Phosphorescence in Semiconducting Diamond[1]

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INTRODUCTION

Photoluminescence in semiconducting diamond (Type IIb) has been studied to establish whether the luminescence of slow decay is phosphorescence or a slow fluorescence and to seek any correlation of this property with other properties of the same specimens. Also, during the present work a red phosphorescence was found which is believed to be unlike that reported in other diamonds.

The properties of diamond have been studied intensively for many years. There are many and varied reasons for the great interest in diamonds. In the first place diamond is the prototype of a class of crystals which have reached a supreme position in modern technology. In particular germanium and silicon, which have the diamond structure, have had a phenomenal development because of their use in transistors and other solid state devices. Much of our understanding of silicon and germanium was the result of early studies of diamond. Another reason for the interest in diamond stems from its crystal structure which enables it to be profitably studied theoretically and experimentally.

In the past diamonds have been generally classified as Type I and Type II. The classification arose mainly from their optical properties, and it was thought by some investigators that there was a fundamental difference in their crystal symmetries. Recent studies have been able to resolve the main differences in terms of crystal imperfections.

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Formerly, diamond was considered one of the great insulators; however, in 1952 J. F. H. Custers in South Africa discovered a diamond which would conduct an electrical current (Custers, 1952). Since it was more like Type II than Type I diamond he classified it as Type IIb and designated the original class of Type II as Type IIa. The Type IIb diamonds are exceedingly rare. R. Smoluchowski and W. J. Leivo (1955) showed that the electrical conductivity was typical of an impurity-activiated semiconductor such as silicon and germanium. Three semiconducting diamonds were used in this investiagtion. DS-1 is an elongated chip which is tinted blue. DS-2 is a rectangular parallelepiped with dimensions of 2.5 × 3.5 × 6.5 mm^3, one end of which is distinctly blue, the rest of the specimen being nearly free of coloration. Diamond DS-3 is a blue marquise-cut stone.

A Brief Discussion of Luminescence

Before considering the results of the present investigation, a discussion of the processes involved in luminescence will be given as well as definitions of terms which will be used. Photoluminescence is the general term given to light emission which is excited by light absorption. Other types of excitation give rise to the terms electroluminescence, thermoluminescence, triboluminescence, and chemiluminescence.

Electroluminescence is a luminescence stimulated by application of an electric field. Thermoluminescence is stimulated in a sample while the sample is being heated. Such luminescence generally decays rapidly when the sample temperature is held constant at some point in the heating process. Triboluminescence is luminescence excited by friction. Such luminescence is common in diamonds and may be stimulated by brisk rubbing with a cloth (Robertson *et al.*, 1934). Chemiluminescence originates in chemical reaction.

The present work has been principally concerned with photoluminescence although some other observations have been made. Photoluminescence may involve any of several energy changes of the system considered, so it is desirable to discuss these processes in connection with an energy level diagram. Fig. 1 shows the energy levels assigned to the unspecified system under consideration. The levels G and E represent respectively the ground state and a particular excited state. M represents a metastable or quasi-stable state from which transition directly to the state G is highly unlikely or forbidden. S represents a possible energy level between G and E. E′ and G′ represent states of slightly higher energy than E and G. Suppose that an element of the system absorbs a photon of energy $h\nu =$ (E-G) and finds itself in the state E. This transition will be denoted G-E and the reverse process will be implied by the reverse order E-G. If the process G-E is followed by E-G the process corresponds to resonance radiation which is a radiation typical of a rarified gas configuration. The process G-E might be followed by two events: E-S and then S-G. This is a typical fluorescence process. Case 1 and case 2 in Fig. 1 illustrate these processes.

Phosphorescence differs from fluorescence in that a metastable or quasi-stable state exists into which the system passes following excitation. This transition E-M, represented by case 3 in Fig. 1, is generally accomplished in the case of a solid sample by loss of energy to the lattice or in the case of a gas by collision. Liberation from state M is dependent upon reabsorption of this energy from the surrounding elements, and the lifetime in such a state M may vary from the order of milliseconds to years depending on the temperature of the sample and the depth of state M below the state E. At a low enough temperature the lifetime associated with the state M may become very great so that the phosphorescence is

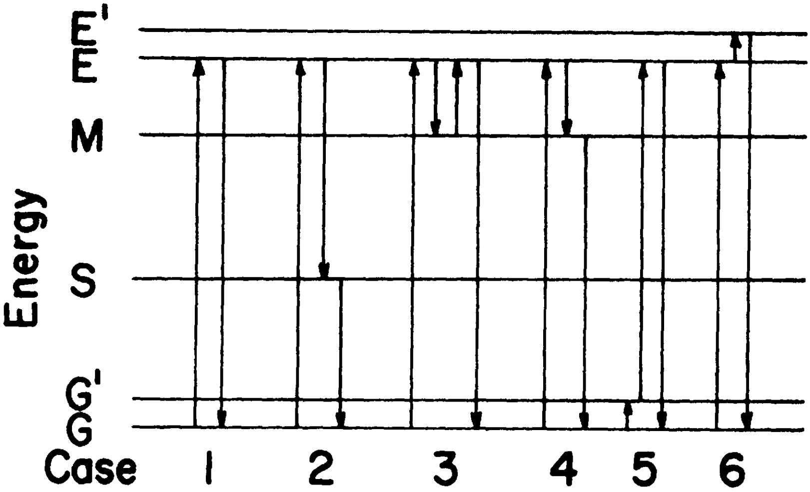

Figure 1—Energy level diagram illustrating six photoluminescent processes.

frozen in. When the sample is subsequently heated, the phosphorescence is liberated. There are minerals which have such "frozen in" phosphorescence at room temperatures, the states having been filled as a result of gamma or x-radiation. When these substances are heated in darkness, a luminescence may be observed during the heating process. If the substance is then cooled and subsequently reheated, no luminescence is observed. This phenomenon is called thermoluminescence. Pringsheim (1949) considers thermoluminescence to be only phosphorescence which is frozen in at normal temperatures. Some other writers take the opposite view that phosphorescence is only a special case of thermoluminescence (Winans and Sedlin, 1958). For the purpose of this work the question is one of definition and need not be further considered.

Fluorescence is not entirely inconsistent with extended lifetimes. Suppose the transition M-G is not extremely unlikely. Indeed, this event might be more probable than the reabsorption of the energy required to permit the transition M-E. In this case a temperature independent fluorescence would be emitted which has a longer than normal lifetime and is called a slow fluorescence by Pringsheim (1949). Slow fluorescence will always be used in the present paper to indicate a fluorescence of longer than normal lifetime, and the process is illustrated by case 4 in Fig. 1.

Observed fluorescence is not adequately explained by the above simple picture. One might think that everything should exhibit fluorescence. The simple picture above largely ignores the effect of the surrounding elements. Only in a rare gas configuration would this be acceptable. Stokes stated the empirical law that fluorescence is always of wave lengths longer than the wavelength of the exciting light. Actually, fluorescence spectra may contain wavelengths shorter than the exciting wavelengths. The term Stokes fluorescence is applied to fluorescence in which Stokes law is obeyed and anti-Stokes fluorescence is applied to emitted wavelengths shorter than the exciting wavelength.

If states E′ and G′ exist immediately above states E and G such that thermal energy may raise the system to G′ just prior to the absorption of a photon, or from E to E′ during the lifetime of the state E, then the emitted radiation may be of shorter wavelength than the exciting radiation. These possibilities are represented by cases 5 and 6 of Fig. 1, and they correspond to anti-Stokes fluorescence.

EXPERIMENTAL PROCEDURE AND RESULTS

Blue Luminescence. Phosphorescence and slow fluorescence frequently have a decay lifetime of a millisecond or longer and are therefore observable after the source of excitation has been removed. In the case of a very short lifetime one must have a means of repeatedly illuminating the sample, removing the illumination, and viewing the sample. An instrument designed for this purpose is called a phosphoroscope. One such instrument, illustrated in Fig. 2, is called a Becquerel type phosphoroscope after its inventor, E. Becquerel. A Becquerel phosphoroscope consists of two disks mounted on a shaft which is in turn mounted on suitable bearings. Each disk has holes or slots which act as windows for illuminating or viewing the sample. The disks are oriented so that the holes in one disk do not line up with the holes in the other disk. A phosphor placed between the disks may then be irradiated from one side of the apparatus and viewed from the other side. Scattered light may be a problem if the sample is a weak phosphor, and in this case a great improvement is achieved by inserting a shield between the disks in such a way that only light which passes through the sample can pass by the shield.

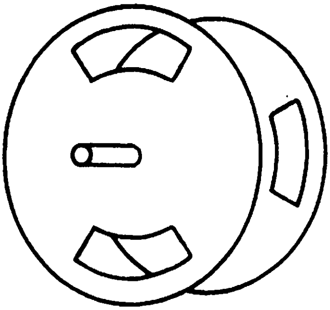

Figure 2—A simplified representation of a Becquerel type phosphoroscope.

The possibility of viewing a phosphorescent sample by merely turning off the lamp used to excite phosphorescence is of no value in the case of samples which have a decay lifetime of the order of a few seconds or less. Lamps will usually glow this long. The use of Kerr cells as a phosphoroscope in the present work was not practical in view of the low transmission and poor cutoff characteristics of Kerr cells and the relatively weak luminescence exhibited by the diamond samples.

Experiments utilizing photographic detection methods were first attempted. The spectrograph used was a Jarrel Ash grating spectrograph which has a nearly linear dispersion of 7 Angstroms per mm throughout the range of the instrument. The film used was Eastman type 103a which is more sensitive to low light levels than are films with higher sensitivity ratings. This film is recommended for exposures which will require more than five minutes time.

Since the luminescence was faint it was expedient to find the optimum position of the sample by the following simple procedure. A tungsten lamp was placed at the position normally occupied by the camera, thus reversing the optical path of the system. It was then easy to find the optic axis of the system and place the sample at the image of the slit of the spectrograph, the image being formed by a suitable lens. The tungsten lamp was positioned so that green light was emitted from the slit, thus matching the region of greatest eye sensitivity.

A Becquerel-type phosphoroscope which gave equal on-off time for observation of luminescence and which operated at 120 cycles per second was placed in position surrounding the sample. Shields were installed to prevent stray light from entering the spectrograph and the sample was then irradiated with a mercury lamp. Exposures were made for as long as 39 hours. Since the phosphoroscope was used, the actual net exposure was for about half of this time. In no experiment was there an image formed on the film from stray mercury light or luminescence of the diamond. Specimen DS-1 was used since it exhibits brighter luminescence than diamond DS-2. A similar experiment in which mechanical shutters were used instead of the Becquerel type phosphoroscope also failed to produce the spectrum of the luminescence. It should be mentioned that with the eyes adapted to darkness, the luminescence passing through the slit of the spectrograph was bright enough to be visible at the position of the collimating mirror but not after dispersion, i.e., from the position of the camera. It was concluded that the energy was too highly dispersed and that possibly no usable image could be formed with exposure times which were practical. Perhaps an experiment utilizing a low dispersion prism spectrograph would be successful. Nayar (1941) was successful in recording phosphorescence of a Type I diamond by similar technique but using a low dispersion instrument and exposures up to six days.

Photoelectric methods of detection were then employed. A Beckman DK-1 spectrophotometer was used which proved to be quite sensitive in the range of wavelengths 220 to 700 millimicrons. An arrangement was devised in which the chopped light from the luminescent sample (DS-1) was focused on the entrance slit of the monochromator. By adjusting the instrument to obtain maximum sensitivity, the spectrum of the luminescence could be obtained. The signal-to-noise ratio was unfavorable, and it was necessary to use a relatively large slit width in order to obtain a response.

The determination of the temperature dependence of the luminescence was investigated. The experiment described in the preceding paragraph was repeated with the addition of an apparatus for cooling the sample. This equipment is illustrated in Fig. 3. Spectrograms of the luminescence were obtained at several temperatures. Three of these are reproduced in Fig. 4. It is interesting to note that no appreciable shift in the maximum occurs, though the intensity decreases sharply with decreasing temperature. In contrast to this behavior the photoconductivity shows a definite shift toward shorter wavelengths as the sample temperature is lowered. The luminescence with the sample at 200° K has essentially zero intensity. As the sample temperature is further reduced the intensity begins to increase and at 90° K the intensity is estimated to be half that at 300° K. Because of extraneous luminescence which appears in the sample mount at the lower temperatures, there is some question about the accuracy of the corresponding measurements; they are therefore not reproduced. The temperature dependence of the luminescent intensity indicates that it is a phosphorescence and not a slow fluorescence. The fact that the intensity increases with decreasing temperature in the range 90° K to 180° K is an indication that a new luminescent process is becoming effective in this temperature range because of the increased lifetime at this low temperature. It should be noted that the phosphoroscope used in these measurements chopped the light beam at 480 cycles per second and that a phosphorescence with decay lifetimes short enough, say less than 100 microsecond, would not be recorded. As was mentioned in a preceding paragraph, because of weakness of the luminescence in our IIb diamonds it was necessary to use a large slit width on the monochromator, and therefore it was not possible to resolve any narrow bands such as those found by Custers (1952).

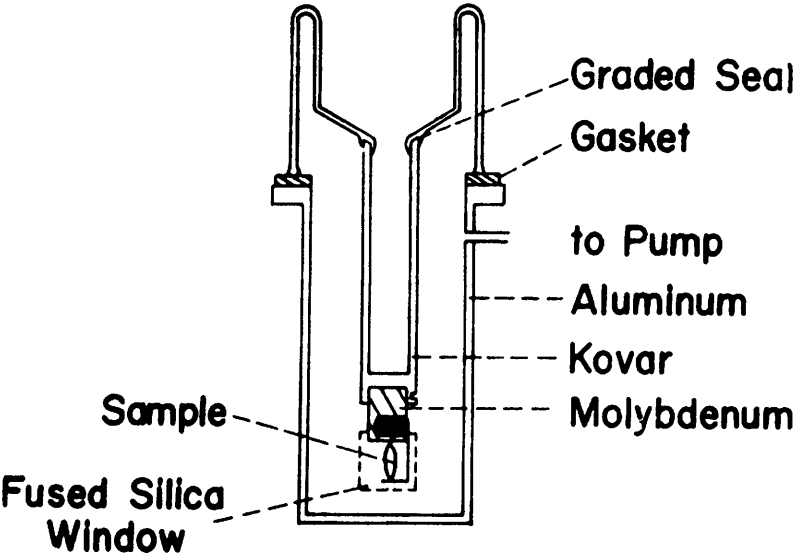

Figure 3—Vacuum sample mount.

Some visual observations regarding the phosphorescence in diamond DS-2 are in order. The blue end of the stone is seen to luminesce much more brightly than the clear end when viewed with a phosphoroscope. The clear end decays much more slowly than the blue end, but its emission is very weak and at the beginning of a decay cycle is completely masked by the luminescence from the blue end. The emission from the blue end is distinctly blue, but that from the clear end of the stone is always so faint that no distinct color is discernible.

The decay lifetimes for the luminescence of DS-1 and DS-2 were obtained at room temperature. A lens and an RCA 1P28 photomultiplier tube were positioned so that an image of the diamond was focused onto the photocathode of the tube. The phosphoroscope was rotated by hand so that the light from the mercury lamp could be rapidly cut off and the phosphorescence from the sample could fall on the photomultiplier tube. A signal from the tube was displayed on an oscilloscope, and the resulting curve was photographed. From the curves obtained in this manner the decay lifetime of the luminescence was found to be 0.7 ± 0.1 sec, the large uncertainty being due to noise in the circuit. It seems doubtful that there is a distinct correlation with the 0.25 second carrier lifetime which was obtained by other investigators (Wayland and Leivo, 1958).

Red Luminescence. During the course of this work a luminescence of slow decay which is red in color was observed in the Type IIb sample

DS-2 and was subsequently found in DS-1, but was not exhibited by DS-3. The red luminescence is most easily observed in conjunction with a phosphoroscope which is rotated by hand so that the diamond may be irradiated and then viewed at will. The blue luminescence masks the red if the viewing rate is too fast.

The following properties are associated with the red luminescence. It is excited by the short ultraviolet wavelengths and is in this respect similar to the blue luminescence; when a filter is placed between the diamond and the mecury lamp to remove the short ultraviolet wavelengths from the incident beam, neither the red nor the blue luminescence is excited.

The red luminescence is temperature dependent in the sense that at room temperature it is not observed in DS-1 and is hardly observable in DS-2, but if the sample temperature is raised to 75° it is easily observed in either sample. The decay lifetime of the red luminescence decreases with increasing temperature, but the red luminescence is found to decay more slowly than the blue throughout the temperature range which has been investigated, 25 to 200° C. The red luminescence appears to be uniformly emitted throughout DS-1, but it is first observed in the blue end of DS-2. At a higher temperature both the blue end and the clear end of DS-2 are seen to exhibit the red luminescence. The decay lifetime for the red luminescence is different in the two ends of DS-2 as it is for the blue luminescence. With the sample temperature at 130° C, for example,

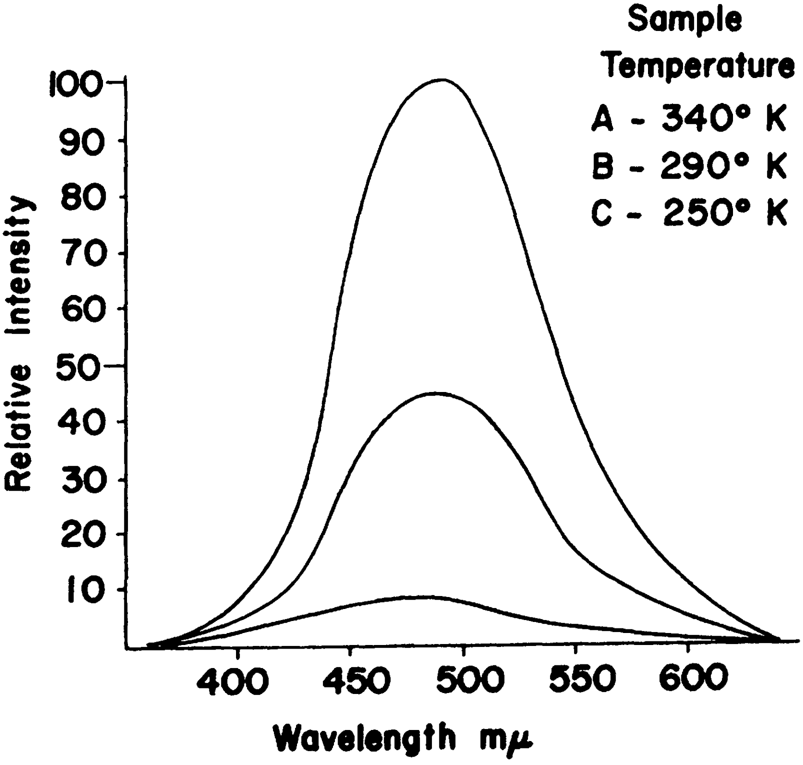

Figure 4—Phosphorescence spectrum of diamond DS-1.

the red luminescence from the blue end of the sample decays quite rapidly, and the blue end appears dark while the red glow from the clear end is plainly visible for several seconds. When the sample is viewed from the edge, the greater sample depth adds to the brightness of the glow and seems to indicate that the emission is a bulk effect. This is difficult to state unequivocally because of the small size of the sample and the high reflectivity of the diamond.

The blue luminescence is always brighter than the red at the beginning of a decay period. This is easily seen when the phosphoroscope is turned to give a viewing rate of 10 to 20 cycles per second. At this rate the blue is quite predominant though at the higher sample temperatures the color appears different to the eye. The red is observed to decay more slowly and is seen only after the blue has decayed. There seems to be still another emission process appearing at the higher temperatures, but it is so faint that no distinct color is apparent.

Because the red luminescence is frozen in at room temperature but quite apparent at higher sample temperature, and because the decay lifetime decreases with increasing temperature, it will be called phosphorescence. An effort was made to observe the red phosphorescence as thermoluminescence, but the rate of heating used thus far is insufficient.

The red phosphorescence has not appeared on the spectrograms recorded on the Beckman DK 1 spectrophotometer. Since the detector used in this work was a 1P28 photomultiplier tube, which is virtually insensitive to radiation of 700 millimicrons and yields only 10% of its maximum response at 650 millimicrons, this is not surprising.

Diamond DS-2 is a much better sample than DS-1 for demonstrating the red phosphorescence for it emits the red phosphorescence at a lower temperature than DS-1 and more brightly at all appropriate temperatures. DS-1, however, is a brighter blue luminescent sample. The red luminescence was not observed to be emitted by DS-3 from room temperature to 175° C though the same techniques and apparatus used with the other two stones were employed. All of these observations were made in a dark room, and some eye accommodation is essential for the observation of either the blue luminescence or the red.

No mention of a similar red luminescence has been found in the literature, and it would be of interest to see the result of other investigations. The present observations are too narrow in scope to classify this red phosphorescence as characteristic of semiconducting diamonds. The only mention of red luminescence which has been found in the literature was in the work of Nayar (1941) previously mentioned. This work involved phosphorescence in Type I diamond and Nayar found a faint band extending from 505 to 630 millimicrons. This does not seem to correspond to the red luminescence reported here which has been found to contain 680 millimicron emission.

SUMMARY AND CONCLUSIONS

The visible blue luminescence in the investigated semiconducting diamonds decreases with decreasing temperature, but there is essentially no shift in the spectral distribution. The decay time, which was found to be 0.7 second at room temperature, decreases with increasing temperature; at 200° K the intensity of the luminescence is zero at all recorded wavelengths. This behavior of the intensity and decay time indicates that the luminescence is a phosphorescence which becomes frozen in at sample temperatures of 200° K or less. As was pointed out in the previous discussion of luminescence, phosphorescence involves states from which transitions directly to lower energy states are forbidden. For example, consider a shallow trap just below the conduction band of a crystal. Excited carriers enter these states with loss of thermal energy to the lattice and are immobile until liberated by thermal energy supplied by the lattice. Not all excited carriers are trapped and some may quickly return to ground states by radiative recombination corresponding to fluorescence. The average time spent in a trap depends on its depth below the conduction band and the vibrational energy of the lattice which is determined by the crystal temperature. As the crystal temperature is lowered, the average time spent in traps becomes longer, and at low enough temperature a trapped carrier may not be thermally liberated. Radiative recombinations which follow the liberation of a carrier from a trap lead to the same emission spectrum observed in fluorescence.

Upon further lowering the sample temperature to 180° K a phosphorescence of the same blue color is again observed, and the intensity increases with decreasing temperature to 90° K, which is the lowest temperature employed in this investigation. Reappearance of the phosphorescence indicates that another trapping level exists which is not as deep as that responsible for the phosphorescence observed above 200° K. It is also possible that at the lower temperatures the reduced lattice vibrations decrease the probability for nonradiative recombination thus allowing relatively more radiative transitions per excitation.

In this investigation an unusual red luminescence was observed and investigated as thoroughly as available instrumentation permitted. The red luminescence was identified as a phosphorescence by the variation of intensity and decay time with temperature. It is more intense and decays more rapidly in the blue end of specimen DS-2 than in the clear end, and is excited by radiation near the fundamental absorption edge at 5.6 ev. These properties are the same in the blue phosphorescence; however, at all temperatures at which the red phosphorescence is observed it decays more slowly than the blue phosphorescence. The weakness of the phosphorescence in the investigated diamonds implies that radiative recombination is not the dominant recombination process by which excited charges return to ground states. This seems consistent with the result of a fluorescence experiment since no evidence of edge mission, emission in the ultraviolet, or light corresponding to the phosphorescence spectrum appeared on the spectrographic film after very long exposures during which time the diamond was continuously irradiated through a monochromator with radiation at 5.6 ev. Edge emission has been observed by carrier injection whereby larger minority carrier densities are possible (Male and Pryor, 1960). The absence of correlation between phosphorescence and photoconductive decay times and the different dependence on temperature of the photoconductive peaks and of the phosphorescence spectral distribution seem to indicate that a nonradiative recombination process is predominant in these diamonds.

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