

The luminescence of diamond—III

SIR C V RAMAN

1. The electronic emission spectra

As was remarked in the first article of the series, the emission band at $\lambda 4156$ discovered by C Ramaswamy in the year 1930 plays the leading role in the blue luminescence of diamond, while the band at $\lambda 5038$ studied later by Dr Nayar and by Miss Mani plays an analogous role in respect of the green luminescence. These bands sharpen when the diamond is held at liquid air temperature and shift to $\lambda 4152$ and $\lambda 5032$ respectively. The $\lambda 4152$ emission also then appears resolved into a doublet, the width and separation of the components varying considerably with the specimen under study. In particular, the doublet is narrow for the diamonds which exhibit the blue luminescence feebly, a circumstance which is favourable for a satisfactory resolution of the associated vibrational spectrum into its discrete components. Absorption bands are also observed at $\lambda 4152$ and $\lambda 5032$ in the spectrum of white light transmitted by the respective diamonds, the strength of such absorption varying *pari passu* with the intensity of the corresponding emission. Hence, one is justified in ascribing them to electronic transitions in the crystal lattice. Where there is an apparent lack of correspondence between the strength of the absorption and of the emission, there is evidence for the existence of self-reversal or other cause affecting the emission intensity.

The investigations of Dr Nayar and of Miss Mani have also shown that $\lambda 4152$ and $\lambda 5032$ are by no means the only electronic transitions recorded in the luminescence spectra, though these stand out by reason of their special intensity and their association with vibrational transitions in the lattice. Lines appearing strongly both in emission and absorption have been observed at $\lambda 4189$, 4197 , 4206 , 4907 , 4959 and 5359 . A fairly strong line at $\lambda 5758$ and numerous others which are less intense have also been recorded in the emission spectra of various diamonds but have not so far been detected in absorption. The electronic emission lines may be divided broadly into two groups, viz., those that appear along with the emission at $\lambda 4152$ and the rest with that at $\lambda 5032$. They are observed respectively with the diamonds exhibiting these two types of luminescence.

The electronic line at $\lambda 4156$ present in the blue luminescence spectrum sharpens and increases in peak intensity when the diamond is cooled down. *Per*

contra, it decreases in peak intensity when the diamond is heated up, until finally at 350° C it merges into a continuous background and ceases to be visible. Its integrated intensity has been investigated by Chandrasekharan and found to remain unaltered over a wide range of temperature. Miss Mani's investigations have shown that the other electronic lines likewise shift towards smaller wavelengths and sharpen when the diamond is cooled down to liquid air temperature. The shift in wave numbers in the various cases is found to be of the same order of magnitude and roughly proportional to the respective frequencies.

2. The electronic absorption spectra

The refractive indices of diamond fit very well into a dispersion formula containing two terms, the major term indicating an absorption at λ 1060, and the minor term with an absorption wavelength at λ 1750. The actually observed absorption in the ultra-violet, however, extends further towards greater wavelengths. Diamonds of the non-luminescent type show a complete cut-off for wavelengths less than λ 2250, while the best specimens of this class exhibit a complete transparency in the visible and near ultra-violet regions of the spectrum. Diamonds which exhibit luminescence, however, show a different behaviour. When the thickness of the plate is reduced sufficiently, the observed transmission extends down to λ 2250. There is, however, a strong absorption at greater wavelengths, and indeed with the largest thicknesses, a complete cut-off is

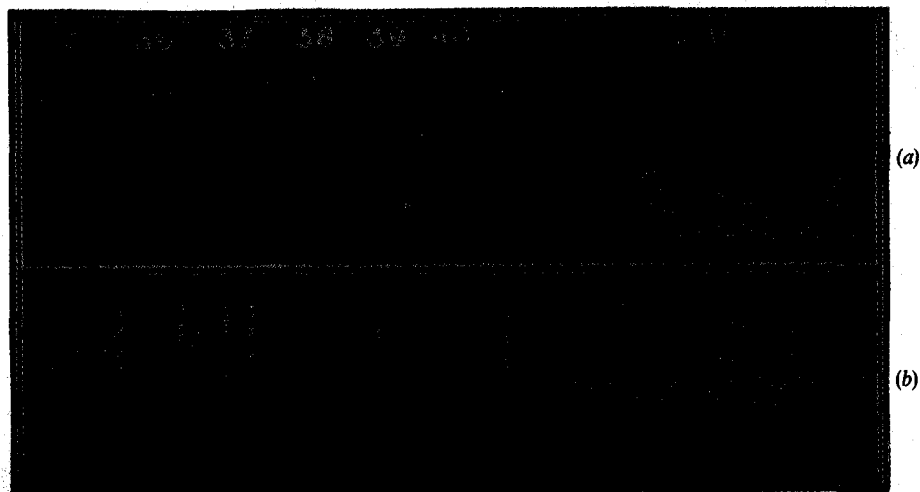


Figure 1. Absorption of visible light by thick diamond. (a) At room temperature, (b) At liquid air temperature.

observed extending to $\lambda 4152$, and feebler absorption bands are noticed at even greater wavelengths. These features are exhibited in figures 1 and 2 taken from a paper by K G Ramanathan.

In moderate thicknesses, however, blue-luminescent diamonds transmit wavelengths greater than $\lambda 3000$ quite freely with the exception of certain absorption lines noticed in the region between $\lambda 3500$ and $\lambda 3000$, and the vibrational bands associated with the $\lambda 4152$ electronic transition.

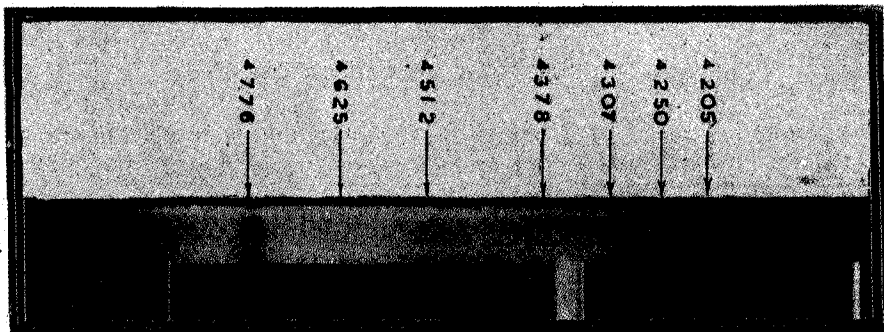


Figure 2. Absorption of visible light by thick diamond under high dispersion.

Some 25 such absorption lines of the first kind can be seen in figure 3 which is reproduced from a paper by Dr Nayar. To record them successfully, it is necessary to hold the diamond at liquid air temperature and to adjust the thickness of diamond traversed as well as the photographic exposure suitably.

Ordinarily, a diamond of the blue-luminescent class should be less than a millimeter thick to show any transmission for wavelengths less than $\lambda 3000$. Very thin diamonds of the same variety exhibit a series of sharply-defined absorption lines in the wavelength region between $\lambda 2370$ and $\lambda 2240$. These are shown in figure 4 reproduced from a paper by K G Ramanathan.

It is noteworthy that a precisely similar set of absorption lines is observed also in the ultra-violet transmission of green-luminescent diamond, but can then be seen with moderate thicknesses of the material.

It should be emphasised that the absorption spectra exhibited in figures 3 and 4 stand on a different footing from those mentioned in the preceding section and those shown in figures 1 and 2. They do not appear as emission lines, and their strength is not directly related to the intensity of luminescence. Indeed, the absorption lines seen in the vicinity of $\lambda 3000$ become weak and diffuse and the transparency extends further into the ultra-violet in the case of strongly blue-luminescent diamonds, as was first observed by Sunanda Bai.

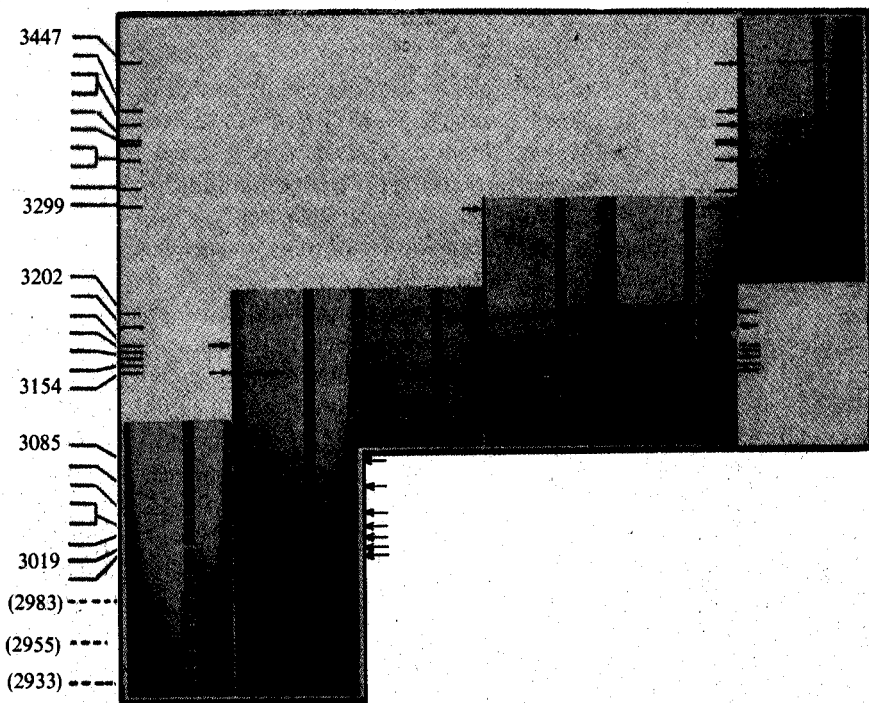


Figure 3. Absorption lines in the ultra-violet.

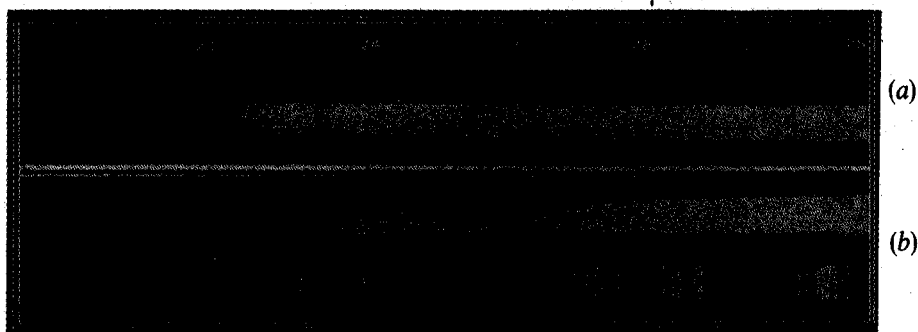


Figure 4. Ultra-violet absorption spectrum of thin blue-fluorescent diamond. (a) At room temperature and (b) liquid air temperature.

3. The infra-red activity of diamond

Polished cleavage plates are particularly suitable for quantitative studies on infra-red absorption. The results obtained by K G Ramanathan with a whole series of such plates are highly significant in relation to our present subject. No important differences are observed as between different diamonds in the infra-red activity in the spectral region between 1400 and 2800 cm^{-1} which covers the octaves and combinations of the fundamental vibration frequencies. There are, however, great differences in behaviour in the spectral region between 700 and 1400 cm^{-1} which covers the first-order vibration frequencies. The diamonds which are non-luminescent are completely transparent in the latter region. On the other hand, the non-birefringent and weakly blue-luminescent diamonds show a strong activity in the latter region, and the absorption-curves exhibit a series of peaks exhibiting a resolution of the vibration spectrum into distinct components (see figure 5). Green-luminescent diamonds show an intermediate behaviour, such as would result from passage successively through two plates of appropriate thickness belonging respectively to the active and non-active types (see figure 6). *Strongly* blue-luminescent diamonds are found to exhibit an infra-red activity which is distinctly less than in the case of diamonds with a weak luminescence. The character of the absorption-curve also shows minor variations accompanying the changes in the colour and intensity of the luminescence.

The diamonds which show the first-order infra-red activity most strongly are those which make the nearest approach to ideal perfection of crystal structure as shown by their freedom from birefringence and their X-ray behaviour. *Per contra*, the diamonds which do not show the first-order activity are those which exhibit the largest departure from ideality as indicated by such tests. In these circumstances, it is clearly not possible to ascribe the infra-red activity exhibited by the

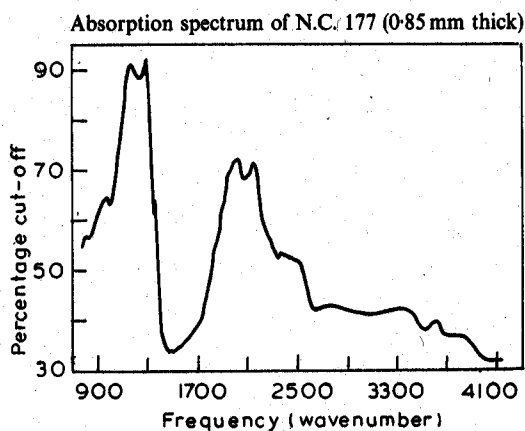


Figure 5. Infra-red absorption spectrum of blue-fluorescent diamond.

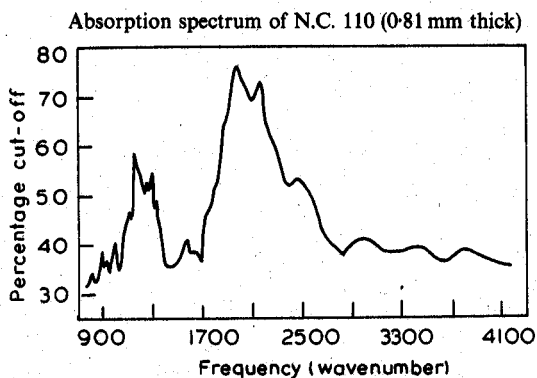


Figure 6. Infra-red absorption spectrum of green-fluorescent diamond.

former class of diamonds to structural imperfections or other accidental circumstances. We are, in fact, compelled to recognize that the difference in behaviour connotes a fundamental difference in crystal structure. The nature of such difference follows from well-established spectroscopic principles, according to which the absence or presence of first-order infra-red activity in a crystal of the cubic class depends on whether the structure of the crystal does or does not possess centres of symmetry. In other words, the observed behaviour in respect of infra-red activity indicates that the electronic structure of the non-luminescent diamond has the highest or O_h type of symmetry, while the electronic structure of the blue-luminescent diamonds possesses only the lower or T_d type of symmetry.

4. The origin of the luminescence

The experimental facts already described do not permit us to accept the belief formerly entertained that the luminescence of diamond arises from the presence of chemical impurities. They also serve to exclude the alternative hypothesis that the luminescence is activated by extraneous impurities. As early as 1941, Dr Nayar suggested that the origin of the blue luminescence studied by him should be sought for in the departure of the crystal structure from ideal perfection. While this suggestion contains an element of truth, the results of subsequent investigations with a wider range of material show that it is not by itself sufficient to cover the facts. It does not, for instance, explain why diamonds which, as judged by optical and X-ray tests, show structural imperfections of the crystal in the highest degree, are precisely those which are non-luminescent. Neither does it account for the green type of luminescence and for the relationship between luminescence and birefringence which has been so clearly established. We are thus forced to look a little deeper to reach a clear understanding of the array of facts revealed by the Bangalore investigations.