

THE THERMOLUMINESCENCE OF DIAMOND

BY V. CHANDRASEKHARAN

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

Received June 13, 1946

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. INTRODUCTION

SOME substances have the property of storing up energy under suitable excitation which they later release. The release of energy as visible light at the temperature of excitation is known as phosphorescence. But, even after the afterglow has decayed, the substance may retain some of the stored-up energy which manifests itself as light on heating the substance in darkness. To this phenomenon is applied the term thermoluminescence. That some diamonds exhibit thermoluminescence has long been familiar to several investigators in the past. In the twelfth century, Albertus Magnus by placing the diamond in hot water noticed the glow, while in the seventeenth century, Robert Boyle held a diamond near a flame and observed its glimmering on removing it quickly to a distance. However, there seems to be no recent work on the subject mentioned in the literature. The present paper describes the results of a study of thermoluminescence undertaken by the author, and these are briefly enumerated below.

Fluorescent diamonds, after exposure to ultraviolet of the sun, glow in darkness with a greenish-yellow colour. In the case of brightly blue-fluorescent diamonds, Sir C. V. Raman discovered that for a brief duration of a few seconds, there is blue light accompanying the greenish-yellow glow which lasts for several minutes. On raising the temperature of the diamond to 270° C., the colour of the visible afterglow changes to blue and it is very bright. This thermoluminescence is observed even if the diamond is heated a few days after activation, by which time the ordinary phosphorescence would have completely disappeared. There is the yellow portion also in the blue thermoluminescence, as can be verified by viewing the diamond through an yellow filter. Another important result of the investigation is that the ultraviolet light below 3200 Å is able to excite thermoluminescence more efficiently than ultraviolet between 3500 and 4000 Å, even though the former excites little phosphorescence at room temperature. X-rays are also able to produce a slight activation. The effect of irradiation of the diamond with light of wavelength greater than 4200 Å is to practically remove the activa-

tion in diamonds even at or below room temperature. Green fluorescent diamonds show a weak greenish-yellow thermoluminescence.

2. PHOSPHORESCENCE

In order to facilitate an understanding of the thermoluminescence, the main facts about the phosphorescence of diamond are briefly stated below. They will be dealt with in greater detail in a separate paper on the subject appearing in the present symposium. The source of light used in the study was sunlight and the arrangement was that described in the paper on phosphorescence patterns also appearing in the present symposium.

Blue-fluorescent Diamonds.—The colour of the light emitted by blue-fluorescent diamonds under the ultraviolet of the sun changes suddenly to greenish yellow when the exciting radiation is cut off. The afterglow can be seen for about half an hour in darkness in the case of the strongly blue-luminescent diamonds. Observation of the diamond through suitable light filters enables us to obtain an idea of the nature of the phosphorescence spectrum. It is found that the glow can be seen with almost undiminished intensity through a yellow filter transmitting above λ 5000 for practically the whole of its duration. On the other hand, through a violet filter cutting off between 4950 and 6300 Å the diamond is visible faintly for a relatively short duration of about 20 seconds. Thus the energy of the phosphorescence is mainly in wavelengths above 5000 Å. This is further confirmed by viewing the diamond through a filter which has its cut-off between λ 5200 and λ 6250. The phosphorescence is then seen more brightly and for a longer duration of a few minutes. On viewing the afterglow through a direct vision spectro-scope, the spectrum is found to extend at first on both sides of λ 5000, but in a few seconds the spectrum on the violet side diminishes in intensity relatively to that on the green side. However, the entire spectrum also becomes very feeble and it is not possible to continue its study after the first few seconds. There is no red phosphorescence, as the glow is invisible through a red filter transmitting above 6300 Å. The brightness of the phosphorescence increases with the intensity of the ultraviolet light used. However, a variation of the time of irradiation from one second to several minutes produced no perceptible increase in intensity of the glow, and the time for which the diamond can be perceived through the various filters remains unaltered. The brightness of the glow in different diamonds increases with the intensity of their fluorescence.

One of the diamonds was cooled by immersing it in liquid air contained in a Dewar flask and then irradiated with ultraviolet light. On shutting

off the light, a greenish-yellow glow was detected for 30 seconds, as has already been mentioned in a paper by Nayar (1941).

Green-fluorescent Diamonds.—Green fluorescent diamonds in striking contrast with the blue ones exhibit a faint greenish-yellow glow which lasts for only 40 seconds even in the case of the most brightly fluorescent specimens. As the glow is faint and of short duration, it cannot be examined through filters.

General Remarks.—In the fluorescence spectra of all diamonds, electronic lines at λ 4152 and λ 5032 with their accompanying bands at longer wavelengths are recorded. In blue-fluorescent diamonds the λ 4152 system is strong but the λ 5032 is also recorded in many cases though weakly. In green-fluorescent diamonds, the λ 5032 system is strong but is always accompanied by the λ 4152 system though with relatively much less intensity. On the other hand, the phosphorescence spectra of strongly blue-fluorescing diamonds recorded by Nayar (1941) and Miss Mani (unpublished work) show both the λ 4152 and λ 5032 system with comparable intensity. Their spectrograms were obtained with a time-interval of the order of a fraction of a second between excitation and observation. The visual observations described in the present paper indicate that with longer time-intervals the λ 4152 grows gradually weaker and disappears after a few seconds and that the subsequent phosphorescence consists exclusively of λ 5032 and its accompanying band system. Further experimental work is necessary to confirm this finding and also to investigate how the duration of the phosphorescence of any diamond depends upon the relative and absolute intensities of the λ 4152 and λ 5032 systems as exhibited in its fluorescence.

3. THERMOLUMINESCENCE

A blue-fluorescent diamond N.C. 67 was activated by exposing it to the ultraviolet light of the sun and was then placed on a hot plate whose temperature was about 100° C. The glow brightened up but the colour remained unaltered. When the temperature of the diamond was raised to 270° C., the glow was very bright and *blue in colour*. However, the diamond could be observed through the yellow filter indicating that the yellow portion must also be accompanying the blue glow. The blue thermoluminescence was perceived for about 10 minutes.

In all the above described experiments, ultraviolet light between 3500 and 4000 Å has been used. To use ultraviolet light below λ 3000, the light from an iron arc was focussed by a quartz lens on the diamond. After shutting off the incident light the diamond showed little phosphorescence.

However, on heating the diamond, bright blue thermoluminescence was observed. When during irradiation, a glass plate was introduced between the diamond and the quartz lens, the intensity of thermoluminescence became extremely small, showing that wavelengths below 3000 Å produce very high activation compared to wavelengths between 3500 and 4000 Å. As a further confirmation of this, the diamond was held close to a water-cooled low-pressure quartz mercury arc and then heated to 270° C. in darkness. A brilliant blue glow was observed.

The diamond N.C. 67 was activated by means of the light of an iron arc and kept in darkness. After 10 days the diamond was heated to 270° C. and a blue glow was observable. Thus some energy can be stored up in the diamond for any length of time. It should be realised, however, that the heating does not produce, but only releases the energy 'frozen in' at room temperature, as the thermoluminescence glow is not persistent at the high temperature like fluorescence, but decays (Pringsheim and Vogel, 1943). Thermoluminescence is nothing but phosphorescence at a high temperature. In support of this view the heated diamond at 270° C. was irradiated with ultraviolet light and on shutting off the light, the phosphorescence was bright blue. P. G. N. Nayar has similarly observed that the phosphorescence at room temperature could be quenched at any stage of its life by immersion in liquid air and the residual part of its life completed on regaining the room temperature.

The effect of X-rays in producing the activation in the diamond was tried. The diamond N.C. 67 was heated for several minutes at 270° C. until no trace of glow was detected and after cooling, it was irradiated by X-rays. It was then again heated to 270° C. in darkness and a faint blue glow appeared which was visible for about a minute.

In the case of a green-fluorescent diamond N.C. 41, a comparatively faint *greenish-yellow* glow was detected for about 10 minutes on heating it to 270° C.

4. THE EFFECT OF RED LIGHT

It has been stated above that the activation in N.C. 67 could be retained for several days and released on heating it. The diamond after activation was exposed for about a minute to bright red light of the sun obtained by the use of a red filter, and on heating the diamond subsequently an extremely faint glow was detected. Thus the activation was practically removed. Similarly, when the phosphorescing diamond was exposed for a minute to red light, the brightness of the phosphorescence was much smaller than what it would otherwise have been. A careful study of the effect of red light will

be prevented in a later paper. It was found by the use of various filters that any wavelength above 4200 Å was able to remove the activation in diamond. In fact, if the diamond after exposure to focussed ultraviolet light of the sun was taken out into bright daylight, the activation disappeared practically as was verified by heating the diamond subsequently.

5. DISCUSSION

The foregoing experiments have made it clear that there are two distinct types of phosphorescence, one blue and the other yellow. The former is faint and observable only for a short time at and below room temperature, while the latter predominates in the glow and lasts for a long time. At high temperatures, the glow is blue showing that the blue then predominates. The ultraviolet light below 4000 Å is able to excite thermoluminescence with greater efficiency than the very near ultraviolet, while the converse is true of phosphorescence at room temperature. These facts have to be remembered in presenting any theory of the phosphorescence of diamond.

The blue phosphorescence and thermoluminescence may be identified with the A 4152 system, while the yellow phosphorescence and thermoluminescence may be identified with the A 5032 system. However, the diamonds which show the latter system brightly in fluorescence compared to the former, show only feeble greenish-yellow phosphorescence and greenish-yellow thermoluminescence.

In the fluorescence of diamond, principally two electronic lines A 4152 and A 5032 are found (Ama-Mann, 1944) and as these come out in absorption also, there are three main energy levels, one ground and two upper ones, in diamond. The usual explanation of phosphorescence is based on the idea that there are metastable levels near the upper levels in which some electrons are trapped. Due to the thermal agitation, these slowly leak to the main levels and from there they drop to the ground state emitting light. This view is supported in the case of the after-glow of diamond as both the 4152 and 5032 lines are observed in phosphorescence. There must also, however, be some traps from which the electrons cannot escape at room temperature. On raising the temperature, however, the electrons are enabled to escape from these levels.

In conclusion the author wishes to thank Sir C. V. Raman, Kt., F.R.S., N.I., for suggesting the problem and for the encouragement given during the work.

6. SUMMARY

Blue-fluorescent diamonds show a greenish-yellow glow at room temperature after exposure to ultraviolet light. In this glow, there is also a blue component which however decays more rapidly. On heating to 270°C , the colour of the glow changes to blue and the glow brightens up. This effect, known as thermoluminescence, can be observed even if the diamond is heated a few days after activation. Remarkably enough, radiations below 3000 \AA are able to produce an activation greater than that produced by radiations between $\lambda\ 3500$ and $\lambda\ 4000$, even though the former give rise only to slight phosphorescence. Even X-rays are able to produce a slight activation. In the case of the green-fluorescent diamonds, the phosphorescence is feeble and greenish yellow in colour. The thermoluminescence of these diamonds is greenish-yellow and is much fainter than that of blue fluorescent ones. Light of any wavelength greater than $\lambda\ 4200$ is able to remove the activation in both varieties of diamond.

REFERENCES

- | | | |
|-------------------------------|----|--|
| Anna Mani | .. | <i>Proc. Ind. Acad. Sci.</i> , 1944, 19 , 231. |
| Chandrasekharan, V. | .. | <i>Ibid.</i> , 1946, 24 , 193. |
| Mellor, J. W. | .. | <i>Treatise on Inorganic and Theoretical Chemistry</i> , 5 , 768. |
| Nayar, P. G. N. | .. | <i>Proc. Ind. Acad. Sci.</i> , 1941, 13 , 534. |
| Pringsheim, P., and Vogel, M. | | <i>Luminescence of Liquids and Solids and its Practical Applications</i> , 1943, 17. |