# ON THE FLUORESCENCE IN DIAMOND EXCITED BY X-RAYS *

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Plate XXI

**ABSTRACT.** The fluorescence of four specimens of diamond of Type I (common) and of one specimen of diamond of Type II (rare) has been excited by X-rays and the spectra have been photographed with a spectrograph of high light-gathering power and moderate dispersion. The spectra have been compared with those excited by ultraviolet light It has been observed that all the four specimens of Type I show continuous fluorescence extending from 5650 Å upto about 3700Å. In the case of two specimens showing strong absorption band at 4156Å, the fluorescence spectrum excited by X-rays shows an absorption band at this position accompanied by a few other similar bands on the shorter wave-length side. The diamond of Type II does not show any fluorescence in the visible region when irradiated by X-rays. These results are contradictory to those published by Ramachandran (1946) who claimed to have observed bands in the spectrum of fluorescence excited by X-rays in diamond of Type I, and weak fluorescence in diamond of Type II.

It is shown that these results can be explained only on the hypothesis that the fluorescence is due to presence of chemical impurities in the lattice of diamond of Type I and that diamond of Type II contains no such impurity.

## INTRODUCTION

It was shown in a paper published earlier (Bishui, 1950) that the fluorescence of diamond is due to presence of some impurity in the lattice, the latter acting as a phosphor in presence of the impurity, and that the absence of fluorescence in diamond of Type II, which is transparent to ultraviolet light beyond 3000 Å, is due to the absence of such impurity. The fluorescence spectrum of diamond excited by X-rays was compared previously by Ramachandran (1946) with the spectrum of fluorescence excited by ultraviolet light in the case of a particular specimen of diamond and it was observed that the 4156 Å band appeared as an absorption band in the spectrum excited by X-rays, although its companions on the longer wavelength side were present as emission bands. In the spectrum excited by ultraviolet light in the same specimen, the 4156 Å band was the strongest of all the bands in the visible region. It is difficult to understand, however, how the same specimen which does not absorb completely the band at 4156 Å excited by ultraviolet rays, can absorb completely the same band excited by X-rays. It was, therefore, thought worthwhile to study the fluorescence spectra of

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a few specimens of diamond of Type I and Type II excited by X-rays in order to understand the mechanism of excitation of the fluorescence in the crystal by these rays. The present paper deals with the results obtained with D I, D II, D V and D VI of Type I and D IV of Type II described in an earlier paper (Bishui, 1950).

### EXPERIMENTAL TECHNIQUE

A commercial medical unit manufactured by Picker X-ray Corporation was used for the irradiation of the crystals with X-rays. The tube is a sealed one and it is provided with a filament cathode and an arrangement for cooling the target with circulating oil. The tube was operated at 4 MA. and 45 KV. A lead disc, about 1 cm. thick and provided with a small hole was placed on the window to get a narrow beam of X-rays, and to stop any light that may come from the inside of the X-ray tube the aperture in the lead disc was closed with black paper. The specimen of diamond was placed on a stand and it was completely covered by a light-tight box provided with two windows through one of which X-rays were passing through the crystal and through the other the light emitted by the crystal came out and was focused on the slit of the spectrograph. As preliminary investigations showed that the fluorescence excited under the conditions mentioned above was weaker than that excited by a mercury arc in quartz tube. An Adam Hilger two-prism glass spectrograph of high light-gathering power was used to photograph the spectrum. Special care was taken to ensure that no day light could in any way enter into the slit of the spectrograph or into the box containing the specimen of diamond. On observing visually through the spectrograph, it was found that the spectrum of the light emitted by any diamond of Type I was a continuous one and it disappeared as soon as the X ray tube was switched off. In the case of D IV, which is of Type II, no fluorescence could be detected on visual observation. The spectra were next photographed, using in each case an exposure of about 15 hours. The width of the slit of the spectrograph had to be increased to about °5 mm in order to diminish the time of exposure to a reasonable value. The spectrum of fluorescence excited by ultraviolet light was photographed with the same slit-width in a particular case for comparison. Gevaert 'superchrome' plates were used.

### RESULTS AND DISCUSSION

The spectrograms obtained in the case of the five specimens excited by X-rays are reproduced in figures 1-5 in Plate XXI and figure 6 shows the spectrogram obtained in the case of D VI excited by light from a mercury arc in silica tube. It can be seen that all the four specimens DI, DII, DV and DVI show continuous fluorescence extending from about 5650 Å upto about 3700 Å, and in the case of DII and DVI the spectrum shows the

absorption band at 4156 Å together with a few other such bands on the shorter wave-length side. These absorption bands are not present in the spectra due to DI and D V, because, as pointed out earlier (Bishui, 1950), these specimens do not show absorption band at 4156 Å at room temperature, although the band appears at −180°C. The spectrogram due to D IV is a blank one, showing that there is no fluorescence in any part of the visible region.

The results mentioned above do not agree with those reported by Ramachandran (1946) who claimed to have observed emission bands in the fluorescence spectrum of diamond excited by X-rays. The spectrum is a continuous one with large intensities in the region between 4200 Å and 5600 Å. Figure 6, however, shows that bands are observed, using the same slit-width of the spectrograph, in the case of excitation by mercury lines. The absence of any fluorescence in the case of D IV irradiated by X-rays is also contradictory to the conclusion arrived at by Ramachandran (1946) that diamond of Type II fluoresces feebly on being irradiated by X-rays. The conclusion arrived at by Bull and Garlick (1950) that all specimens of diamond of fluorescent and non-fluorescent types fluoresce when irradiated by X-rays is not generally true, because DIV, which is transparent in the region of 2250 Å, does not show any fluorescence in the visible region under X-ray excitation.

It is evident from the above facts that for the appearance of bands in the fluorescence spectrum of diamond the exciting energy should be of such a magnitude that it should raise the electron to the excited state corresponding to the absorption band at 4156 Å or to the sub-levels lying above it. If the excitation energy is much higher than this the electron is raised to the conduction level and it produces a continuous spectrum in the fluorescence. This statement is supported by the fact observed earlier (Bishui 1950) that when the Hg line 4046 Å is used for excitation only sharp bands appear in the fluorescence spectrum in the case of diamond of Type I, but when the whole ultra-violet light emitted by the mercury arc in silica tube is used for excitation, the fluorescence spectrum consists of bands superposed on a continuous background. In the case of X-ray excitation the electrons are raised only to conduction levels. The fact that the absorption band at 4156 Å with its companions on the shorter wave-length side appear in the continuous fluorescence excited by X-radiation in diamond of Type I shows that the ground and excited levels of these bands are not affected by the presence of photo-electrons in the lattice. The absence of the emission bands, however, shows that the photo-electrons do not return to the upper metastable states from which they can jump back to the ground level to produce the bands. If the electrons would return from conduction level to the ground level including its sub-levels a continuous spectrum with its long wavelength limit somewhere at 4200 Å would be produced. Since a continuous spectrum extending from about 3700 Å upto about 5650 Å is emitted by diamond of

Type I irradiated by X-rays, we have to postulate a different type of transition to explain the origin of the portion of the continuous spectrum having wavelengths longer than 4200 Å. It is essentially necessary to assume the presence of chemical impurities to account for this portion of the continuous fluorescence spectrum. Probably the conduction electrons find atoms of impurity around them and are captured by these atoms more easily than by the carbon atoms and the corresponding radiations produce the continuous spectrum extending from 4200 Å upto about 5650 Å. Radiation of wavelengths shorter than 4156 Å is also present in the spectrum of fluorescence and this may be due to transitions of the conduction electron to the ground level of the diamond lattice corresponding to the absorption band at 4156 Å. Had the fluorescence been due to pure diamond lattice without any impurity, the fluorescence spectrum would be the same for both ultraviolet and X-ray excitation, because Roth (1949) has come to this conclusion in the case of pure anthracene crystal.

The occurrence of transport of energy through solids has been demonstrated by the results reported by Bowen *et al* (1949). It has also been shown by several authors (Kallman and Furst, 1950, Ageno, Chiozotto and Querzoli, 1949) that some liquids containing small quantities of impurities fluoresce appreciably on being irradiated by X-rays or $\gamma$-rays. The phenomenon has been explained on the assumption that the pure liquid itself does not fluoresce owing to self extinction, but the energy absorbed by the molecules of the solvent is transferred to the impurity molecules in which the energy is trapped and is thus radiated by the latter molecules as fluorescence. In the case of diamond excited by X-rays probably similar transfer of energy takes place. The band at 4156 Å and its companions may be due to the carbon atoms of diamond lattice linked in some way to impurity molecules. The impurity atoms or molecules may have independent fluorescence radiation which is ordinarily weak but brightens up when the energy absorbed by most carbon atoms is transferred tot hose impurity atoms or molecules. Such a process may give rise to the continuous fluorescence which is observed in the region from 4200 Å to 5650 Å.

Ramachandran and Chandrasekharan (1946) and later Bull and Garlick (1950) have concluded that as the fluorescence band at 4156 Å is a doublet, it may be due to transitions $^1S_0 - {}^3P_1$ and $^1S_0 - {}^3P_2$ in the carbon atom, these forbidden transitions being allowed in the lattice owing to influence of lattice-defect. It was pointed out, in an earlier paper (Bishui 1950) however, that the fluorescence band at 4156 Å is not a doublet, but it is a single one and its appearance as a doublet in thick crystals is due to self-reversal. Their hypothesis that only lattice-defect without the presence of any chemical impurity is the cause of fluorescence can not explain the facts observed in the present investigation. First, the portion of the continuous spectrum of wavelength longer than band 4156 Å cannot be due to transitions.
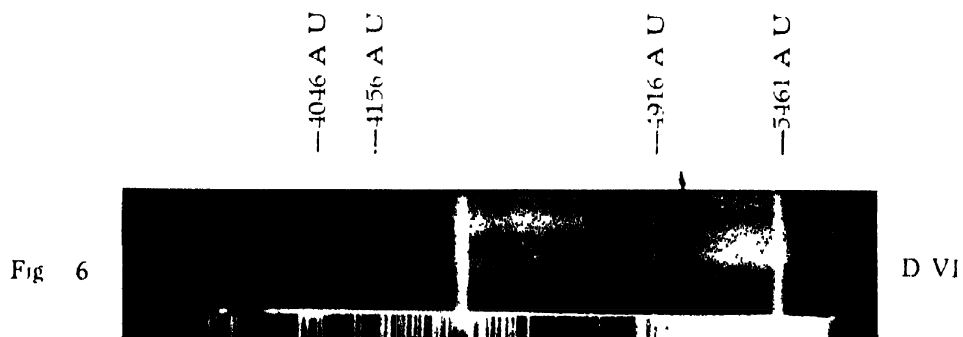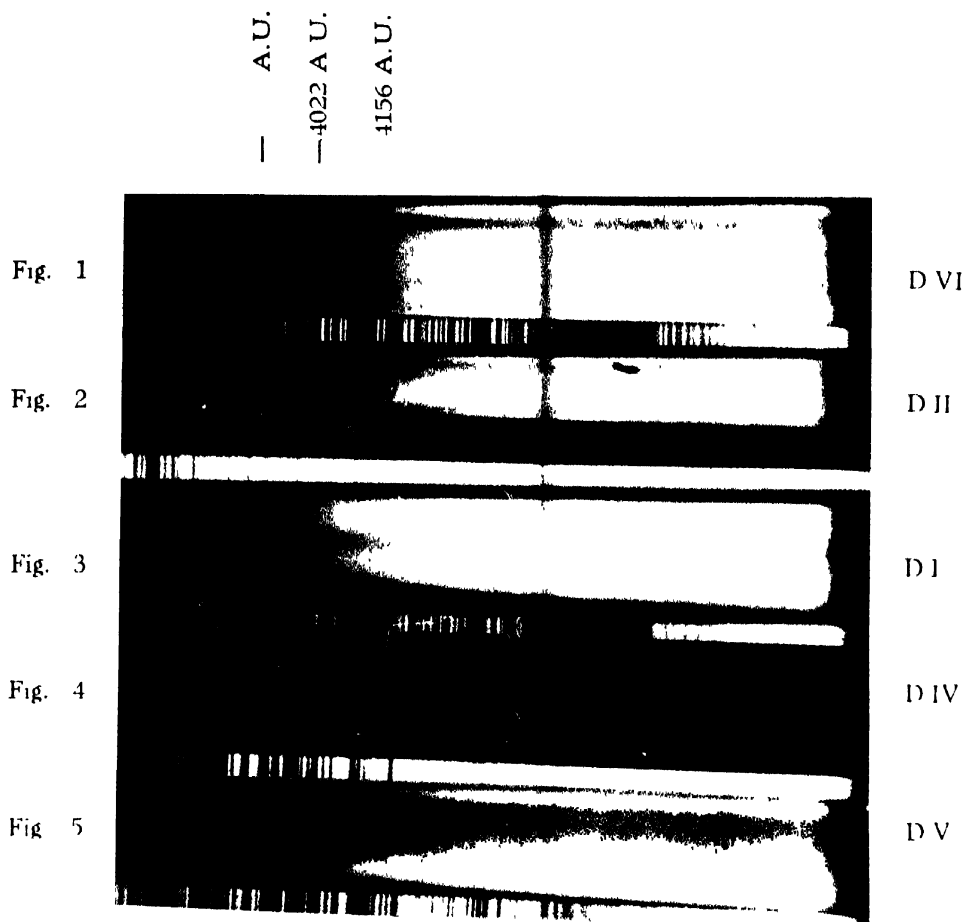
Fluorescence of diamond

Figs. 1—5.  Fluorescence excited by X-rays

Fig. 6.          „          „          „ Ultraviolet light

from conduction levels to any sub-level of the ground level of the absorption band at 4156 Å. Secondly, the total absence of the fluorescence in D IV under X-ray excitation cannot be due to want of lattice-defect in the crystal, as the crystal is highly birefringent and is full of local flaws. The fact observed by Blackwell and Sutherland (1949) that a particular specimen of diamond, which does not show fluorescence and absorption bands at 4156 Å and yet exhibits yellow fluorescence, cannot be explained by assuming the fluorescence to be due to lattice-defect in pure diamond lattice, because such lattice-defect would produce, according to the hypothesis of Bull and Garlick (1950), only blue fluorescence. Probably, impurities of different types are responsible for the fluorescence in the blue and yellow regions and when both the impurities are present in the same specimen it exhibits fluorescence in both the regions, as observed in the case of D I and D VI earlier (Bishui, 1950). The absence of the bands in the spectrum of fluorescence excited by X-ray in diamond of Type I and the presence of strong continuous spectrum on the longer wavelength side of 4200 Å thus show that chemical impurities are responsible for such emissions.

Another feature of the fluorescence of some specimens of diamond observed by Sir C. V. Raman (1951) can be explained on the hypothesis mentioned above. It was observed by him that in some specimens showing banded green luminescence there was correlation between birefringence and luminescence observed at different parts of the crystal for its different orientations. As pointed out earlier (Bishui, 1950), the birefringence may be due to frozen-in ultrasonic waves and any trace of impurity present in the melt is likely to collect at the nodes of these stationary ultrasonic waves. In such a crystal the planes containing the impurities are likely to be highly birefringent and regions in the neighbourhood of these planes will also fluoresce strongly according to the hypothesis given above. The fluorescent portions of such a crystal will, therefore, appear to have a banded structure.

The hypothesis of presence of chemical impurity in diamond of Type I and its absence in diamond of Type II can also explain the nature of photoconductivity of these two types. Photo-electrons ejected in the lattice fall into traps created by the impurities and are recaptured in the atoms in diamond of Type I, while in diamond of Type II, the number of the photoelectron is not diminished in this way and, therefore, Ohm's law is obeyed, as shown by Robertson Fox, and Martin (1934).

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## REFERENCES

Ageno, Chiozzotto and Querzoli, 1949, *Acc. dei Lincei*, **6**, 626.

Bishui B. M., 1950, *Ind. J. Phys.*, **24**, 441.

Blackwell, E. D. and Sutherland, G.B.B.M., 1949, *Jour. de Chimie Physique*, **46**, 9.

Bowen, E J., Mikiewicz, E. and Smith, F W , 1949, *Proc. Phys. Soc. A*, *(London)* **62**, 26.

Bull, C. and Garlick, G.F.J., *Proc. Phys. Soc. A.* (London), **63**, 1283.

Kallman, H. and Furst, M, 1950, *Phys. Rev.*, **79**, 857.

Ramachandran, G. N., 1946, *Proc. Ind Acad. Sc.*, **24A**, 81.

Ramachandran, G. N. and Chandrasekharan, V., 1946, *Proc Ind. Acad. Sc* , **24A**, 176.

Raman, Sir C. V., 1951, *Current Science*, **20**, 55.

Robertson, R., Fox J. J. and Martin, A. E., 1934, *Phil. Trans. Roy. Soc. A*, **232**, 463.

Roth, L., 1949, *Phys. Rev.*, **75**, 983.