

# THE PHOSPHORESCENCE OF DIAMOND

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## 1. INTRODUCTION

A REMARKABLE property of many diamonds is their power to store up energy under ultraviolet irradiation, a portion of which is released as visible light on shutting off the exciting radiation. This phenomenon, known as phosphorescence, has been remarked upon by several early workers like Robert Boyle, Crookes, Becquerel and others. However, the rest of the energy is retained in the diamond even for several days and released as visible light on either heating or more effectively on re-illuminating the diamond with long wavelength radiations even at or below room temperature. The former effect of heating has been dealt with in the paper on thermoluminescence appearing in the present symposium, while the latter is mainly dealt with in this paper. The main facts about phosphorescence already summarised in the paper referred to are also presented here more fully.

Diamonds which show bright blue fluorescence under ultraviolet light exhibit a greenish-yellow afterglow for about 30 minutes in which there is also a blue component during the first few seconds. Sir C. V. Raman discovered this fact by the use of a violet filter and this technique of viewing the diamond through filters has been found extremely useful in studying the effect of re-illumination. The green-fluorescent diamonds show only a feeble phosphorescence. When blue-fluorescent diamonds after exposure to ultraviolet light are re-illuminated with red light and viewed through a filter complementary to the red, a very bright blue flash is observed which dies away in a few minutes. In the case of green-fluorescent diamonds, the flash is green. Both varieties of diamonds on heating lose their activation in the form of thermoluminescence. Ultraviolet light below 3000 Å produces activation several times greater than that produced by radiation between 3500 and 4000 Å. X-rays are also able to produce a slight activation. Any wavelength above 4200 Å is able to remove the activation in diamonds.

## 2. PHOSPHORESCENCE

The main facts about the phosphorescence of diamonds have already been stated in the paper on thermoluminescence appearing in the present symposium. As the specimens N.C. 67, N.C. 68, and N.C. 41 have been

used in the study of re-illumination with long wavelength radiations, their phosphorescence is described below. The former two are small brilliants and are intensely blue-fluorescent, while N.C. 41 is a moderately large crystal which is brightly green-fluorescent. N.C. 67 and N.C. 68 after exposure to ultraviolet light of the sun exhibit a greenish yellow glow and the change of colour from the blue fluorescence to greenish yellow phosphorescence is very striking. To find whether any blue phosphorescence is present in the glow, the diamond is viewed through a violet filter having a cut-off between 4950 and 6300 Å; a faint glow is then detected lasting for about 20 seconds. The main bulk of the emitted energy is, however, in the yellow, as the brightness of the glow is practically undiminished by the interposition of an yellow filter transmitting wavelengths greater than 5000 Å. The green-fluorescent diamond shows a faint greenish yellow glow lasting for about 40 seconds which is, however, too faint to be studied with filters.

It is found that the decay of the afterglow in all cases is extremely rapid in the first few seconds. It is proposed to take up the exact nature of the decay in a further communication.

The fluorescence spectra of diamonds taken by Miss Mani (1944) reveal mainly a line at  $\lambda$  4152 and a system of bands associated with it and also another line at  $\lambda$  5032 and an accompanying band system. In the phosphorescence spectrum of N.C. 68 taken by Miss Mani (unpublished work), both systems appeared. As the time interval between irradiation and exposure was only a fraction of a second, the violet phosphorescence was present and was recorded as the 4152 system. The green glow may be identified with the 5032 system which presumably has a long lifetime in the phosphorescence of blue-fluorescent diamonds.

### 3. THE EFFECT OF RED LIGHT

In order to follow the effect of re-illumination, it is important to recall the Stokes law of fluorescence. The wavelength of the exciting radiation should be near about or less than the wavelength of fluorescence. Thus red light is unable to excite any visible fluorescence, and similarly green light cannot produce any violet fluorescence.

*Blue-Fluorescent Diamonds.*—The diamond N.C. 67 is exposed to ultraviolet light of the sun for about a minute and after shutting it off, red light obtained by passing sunlight through a red filter transmitting above 6300 Å is focussed on it. On viewing the diamond through a 3 cm. filter of saturated copper sulphate solution which is complementary to red light, a bright blue flash is observed which decays very rapidly in the beginning and is visible for about four minutes. As red light cannot produce an

fluorescence, the flash is due to the release of the stored-up energy in the diamond by red light. Even though the colour of the flash is blue, it also contains wavelengths from 5000 to 6000 Å. This is shown by the fact that the glow can be observed both through a blue filter of ammoniacal copper sulphate solution transmitting wavelengths less than 4600 Å and through a green filter transmitting 5000 to 6000 Å.

On illuminating the activated diamond with green light (5000 to 6000 Å) of the sun and observing through a complementary violet filter, a bright violet flash is observed for about two seconds, and subsequently there is a persistent faint red colour due to fluorescence produced by the green light. The violet flash is, however, due to the release of activation energy by the green light as is indicated by the decaying of the flash.

The effect of both green light and red light can be noticed even a few days after activation by ultraviolet light. This indicates that the stored-up energy is retained by the diamond and is released by exposure to green light for a sufficient time, since red light has subsequently no effect; also, *vice versa*. If similarly the activated diamond is exposed to blue light (4100 to 5000 Å) for about a minute, any flash occurring during the exposure cannot be observed through a complementary filter owing to the presence of a persistent green and red fluorescence produced by blue light. However, after such exposure, the diamond no longer shows any flash on irradiation with red light, thereby indicating that blue light is able to remove the stored-up energy presumably as a flash. Using a monochromator with sunlight as the source, a preliminary study of the efficiency of different wavelengths in removing the activation in the blue-fluorescent diamond N.C. 68 has been made. Green light near about  $\lambda$  5500 appears to be the most efficient, but a more thorough examination of the facts will be published later. It is also found that for a given wavelength, the brightness of the flash increases with intensity of the light used while the duration of visibility diminishes, showing that the whole of the stored-up energy is released in a shorter interval of time by a more intense source of light.

The activation in diamond is increased on increasing the intensity of the activating ultra-violet light. However, as in the case of phosphorescence, the time of irradiation need only be a second. Increased exposure times do not result in an observable increase in the intensity of the flash which results from illuminating the diamond with a constant source of red light.

When the radiations from a low pressure quartz mercury arc are used for activation, it was found that the blue flash obtained by subsequent irradiation with red light (above 6800 Å) is much brighter than when the

near ultraviolet between 3500 and 4000 Å is employed for activation. In fact, the blue colour is clearly seen for a few seconds even in the presence of the intense red light in the former case, while a filter of copper sulphate solution has to be used to cut out the red light if the blue flash is to be observed in the latter case. A very large part of the high activation produced by the quartz mercury arc is due to radiations below 3000 Å. This is shown by the fact that when a glass plate which cuts off these wavelengths is interposed between the diamond and the mercury arc, the activation is reduced to a very small fraction of its former strength. It is also found that subsequent exposure to light between 3500 and 4000 Å reduces the large activation produced by radiations below 3000 Å.

During any part of a flash if the illuminating light is cut off, the flash disappears instantaneously as far as the eye can judge. The remaining part of the flash can be completed at any later time by illuminating again with the light.

X-rays are also able to produce a slight activation. This can be verified by removing all previous activation in the diamond by exposure to bright red light for about half an hour and then irradiating it with X-rays for a few seconds. Subsequently, when red light is allowed to fall on the diamond, a feeble blue flash is observed through the copper sulphate filter.

*Green-fluorescent Diamonds.*—The green fluorescent diamond N.C. 41 behaves in exactly the same way with regard to all the above effects except for the fact that the flash is green as observed through copper sulphate solution and not blue. The major portion of the energy of the flash is hence in the green.

*Spectrum of the Flash.*—The diamond N.C. 67 after activation by focussing the light of a quartz mercury arc on it with a quartz lens, was placed very close to the slit of a Zeiss three-prism spectrograph. The light of a carbon arc was passed through a red filter transmitting wavelengths greater than 6300 Å and focussed on the diamond. After one minute of exposure, the diamond was activated again and the experiment repeated 30 times. A faint spectrum (not reproduced) was obtained in the violet part and showed the 4152 line and its system of bands. To prove that the spectrum was not due to fluorescence, a blank experiment was performed in which the diamond was not activated with the mercury arc but a continuous exposure of one hour and a half was given with red light focussed on the diamond as before. In the spectrum, no trace of the violet portion was found and only the band in the red region due to the incident light appeared,

In the case of the brightly green-fluorescent diamond N.C. 41, the 5032 line and its bands were found faintly with an exposure repeated 50 times in the manner described above.

#### 4. THE EFFECT OF HEAT

It has been stated that the diamonds retain energy for several days after activation. The activated blue-fluorescent diamonds on heating to 270° C. exhibit blue thermoluminescence as stated in the paper on thermoluminescence. After a few minutes the glow disappears, and after cooling the diamond shows no longer any flash on irradiating with red light and observing through copper sulphate solution. In the case of the green-fluorescent diamond N.C. 41, a faint greenish yellow thermoluminescence is observed on heating to 270° C. and subsequently the usual flash with red light is absent. Thus at 270° C. the diamonds lose their activation.

On cooling the diamonds by immersing in liquid air, they showed every one of the usual effects resulting from activation.

In conclusion, the author wishes to express his deep gratitude to Professor Sir C. V. Raman for his inspiring guidance and for his helpful interest in the problem.

#### 5. SUMMARY

Fluorescent diamonds retain some energy after ultraviolet irradiation, a part of which is released at room temperature as phosphorescence. However, a greater part of the energy remains with the diamond for any length of time until it is illuminated with long wavelength radiations; it is then emitted as a flash of visible light. This can be observed through a proper filter complementary to the illuminating light. Any wavelength above 4200 Å is able to remove the activation in diamonds. Ultraviolet light below 3000 Å produces activation several times greater than that produced by the very near ultraviolet between 3500 and 4100 Å. X-rays are also capable of producing a weak activation. All these effects are observed even at liquid air temperature. However, the activation in diamond can be removed by heating it to 270° C. when thermoluminescence is observed. In the case of blue-fluorescent diamonds, the stored-up energy is given out mainly as a blue flash on illuminating them with long wavelength radiations and the spectrum of the flash reveals mainly the 4152 system, while in green-fluorescent diamonds, green light is mainly emitted and the 5032 system is found in the spectrum of the flash.

#### REFERENCES

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