

The luminescence of diamond—I

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1. Introduction

No less than seventy-five distinct papers which concerned themselves with the structure and properties of diamond were communicated by the present writer and his collaborators and published in the *Proceedings* of the Indian Academy of Sciences between the years 1934 and 1948. Review articles surveying the work of the latter part of this period appeared from time to time in the pages of *Current Science*. Investigations on the diamond have once again been taken up and fresh results have been reported in the *Proceedings* of the Academy for August 1950.* It appears appropriate in these circumstances to give an account of this recent work in the light of the earlier investigations. In doing so, we shall not trouble to quote literature references, since the interested reader will find a complete bibliography classified under various headings on pages 269 to 287 of the *Proceedings* of the Academy for December 1948.

When the phenomenon of the luminescence of diamond first came under the notice of the present writer in the year 1930, it was not regarded as a subject offering scope for research. Actually, it presented itself as an impediment to the researches then in progress which had for their object the spectroscopic study of the scattering of light in diamond with a view to discover the nature of the *complete vibration spectrum* of that substance. The realisation of this aim had indeed to wait for many years until some non-luminescent diamonds came into the possession of the writer. That the luminescence was itself a phenomenon worthy of study did not suggest itself till the year 1940 when Mr P G N Nayar took up the problem at the instigation of the writer. It soon became apparent that a most fertile field of research awaited exploration.

The photographs reproduced in figure 1 exhibit one of the remarkable features of the luminescence of diamond, namely, the enormous variations in its intensity.

The first of the six pictures in the figure shows a group of 88 South African diamonds set within a circlet of pearls as seen by daylight. The remaining five pictures show the same diamonds made visible by their emission when irradiated

**Memoirs of the Raman Research Institute*, No. 9. "The luminescence of diamond and its relation to crystal structure," by Sir C V Raman and A Jayaraman.

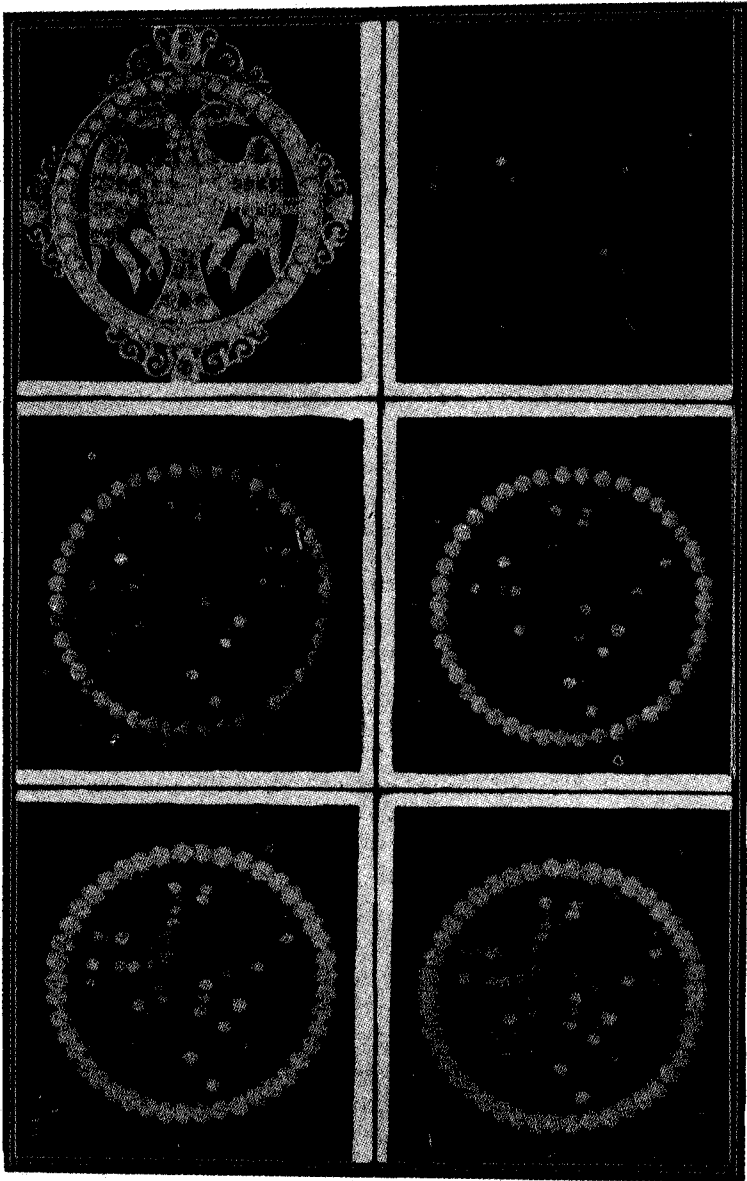


Figure 1. Luminescence of South African diamonds.

by sunlight filtered through a plate of nickel-oxide glass. The five pictures were recorded respectively with exposures of 5 seconds, 15 seconds, 30 seconds, 120 seconds and 1,800 seconds. Only in the last and most heavily exposed picture is it possible to recognise the original pattern seen by daylight.

Equally noteworthy are the variations in the colour of the luminescence of diamond. While the majority of clear white diamonds show a blue luminescence, others exhibit a greenish-blue, green or greenish-yellow luminescence under ultra-violet irradiation, while a small minority are definitely non-luminescent. In June 1942, the writer had the opportunity of examining a great many diamonds of Indian origin at Panna, and was much impressed by the fact that all the 52 diamonds of the highest quality and of great size in the necklace owned by the Maharaja of Panna were blue-luminescent, though the intensity of such luminescence varied largely. During a visit by the present writer to London in May 1948, the opportunity arose of examining the luminescence of a very large number of diamonds of high grade from the Congo area in their natural form as crystals. The stones had been sorted and arranged in cages in the order of their excellence as judged by their water and freedom from colour. Each cage contained some fifty to sixty crystals. All the diamonds without exception from the first six cages showed a luminescence of blue colour. Examples of green or yellow luminescence were very few even in the cages containing the lower grades, a blue or bluish-green luminescence being by far the commonest effect observed. The similarity between these results and those observed with the Panna diamonds in June 1942 was so striking that one could scarcely doubt that the blue luminescence was a characteristic property of diamond of the first quality.

2. Luminescence and absorption spectra

Examination of the spectrum of the light emitted by luminescent diamonds reveals the cause of the variations in its colour. In figure 2 are reproduced a set of seven pictures recorded in some recent studies by Mr A Jayaraman. The first of these pictures is that of a typical blue-luminescent diamond, while the third spectrum is that of a diamond exhibiting an intense green luminescence. These types of emission were those very thoroughly studied by Mr P G N Nayar and Miss Anna Mani respectively. It is evident that the second and fourth spectra in the figure are superpositions in different intensity ratios of the blue and green types of luminescence. The last three spectra in the figure represent other types of luminescence which are less common but are also of great interest. It would seem that they arise from a progressive extinction of the shorter wavelengths in the second or green type of spectrum with a consequent approach of the colour of the luminescence to a pure yellow or orange.

The spectra reproduced in figure 2 were recorded with the diamonds held at room temperatures. Lowering the temperature of the crystal to that of liquid air

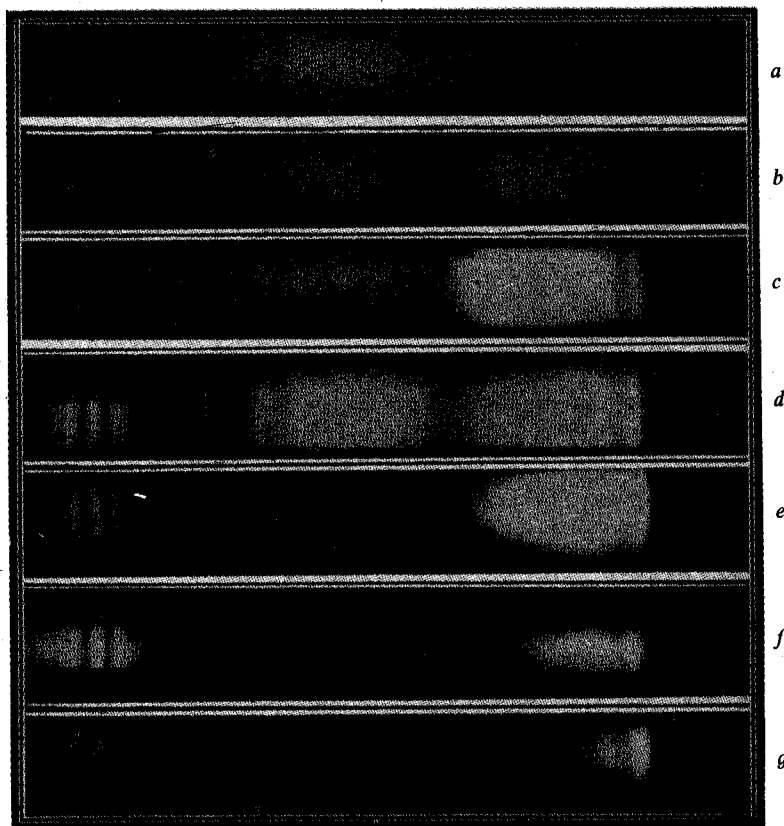


Figure 2. Luminescence spectra of diamonds.

(a) Blue, (b) Bluish-green, (c) Green, (d) Bluish-white, (e) Greenish-yellow, (f) Yellow, (g) Orange.

results in the sharpening of the bands, whereby the true character of the spectra stands clearly revealed. Lowering of the temperature has an analogous effect on the corresponding absorption spectra exhibited by the same diamond. Inter-comparison of the emission and absorption by the same diamond at low temperatures reveals the remarkable connections between the two. These features are apparent from figures 3, 4 and 5 reproduced from the papers of Mr P G N Nayar and Anna Mani. In figure 3, the upper of the two spectrograms represents the emission spectrum and the lower the absorption spectrum. The former exhibits the bright lines at λ 4152 and λ 5032 characteristic of the blue and green types of luminescence respectively. The lower spectrum, on the other hand, exhibits dark lines in absorption at the same wavelengths. It will be seen from the same figure that the emission at λ 4152 and λ 5032 are accompanied by subsidiary bands towards the longer wavelengths. In absorption, on the other hand, the subsidiary bands appear towards shorter wavelengths. The subsidiary bands in

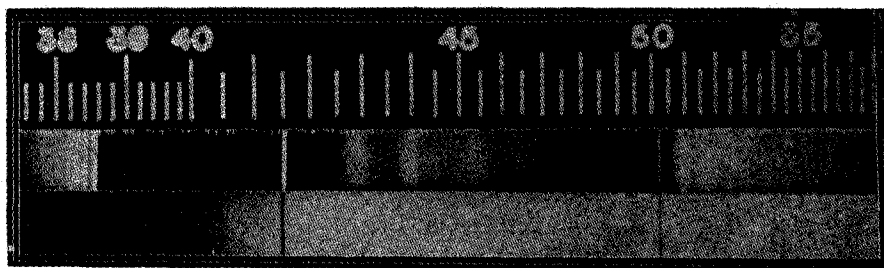


Figure 3. The fluorescence and absorption spectra of diamond.

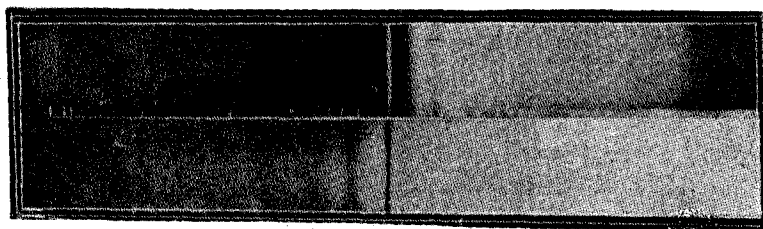


Figure 4. The 5032 system in emission and absorption at liquid air temperature showing mirror image symmetry.

emission and absorption exhibit mirror image symmetry about $\lambda 4152$ and $\lambda 5032$ as the case may be, their frequency shifts with respect to these being equal and opposite. This is clearly seen from figure 4 in the case of $\lambda 5032$ and from figure 5 in the case of $\lambda 4152$. In the latter figure, the absorption spectrum has been reversed so as to exhibit the mirror image symmetry about $\lambda 4152$ line by the coincidence of the dark bands in absorption with the bright bands in emission.

The relationship between the emission and absorption spectra of diamond is also illustrated in a striking manner by studying the effect on the intensity of the luminescence of exciting the same with monochromatic light the wavelength of which can be altered. Anna Mani carried out a series of experiments of this kind and found that the intensity of the blue luminescence passes through a series of maxima and minima when the exciting radiation is on the short wavelength side of $\lambda 4152$ and is gradually shifted towards that wavelength. It reaches a large maximum when the exciting band coincides with $\lambda 4152$ and then drops suddenly to a small value when shifted to greater wavelengths. Similar effects in respect of the green luminescence are noticed when the exciting radiation lies on one side or the other of the principal absorption at $\lambda 5032$ which goes hand in hand with that luminescence. The facts recited show that the absorption and emission centred at $\lambda 4152$ and $\lambda 5032$ respectively represent electronic transitions, while the subsidiary bands represent the vibrational transitions of the crystal lattice which are coupled with these electronic transitions.

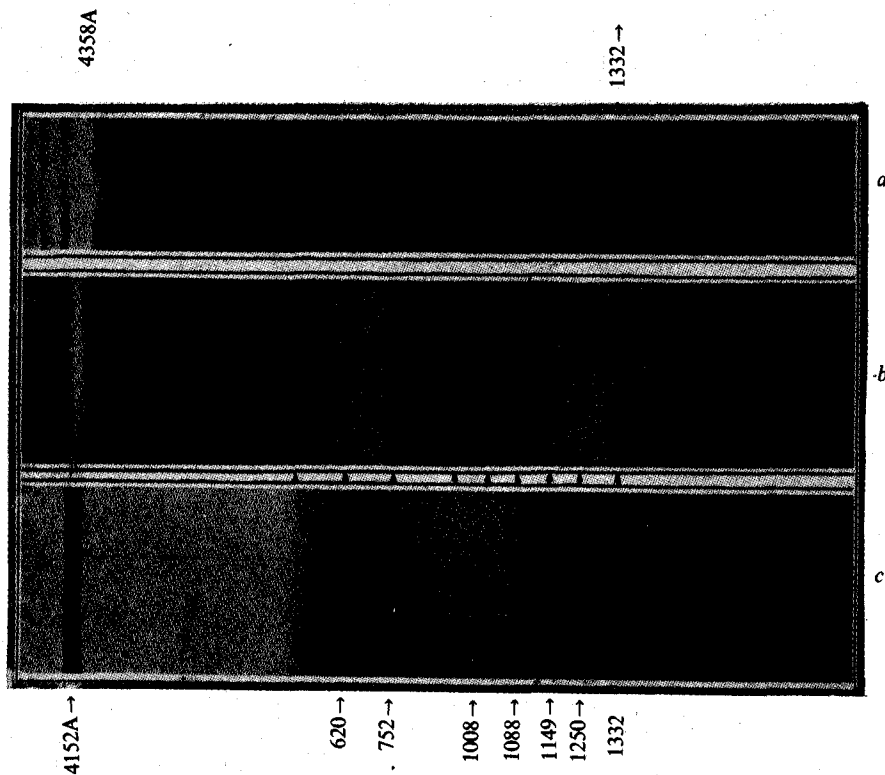


Figure 5. (a) Raman spectrum of diamond. (b) emission spectrum and (c) absorption spectrum (reversed).

3. The lattice spectrum of diamond

The foregoing interpretation of the observed facts finds confirmation in the agreement of the frequency differences (positive and negative respectively) derived from the luminescence and absorption spectra with the lattice frequencies in diamond as determined from studies on the scattering of light and on the infrared absorption in the substance. The electronic absorption and emission lines are diffuse at room temperatures and exhibit a readily observable width and structure when it is cooled down to liquid air temperature. This introduces some uncertainties in the lattice frequencies as deduced from the studies on luminescence or the corresponding absorption. Such uncertainties are even greater in the case of the green luminescence, the λ 5032 line being diffuse even at liquid air temperature. Nevertheless, the results are sufficiently definite to give us an indication of the nature of the vibration spectrum of the diamond lattice.

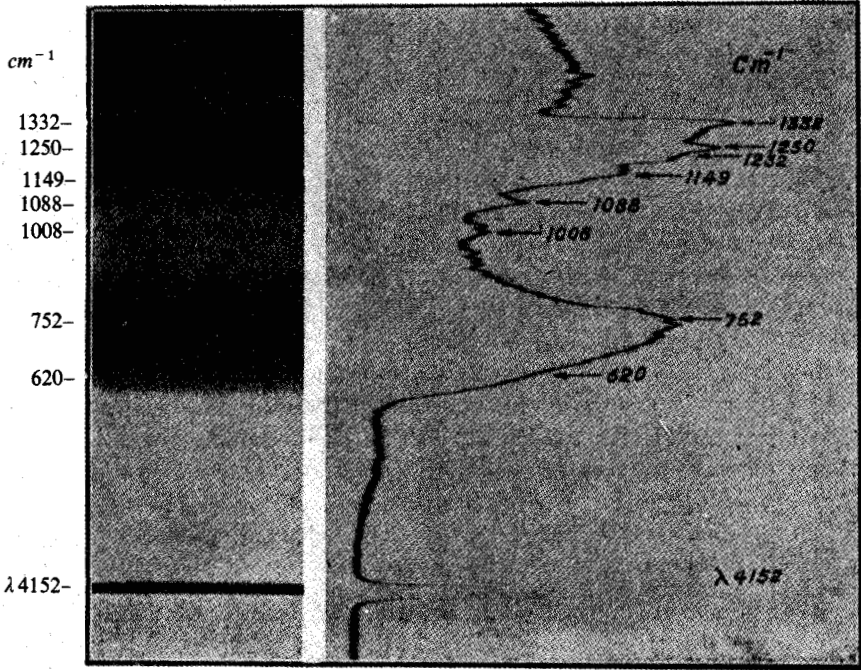


Figure 6. The emission spectrum of blue-luminescent diamond.

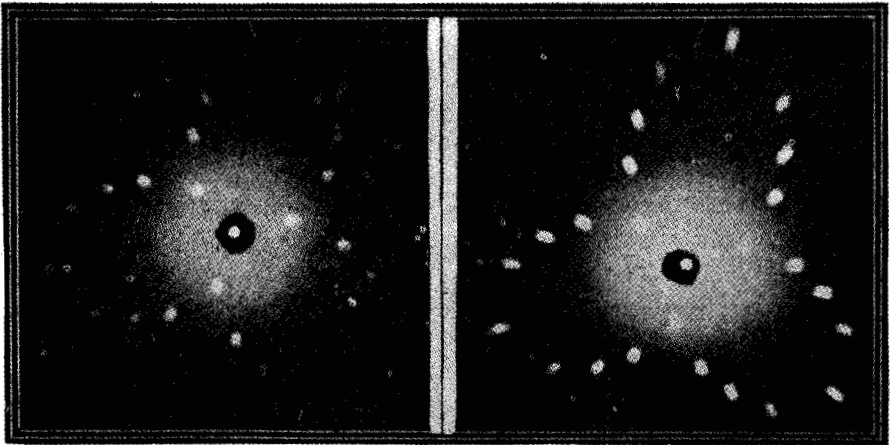


Figure 7. Laue photographs of two blue-fluorescent diamonds.

Particularly remarkable is the appearance in the emission spectrum of blue luminescence, of a series of well-defined bands. These are shown in figure 6 taken from a paper by K G Ramanathan. Their positions are marked in the figure and their sharpness is evident from the accompanying microphotometer record. As already remarked, the finite width of the λ 4152 line sets a limit to the sharpness with which the vibrational transitions are recorded. The sharpness is even less satisfactory in the case of the λ 5032 line and the accompanying vibrational transitions. Hence, the evidence from the luminescence spectra regarding the discrete character of the lattice vibration spectrum of diamond must be regarded as indicative rather than as demonstrative. The real proof of the discrete line-character of the lattice vibration spectrum of diamond comes from the studies on light-scattering, where the sharpness of the recorded lines is determined by the monochromatism of the incident light which is very high.

The spectroscopic facts set forth above make it clear that in spite of the enormous variations in the intensity and colour of the luminescence of diamond, we are dealing with a well-defined phenomenon namely, certain electronic transitions and associated vibrational transitions, the positions of which do not vary either with the particular specimen or with the locality of its origin. What varies is the intensity of these transitions. Thus, we are naturally led to infer that the luminescence is a phenomenon characteristic of the diamond itself, and that the variations observed arise from corresponding variations in the fine structure of the crystal. This conclusion is powerfully reinforced by X-ray studies especially those made and reported in various papers by Dr G N Ramachandran. It is found that there is a precise quantitative correlation between the strength of the blue luminescence exhibited by diamonds with the intensity of the X-ray reflections, both of the Laue and the Bragg types, given by their crystal planes. This is illustrated for the Laue reflections in figure 7. The two photographs reproduced were recorded with equal exposure, with two diamonds of equal thickness but differing in the intensities of their blue luminescence. It is seen that the Laue reflections of the two diamonds differ greatly in their intensity. Dr G N Ramachandran has also shown that the angular divergence of the Bragg reflection given by the diamond with monochromatic X-rays is least for faintly blue-luminescent diamonds and increases with the intensity of that type of luminescence. In other words, the former represent the nearest approach to an ideally perfect crystal structure.