighbourhood of 7930 Å.

The second condition for the emission of the infra-red line was also verified. Using the light from a carbon arc filtered through a green filter (which transmitted strongly from 4800 Å to 6000 Å and weakly upto 7000 Å) as the exciting radiation, an exposure of 3 hours only brought out the continuous spectrum in the infra-red weakly. An exposure of 8 hours was required to record the continuous spectrum with about the same intensity as with ultraviolet excitation, but yet the line at 7930 Å was not recorded [see Fig. 2 (c)].

These observations strongly support the idea that the transition is one occurring from the higher excited level to an intermediate level. In Fig. 1 (b) are shown the energy levels in diamond as calculated from the results reported in this paper.

Our grateful thanks are due to Prof. Sir C. V. Raman for the kind interest that he took in this investigation.

SUMMARY

Arguments are adduced to show that the doublet centred at 4152 Å occurring in the spectrum of all fluorescing diamonds arises from 'forbidden' transitions analogous to the forbidden $^3P-^1S$ transitions in the spectrum of CI. On the basis of this analogy, fluorescence lines are also expected to occur at about 8816 Å and 7849 Å, analogous to the $^3P-^1D$ and $^1D-^1S$ transitions in CI. Of these, the former should also occur in absorption, while the latter should not occur in absorption and should be emitted only if the exciting radiation has a wavelength shorter than 4152 Å. A line has actually been found at 7930 Å, satisfying the latter conditions. The former line could not be recorded being outside the limit of sensitivity of the photographic plate.

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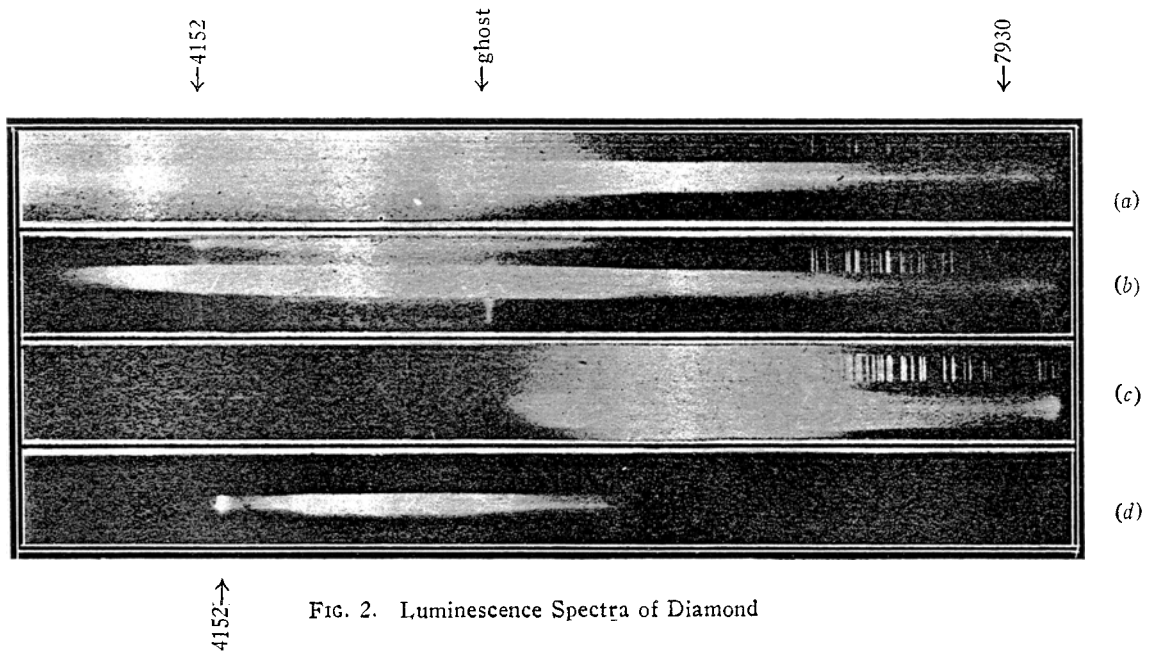


FIG. 2. Luminescence Spectra of Diamond