

LUMINESCENCE IN SEMICONDUCTING

DIAMOND

By

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## CHAPTER I

### INTRODUCTION

Unusual phosphorescence in a diamond led to the discovery of semiconducting diamonds and the present work is concerned with investigation of this luminescence. Diamonds were classified as type I or type II in 1934 by Robertson, Fox and Martin (1) who made an extensive as well as intensive study of their various properties. A brief explanation will be given. The classification was made by optical properties in the following way: The more common type I diamond absorbs wavelengths shorter than about  $0.3 \mu$  and has certain absorption peaks in the visible region of the spectrum and in addition has several absorption bands in the infrared region. One group lies in the range from 2 to  $5 \mu$  and another is near  $8 \mu$ . Type II diamond is transparent to about  $0.225 \mu$ , has the same absorption bands as type I diamond in the 2 to  $5 \mu$  spectral region but the  $8 \mu$  group is absent, as are the absorption peaks in the visible region of the spectrum. Variations in certain properties of type II diamonds have been noted by many workers, but further subdivision of type II was not made for nearly twenty years after the work of Robertson, Fox and Martin. The present classification generally recognized, though in some respects unsatisfactory, identifies three distinct types of diamonds. These are type I and type IIA which are very good electrical insulators,

and type IIb which is a semiconductor and is under consideration in the present work.

Semiconducting diamonds have been studied by many investigators since they were first recognized due to their unusual phosphorescence as a unique type of diamond by Custers (2) in 1952. Leivo and Smoluchowski (3) established the fact that type IIb diamonds behave like impurity activated semiconductors with low impurity concentration. They found the slope of the dependence of  $k \ln R$  on  $1/T$  to be about 0.35 ev. That these diamonds are p-type semiconductors was found by Venable, Smoluchowski and Leivo (4) from experiments involving the Hall effect. In most cases the investigations involved different diamonds, and it was decided that a thorough investigation should be made of the properties of a few suitable semiconducting diamonds in order to better appraise the observations.

Two of the stones were made available by Dr. J. F. H. Custers of the Diamond Research Laboratory, Johannesburg, South Africa. One of these two which hereafter will be designated as D-0 is a rectangular parallelepiped with dimensions  $6.5 \times 3.5 \times 2.5 \text{ mm}^3$ . About three fourths of the diamond is clear or water white, one end being slightly blue. The second diamond, which will be called the Chip, is an irregular and somewhat cigar shaped unpolished stone and has only three surface regions which are smooth. The Chip is more distinctly blue and has a higher conductivity than D-0. The third type IIb diamond is a marquise cut stone from the U. S. National Museum, Washington, D. C. It is also a blue stone and will be called the Blue Marquise.



## I. Optical Transmission Studies

Stein and Leivo (5,6,7) studied the optical transmission of the diamond D-O from the fundamental cut-off at about  $0.23 \mu$  to  $13 \mu$ . A less intensive study was made of the Chip which is not well suited to optical studies since it is irregular in shape.

After the initial rise in the region of optical cut-off near  $0.23 \mu$  the transmission curve for the blue end shows a gradual increase in transmission to about  $0.45 \mu$  and then a gradual decrease with increasing wavelength to the near infrared. The transmission in the clear end of the sample differs from this by steadily increasing from the cut-off region to about  $1.2 \mu$  and remaining essentially constant until a series of absorption peaks begins around  $2.5 \mu$ . Thus the transmission curve for the blue end of the diamond may be qualitatively described as being concave downward from  $0.23 \mu$  to  $1.5 \mu$  and the transmission curve for the clear end is roughly linear in this same spectral region. Infrared absorption peaks in the blue end of D-O are somewhat more pronounced and some absorption peaks appear in the spectrum of the blue end which are absent in the clear end. The extra absorption peaks in the blue end were found by Stein to occur at  $2.43$ ,  $3.40$ ,  $3.56$  and  $4.07 \mu$ . Clark, Ditchburn and Dyer (8) have found similar peaks for type IIb diamond at  $2.44$ ,  $3.6$  and  $4.05 \mu$ . These absorption peaks together with a few others of less intensity, which are also found in this spectral region, are characteristic of type IIb diamond. The absorption spectrum for the clear end of D-O is thus tending toward that of type IIa diamond. The  $8 \mu$  absorption band which is characteristic

of type I diamond is not present in either type IIa or type IIb diamonds.

## II. Rectification and Photoeffects

Bell (9,12) investigated rectification and photoeffects. Most of his work was on the Chip; however, some observations were made on the other two samples. The direct current measured as a function of the applied potential followed the usual rectification curve rather well within certain limits of potential. The current density equation which is derived from the theory of a rectifying barrier is of the form

$$j = j_s [ e^{qV/kT} - 1 ]$$

in which  $q$  is the electronic charge,  $V$  is the applied potential,  $k$  is the Boltzmann constant, and  $T$  is the temperature in degrees Kelvin, and finally

$$j_s \propto e^{-\phi/kT}$$

$\phi$  being the absolute value of the difference between the Fermi levels in the metal probe and the semiconductor. Derivation of the above relationships is not appropriate to this paper and may be found in the work of Bell (9) or in many current texts on semiconductors. The expression for  $j_s$ , the reverse saturation current density, implies great sensitivity to variations in  $\phi$ . That this does not in general prove to be the case was discovered by Meyerhof (10) and subsequently explained by Bardeen (11). Bardeen proposed that surface states could be formed with density such that the potential barrier was formed between the surface of the semiconductor and the interior region and that rectification would thereby be almost

independent of the metal used for the probe. Bell indeed found this to be the case with the diamond. He therefore concluded that rectification was due to the barrier set up by surface states on the diamond. Bell also found that the characteristics vary over the surface of the diamond, implying inhomogeneity of surface states. The exact nature of these states is still unknown.

This same inhomogeneity in the surface characteristics also appeared in the investigation of Bell on the photovoltaic effect, some regions of the diamond giving opposite polarity to that at other regions. He did find a spectral dependence for photovoltaic effect. A peak response was found at  $0.44 \mu$  and  $0.64 \mu$  and a minor peak occurred at  $0.89 \mu$ . In the ultraviolet region of the spectrum the peak response occurred at  $0.23 \mu$  which is the region of optical cut-off for the diamond. No photovoltaic effect was found using excitation from  $1.3 \mu$  to  $12 \mu$  at room temperature.

Photoconductivity varied when different regions of the diamond were investigated, but a maximum response was obtained in all regions of the diamond at excitation wavelengths  $0.63 \mu$  to  $0.64 \mu$ , and in certain parts of the clear end of diamond D-0 a minor peak occurred at  $0.89 \mu$ . In the ultraviolet spectral region two peaks were found when the whole diamond was irradiated. These peaks were at  $0.224 \mu$  and  $0.228 \mu$ . The room temperature resistivity is about  $65 \text{ ohm cm}$  in the blue end of D-0 and  $3.6 \times 10^5 \text{ ohm cm}$  in the clear end.

### III. Hall Effect

Young (13) studied the Hall effect in diamond D-O and found p-type conductivity. The slope of the plot of  $k \ln R_H T^{3/2}$  versus  $1/T$  was 0.35 ev.  $R_H$  is the Hall constant,  $T$  the Kelvin temperature and  $k$  is the Boltzmann constant. The mobility value which Young computed on the basis of the measured resistivity and the Hall constant was too low; however, it was subsequently found by Wayland (18), another member of this laboratory, that when more contact pressure was used on the potential probes that Hall measurements led to a value for the hole mobility of  $1300 \text{ cm}^2/\text{volt-sec}$ . Austin and Wolfe (14) have obtained a value of  $1550 \pm 150 \text{ cm}^2/\text{volt-sec}$  for the hole mobility in a semiconducting diamond specimen which had a room temperature resistivity of 270 ohm cm.

### IV. Photoconductivity

Johnson (15,16) investigated photoconductivity and its temperature and directional dependence in the diamond D-O. Johnson found that the photoconductivity is a linear function of the electric field and also of the intensity of illumination. The latter implies that the lifetime of the majority carriers does not change with increasing light intensity. At room temperature, peak response in the ultraviolet was found at 224 m $\mu$  and 228 m $\mu$ , corresponding to 5.58 ev and 5.45 ev respectively. At this temperature a broad maximum was found near 0.6  $\mu$  and two very weak maxima were at 1.46  $\mu$  and 1.75  $\mu$ . No photoconductivity was found in the spectral regions 245 m $\mu$  to

350 m $\mu$  and 5.1 to 12  $\mu$ . Johnson found that the photoconductivity increased with increasing temperature up to 400° K with no appreciable increase in the half width of the peaks. Above 405° K the signal to noise ratio became intolerable. The photoconductivity peaks were found to decrease in magnitude and shift to shorter wavelengths as the temperature of the diamond was lowered, this effect becoming observable at 250° K, with the 0.6  $\mu$  peak appearing at 0.59  $\mu$ . Ultraviolet induced photocurrent was not measurable at temperatures less than 240° K. At 223° K the 0.6  $\mu$  peak appeared at 0.58  $\mu$  and two new peaks, 1.84 and 2.02  $\mu$ , were resolved. There was also indication of a 1.24  $\mu$  peak. At 150° K peaks appeared at 0.52, 0.92, 1.64 and 2.16  $\mu$  with a slight indication of a 1.24  $\mu$  peak. Measurable photocurrent was found at 2.4  $\mu$  whereas it began at 2.08  $\mu$  when the diamond was at room temperature. At 127° K the 0.52  $\mu$  peak was not measurable. The dominant peak was at 0.88  $\mu$  with ancillary peaks at 1.68  $\mu$  and about 2.1  $\mu$ , the last of these three being comparatively broad.

When measurements were made only on the blue end or the clear end of the sample, Johnson found that at room temperature there was a 0.6  $\mu$  peak in the blue end and a 0.66  $\mu$  peak in the clear end. At 148° K the peak in the blue end was essentially unchanged and no infrared peaks appeared, while the peak in the clear end had been reduced in magnitude, and some of the infrared peaks appeared. These peaks in the clear end were at 0.7, 1.28, 1.56 and 1.74  $\mu$ . At 123° K photocurrent was reduced so much that it was not measurable. In this group of measurements the diamond had been investigated by sections, each of which represented about one sixth of

the length of the diamond, and not all of these last peaks appeared in each section.

Regarding photovoltaic effects, Johnson found that the blue end of the diamond gave the greatest response to excitation of  $0.4 \mu$  wavelength but that the spectral distribution of photovoltage on the clear end is very similar to that for photocurrent.

Johnson concludes that the photocurrent per incident photon is much greater for the peaks found in the ultraviolet region of the spectrum than for the peaks found at longer wavelengths.

#### V. Carrier Lifetimes

Wayland (17,18) studied carrier lifetimes by three methods. Two of these methods were beset with difficulties which were insurmountable since the sample itself could not be modified. The pulse response method, however, yielded information of interest to the present study.

Wayland at first used an  $8 \mu$ sec light pulse derived from a spark gap as a light source. Photocurrent was determined by recording on an oscilloscope the voltage across a fixed resistance which was in series with the diamond. One pulse and the subsequent decay constituted a complete experiment. Photographic record of the curve was made, and from this the carrier decay lifetime could be determined. Wayland found the decay lifetime to be 0.25 seconds at room temperature. This value changed to 0.4 seconds when the diamond was cooled to  $260^{\circ}$  K. These measurements were made using large painted contacts on each end of the diamond.

These values are very much longer than one would expect

for free carrier lifetimes in a natural semiconductor. The addition of a steady ambient tungsten light had no effect on the decay lifetime. Wayland felt that trapping by "deep lying" traps might be the cause of this long decay constant, and extended his work in order to investigate trapping.

First, Wayland used a tungsten lamp to excite photocurrent. The resulting decay curve was the sum of several exponentials, but if treated as an exponential curve, the corresponding decay lifetime was thirty nine minutes. Wayland then repeated the experiment using monochromatic light to correspond with the photovoltaic peak response found in the blue end at  $0.44 \mu$  and the photoconductive maxima at  $0.63$  and  $0.8 \mu$ . The respective decay lifetimes were thirty nine minutes, six minutes and about thirty seconds. This indicated that the decay lifetime found with full spectrum excitation was due principally to the lifetime associated with the  $0.44 \mu$  peak. These times are possibly majority carrier lifetimes or recombination times. Using the full spectrum of a mercury arc lamp which contains photons of sufficient energy to excite carriers across the forbidden energy gap and once more assuming the decay curve to be a true exponential, the lifetime was found to be eighty four minutes. The decays associated with the  $0.224$  and  $0.228 \mu$  photoconductive peaks were each of this order. Other decay times obtained were  $125$  and  $800 \mu\text{sec}$ , and  $12$  minutes. All of these values associated with excitation in the short ultraviolet undoubtedly include trapping of carriers and as such are not free carrier lifetimes. From the rise time of the photocurrent using light from a short duration spark a lifetime of  $9 \mu\text{sec}$  was obtained, and is possibly largely independent of trapping.

## VI. Scope of the Present Work

The purpose of the present work has been to investigate luminescence phenomena in the diamond. Although some of the fore-named investigators had made some observations regarding luminescence no detailed study had been made. In particular it should be remembered that type IIb diamond was discovered by Custers (2) as a result of an unusual luminescence of slow decay, which could be excited by a "full spectrum" mercury arc lamp. He identified this luminescence as phosphorescence. Since no data on the temperature dependence of the intensity and decay time of the luminescence was available it was felt desirable in the present work to obtain this information and determine whether phosphorescence or slow fluorescence is the process giving rise to the light observed by Custers, and observed subsequently by many people in diamond studies. This knowledge would indicate the process by which excited electrons and holes return to the ground states and would help to determine the proper model for type IIb diamond.



## CHAPTER II

### A BRIEF DISCUSSION OF PHOTOLUMINESCENCE

Preceding the discussion of the present work, a discussion of luminescence is needed to present clearly the processes implied by the 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 (1). 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. Figure 1 shows the energy levels assigned to the unspecified system under consideration. The levels G and E represent respectively the ground state and a

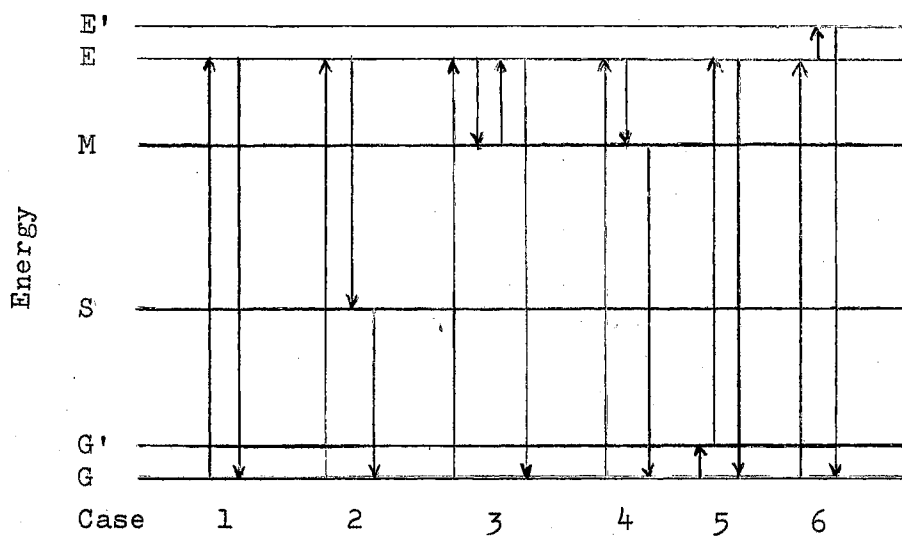


Fig. 1. Energy level diagram illustrating six processes involving radiant emission resulting from photon absorption.

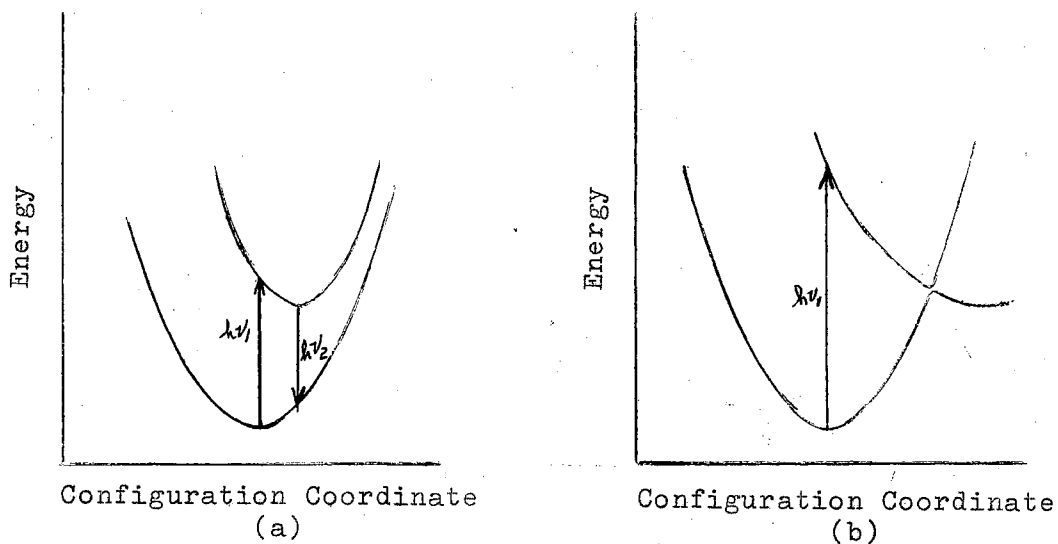


Fig. 2. Possible arrangement of normal level and the level of an exciton at rest. In a fluorescent emission follows excitation, but in b no fluorescence can occur.

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 such 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 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 (19) 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 (20). For the purpose of this work the question is philosophical and need not be further considered.

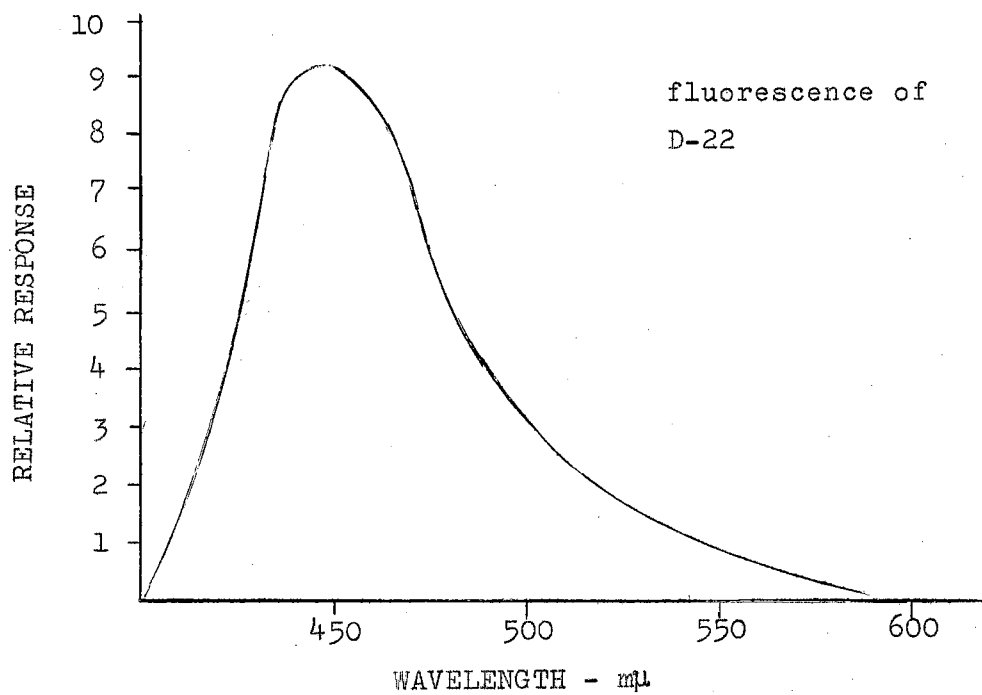
Fluorescence is not entirely inconsistent with extended lifetimes. Suppose the transition M-G is not extremely unlikely. Indeed, this event might be more probable than the reabsorption of the energy required to permit the transition M-E. In this case a fluorescence would be emitted which has a longer than normal lifetime and is called slow fluorescence by Pringsheim (19). 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 all but 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 wavelengths 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

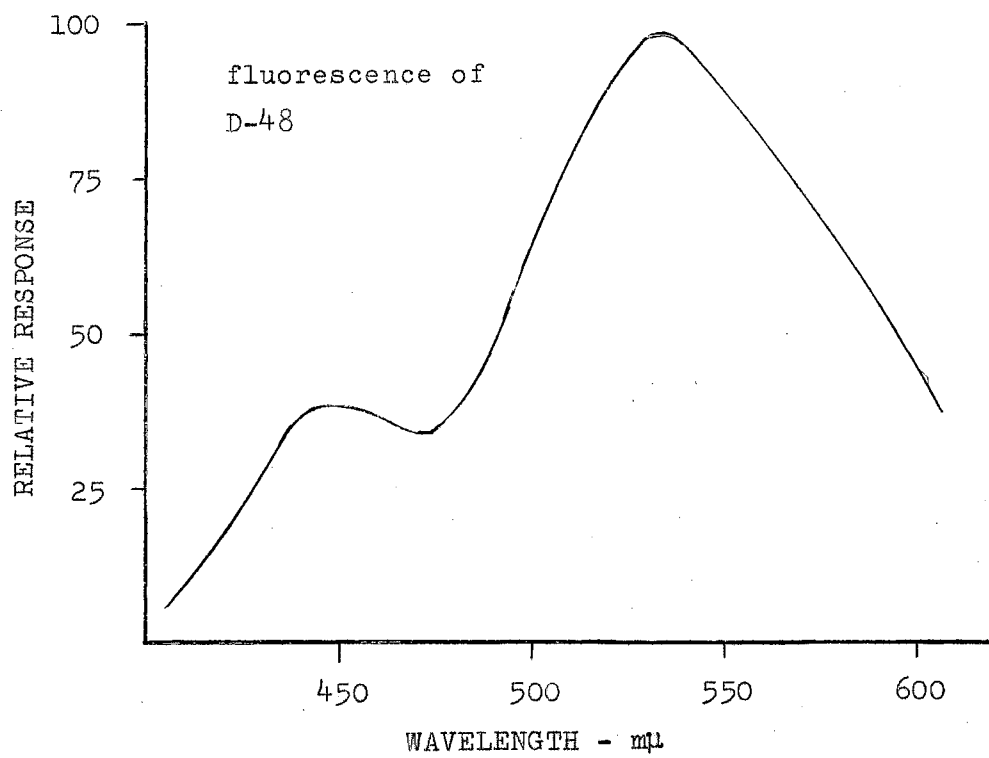
shorter than the exciting wavelength.

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.

The Stokes shift is generally observed in solid fluorescent samples. Type I diamond demonstrates the Stokes shift nicely. Figure 3 displays the spectrum of the fluorescence of two type I diamonds. The fluorescence was excited by a narrow band of radiation from a mercury arc lamp. The band was centered at 365 m $\mu$ . A qualitative explanation of the Stokes shift and indeed the fact that so many substances do not exhibit fluorescence is obtained in connection with the configuration coordinate curve which is exemplified by the curves in Fig. 2. The abscissa is the configuration coordinate which represents the configuration of the atoms which determine the energy of a state. The ordinate represents the energy of the system. By the Franck-Condon principle transitions are vertical, but during the lifetime in the excited state readjustment of the atoms takes place, and thermal equilibrium is established. Emission then takes place on the average from the energy minimum of the upper curve thus giving rise to the longer wavelength of emission. If the two curves cross in the manner indicated in part b of Fig. 2 radiationless transition to the ground state will occur, all of the energy being absorbed by the system as thermal energy.



(a)



(b)

Fig. 3. Fluorescence in type I diamonds.

## CHAPTER III

### EXPERIMENTAL PROCEDURE AND RESULTS

#### I. Fluorescence

In order to observe fluorescence a means must be provided to separate the exciting wavelengths from the fluorescence. Typically a narrow band of wavelengths to excite fluorescence is provided by interposing a narrow band pass filter or monochromator between the sample and a suitable light source. In the case of type I diamond the fluorescence may be excited by light from a mercury arc lamp passed through a Corning number 5840 absorption filter. This filter transmits wavelengths from 300 to 400 m $\mu$  with maximum transmission near 365 m $\mu$ . Cutoff is virtually complete at 400 m $\mu$  and the fluorescence is therefore not masked by visible radiation from the mercury lamp.

In the course of the present work fluorescence spectra were obtained for several type I diamonds. Two of these are reproduced in Fig. 3. The sample D-22 is seen to exhibit blue emission while D-48, which appears green when the fluorescence is observed visually, emits blue as well as green light. The curves are typical of type I diamond, and were obtained using a Beckman DK 1 spectrophotometer equipped with a fluorescence attachment. In order to maintain a tolerable signal to noise level it was necessary to use somewhat

large slit openings on the monochromator of the instrument, and the peaks obtained by Dyer and Matthews (21) were not resolved.

It was desired to determine whether the type IIb samples exhibited a fluorescence when irradiated with this same near ultraviolet light (365 m $\mu$ ). No response on the DK 1 was found to indicate such fluorescence in type IIb diamond. This experiment was performed on diamond D-0 and the Chip. Dyer and Matthews (21) also found no indication of such fluorescence for type IIb diamond. This negative result is not too surprising in view of the difference in the absorption spectra of type I and type IIb diamond (8,5). The absorption spectrum for type I diamond has sharp absorption peaks at approximately 414, 408 and 403 m $\mu$  as parts of a strong band 0.7 ev wide. Type IIb diamond shows no such sharp change in the absorption coefficient in this spectral region. It might further be mentioned that type IIa diamond, although once thought not to exhibit fluorescence (22), has been found to exhibit a weak fluorescence analogous to that found in type I diamond (8).

The possibility of emission associated with excitation at wavelengths corresponding to the fundamental absorption edge was investigated. Light from an iron arc was passed through a quartz monochromator and directed onto the sample. A Jarrell Ash grating spectrograph equipped with a 35 mm camera was used to record the spectrum. The film used was type 103a which was procured from the Eastman Kodak Company. Exposures as long as twelve hours failed to produce anything except the iron spectrum which passed through the monochromator as scattered light. It was concluded that any emission from the diamond was of extremely low intensity if it



existed at all. It should be noted that such fluorescence would not necessarily be expected to exist. Seitz (23) points out that fluorescence has not been observed unambiguously to accompany absorption in the fundamental bands of ideal crystals, and he uses this as an indication that the exciton level curve which he has proposed (Fig.2b) is generally applicable.

## II. Phosphorescence and Slow Fluorescence

Phosphorescence and slow fluorescence are typically described as luminescence with decay lifetime of a millisecond or longer, and are therefore observable after the source of excitation has been removed. In the case of 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 which is illustrated in Fig. 4 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.

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.

It became apparent early in the course of the investigation that it was most important to find a light source with strong emission in the wavelength range 220 to 235 m $\mu$ . The two sources most thoughtfully considered were the mercury arc lamp and the iron arc. The spectrum of iron is rich in ultraviolet lines compared to the mercury spectrum; however, the mercury lamp is found to excite much brighter luminescence in the type IIb diamonds than the iron arc even when currents up to 4 amperes are used in the iron arc. The mercury lamp used was a Type 7606, 140 watt, Hanovia lamp which is ac operated.

In the course of this investigation both photoelectric and photographic detection methods were utilized. The spectrograph used was a Jarrel Ash grating spectrograph which has 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. At a given temperature all films tend to lose sensitivity when light levels become too low. To give a qualitative

explanation of this, a brief account of a theory expressed by Mott and Gurney (24) will be given. During the photographic exposure photoelectrons are liberated to the conduction band from the halide ions in the silver halide crystal grains. They migrate to silver specks found in general on the grain surface. There they are captured and in turn set up an electric field which attracts a current of silver ions. If the time between arrival of photoelectrons is too long, corresponding to very low light levels, the electrons may be thermally liberated from the silver specks and subsequently recaptured by halide atoms, thus in effect being wasted. It is possible therefore to have no net exposure when light levels are too low.

It is not difficult to properly position an intense light source on the optic axis of a spectrograph in such a way that suitable intensity levels are obtained at the film location. When the light source is faint, as in the case of the luminescent type IIb diamond, it is expedient to find the optimum position of the sample by a simple procedure to be described. A tungsten lamp is placed at the position normally occupied by the camera, thus reversing the optical path of the system. It is 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 may be positioned so that green light is emitted from the slit, thus matching the region of greatest eye sensitivity.

The above precautions were observed in locating the optimum position for the sample in front of the spectrograph. A Becquerel type phosphoroscope which gave equal on-off time for observation of luminescence and which operated at 120 cycles per second was

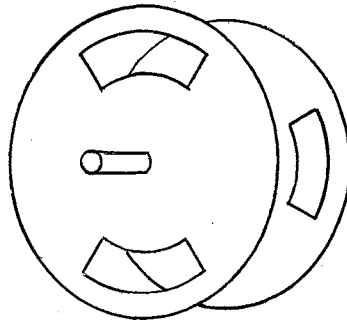


Fig. 4. A simplified representation of a Becquerel type phosphoroscope.

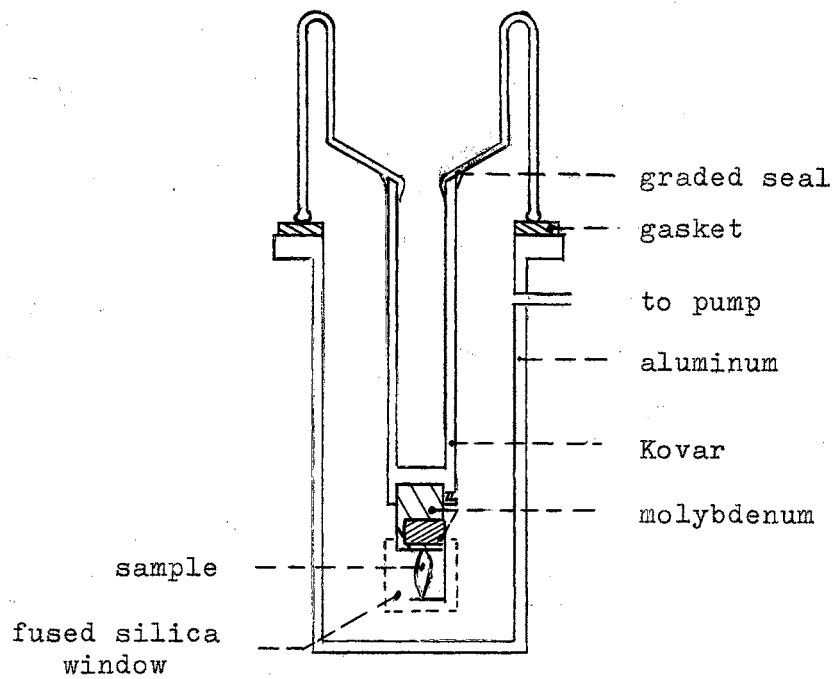


Fig. 5. Vacuum sample mount

placed in position surrounding the sample. Shields as described previously were installed to prevent stray light from entering the spectrograph. The sample was then irradiated with the mercury lamp previously described. 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. The Chip was used since it exhibits brighter luminescence than diamond D-O. 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. Possibly an experiment utilizing a low dispersion prism spectrograph would be successful. Nayar (25) in 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.

The Beckman DK 1 spectrophotometer previously mentioned was found to be quite sensitive in the range of wavelengths 220 to 700 m $\mu$ . An arrangement was devised in which the chopped light from the luminescent sample ( the Chip) was focused on the entrance slit of the monochromator of the DK 1, and by adjusting the instrument

to obtain maximum sensitivity the spectrum of the luminescence was obtained. The signal to noise ratio was unfavorable, and it was necessary to use a large slit width in order to obtain any response.

In chapter I the desirability of determining the temperature dependence of the luminescence was indicated. The experiment described in the preceding paragraph was repeated with the addition of an apparatus to allow the sample to be cooled. This equipment is illustrated in Fig. 5. Spectrograms of the luminescence were obtained at several temperatures. Three of these are reproduced in Fig. 6. It is interesting to note that no appreciable shift occurs in the maximum, though the intensity decreases sharply with decreasing temperature. In contrast to this behavior the photoconductivity was found to show a definite shift toward shorter wavelengths as the sample temperature was lowered. The luminescence with the sample at  $200^{\circ}$  K has essentially zero intensity. As the sample temperature is further reduced the intensity begins to increase, and at  $90^{\circ}$  K the intensity is estimated to be half that at  $300^{\circ}$  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 slow fluorescence. The fact that the intensity increases with decreasing temperature in the range  $90^{\circ}$  K to  $180^{\circ}$  K is an indication that a new luminescent center 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 lifetime short enough, say less than 100  $\mu$ sec, would not be recorded. As was mentioned in a preceding paragraph, 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 (2).

Some visual observations regarding the phosphorescence in diamond D-0 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, as Stein (5) mentions, 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 D-0 and the Chip 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 dc 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  $0.7 \pm 0.1$  sec, the large error factor being due to noise in the circuit. It seems doubtful

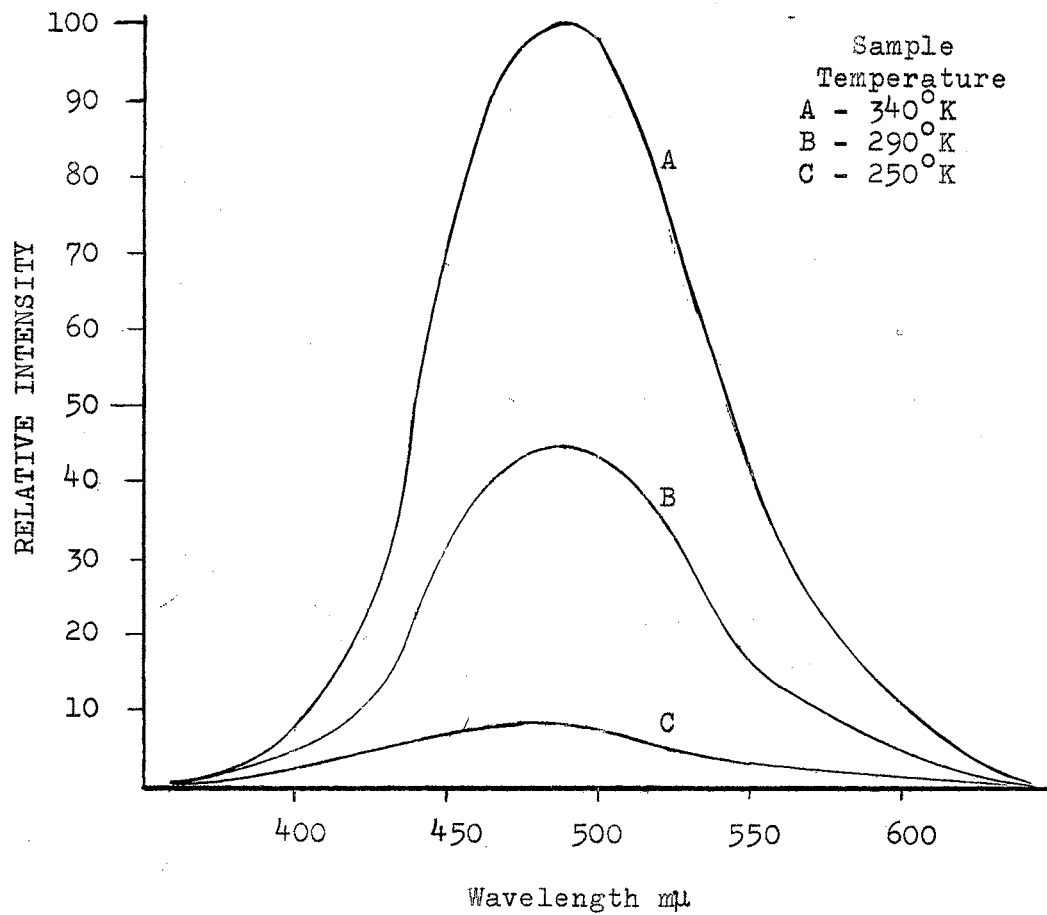


Fig. 6. Phosphorescence spectrum of the Chip.



that there is a direct correlation with the 0.25 second carrier lifetime which Wayland obtained using the 8  $\mu$ sec pulse.

### III. 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 D-0 and was subsequently found in the Chip, but has not been found to be exhibited by the Blue Marquise. 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 property similar to the blue luminescence, for when a filter is placed between the diamond and the mercury lamp in order 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 the Chip and is hardly observable in D-0, but if the sample temperature is raised to 75° C 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 the Chip, but it is first observed in the blue end of D-0. At a higher temperature both the blue end and the clear end

of D-O are seen to exhibit the red luminescence. The decay lifetime for the red luminescence is different in the two ends of D-O as it was for the blue luminescence. With the sample temperature at  $130^{\circ}$  C, for example, 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 phosphoscope 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 spectrographs

which have been obtained. These were recorded on the Beckman DK 1 spectrophotometer, and the detector used in this work was a 1P28 photomultiplier tube which is virtually insensitive to radiation of 700 m $\mu$  and yields only 10 % of its maximum response at 650 m $\mu$ , so that this is not surprising.

Diamond D-0 is a much better sample than the Chip for demonstrating the red phosphorescence for it emits the red phosphorescence at a lower temperature than the Chip and more brightly at all appropriate temperatures. The Chip, however, is a brighter blue luminescent sample. The red luminescence was not observed to be emitted by the Blue Marquise 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 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 (25) previously mentioned. This work involved phosphorescence in type I diamond, and Nayar found a faint band extending from 505 m $\mu$  to 630 m $\mu$ . This does not seem to correspond to the red luminescence reported here which has been found to contain 680 m $\mu$  emission.

#### IV. TRIBOLUMINESCENCE

In the early literature the observation is made that most diamonds exhibit triboluminescence. Twenty two diamonds, some of type I and some type IIa, and the three type IIb diamonds were checked and found without exception to exhibit triboluminescence. The intensity varies between samples and is in every case quite low; therefore, observation of this effect must be made in a dark room with thorough eye adaptation. Spectral analysis seems out of the question at this time.

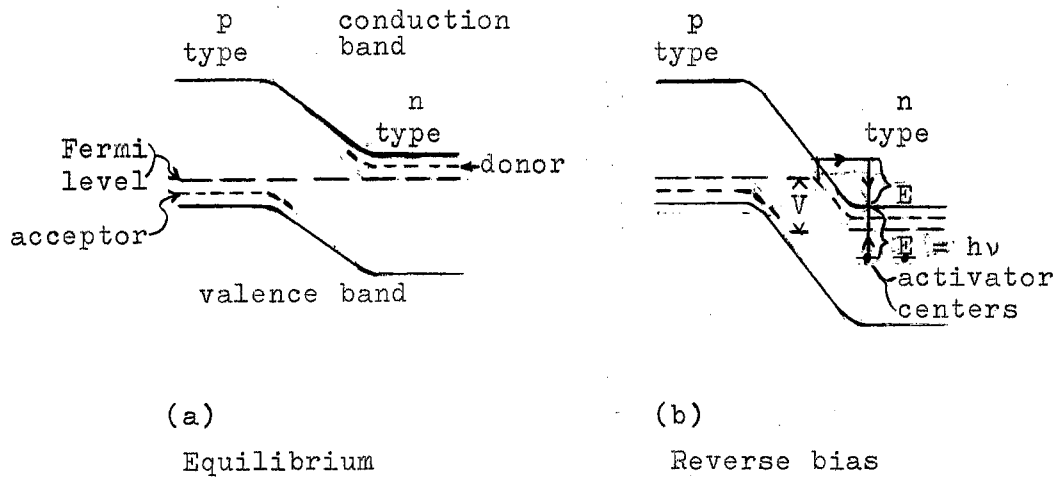
#### V. ELECTROLUMINESCENCE

Electroluminescence, hereafter indicated by EL, is generally believed to be explained by two processes, and the corresponding EL is called intrinsic or carrier-injection EL (26). In intrinsic EL, activator centers are emptied by impact of electrons in the conduction band. These impact electrons are supposed to be liberated thermally or by electric field from shallow traps just below the conduction band. Those which are in regions of the crystal where high electric fields exist may then be sufficiently accelerated to ionize the activator centers upon collision. Sufficiently large electric fields may be found at a p-n junction or a metal to semiconductor contact in reverse bias. The spectrum of such EL is generally similar to the photoluminescence spectrum.

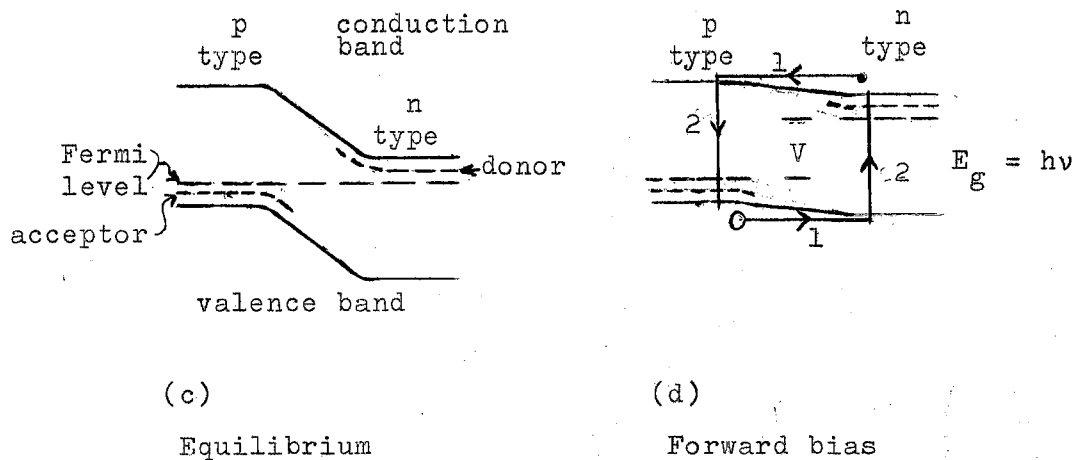
Carrier-injection EL can occur as a result of injecting minority carriers into a semiconductor. This corresponds to a rectifying junction in forward bias. Direct recombination of

electrons and holes leads to "edge emission" which is so called because the associated wavelength lies at the edge of the fundamental optical absorption band. Since recombination is greatly facilitated by the presence of a third body which may be a crystal imperfection or a crystal surface state, activated emission normally predominates over edge emission. Haynes and Briggs (27) found EL corresponding to edge emission in both germanium and silicon. Figure 7 represents the two processes. Effects which involve the use of photon excitation and application of an electric field ( electrophotoluminescence ) such as the Gudden and Pohl effect are not being considered.

EL observed in the investigated samples D-O and the Chip is obtained with a negative probe. This corresponds to forward bias and is indicative of carrier-injection EL. It was found that the efficiency of EL varied as the probe was moved over the surface of either sample. Some regions exist where a comparatively bright luminescence is obtained with currents of less than one milliamperere, but other regions are found in which currents of one and a half milliamperere yield only feeble luminescence. Observation of EL under a microscope shows the luminescence to be confined in general to a bright spot at the probe; however, one region was found on D-O which gave finger-like luminescent streaks extending outward from the probe. Thus we see further indication of inhomogeneity of surface states which was observed in the photovoltaic and photoconductivity investigations.



High electric fields exist in reverse biased p-n junctions. A thermally liberated electron in the junction may be accelerated sufficiently to obtain energy  $E$  necessary to ionize an activator center upon collision.



With the junction in forward bias, majority carriers cross the junction [step 1 in d] to become minority carriers. In step 2 they combine with majority carriers.

Fig. 7. P-n junction in equilibrium ( a and c ), reverse bias ( b ) and forward bias ( d ).

## VI. SUMMARY AND CONCLUSIONS

The temperature dependence of the intensity, decay lifetime and the spectral distribution of the visible blue luminescence in semiconducting diamond was recorded in this investigation. Three of the spectrograms obtained using the sample previously identified as the Chip are reproduced in Fig. 6. It was found that the intensity of the luminescence 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. When the sample temperature is reduced to  $200^{\circ}$  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 phosphorescence which becomes frozen in at sample temperatures of  $200^{\circ}$  K or less. This is explained in terms of the discussion of luminescence in Chapter II. There it was pointed out that 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 by loss of thermal energy to the lattice, and are immobile until liberated by thermal energy supplied by the lattice. Not all excited carriers will be trapped and some may quickly return to ground states by radiative recombination corresponding to fluorescence. The average time

spent in a trap will depend 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.

It was found that upon further lowering the sample temperature to  $180^{\circ}$  K a phosphorescence of the same blue color is again observed, and the intensity increases with decreasing temperature to as low as  $90^{\circ}$  K which is the lowest temperature at which observations were made during this investigation. The reappearance of the phosphorescence indicates that another trapping level exists which is not as deep as that which is effective in the phosphorescence observed at sample temperatures above  $200^{\circ}$  K. It is also possible that at the lower temperatures the reduced lattice vibrations might reduce 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 D-0 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 the fluorescence experiment, for no evidence of edge emission, emission in the ultraviolet or light corresponding to the phosphorescence spectrum appeared on the spectrographic film after very long exposures during which the diamond was continuously irradiated through a monochromator with radiation at 5.6 eV. The absence of correlation between phosphorescence decay lifetime and Wayland's (18) measurements for photoconductive decay times, and the different behavior under changes in sample temperature of the photoconductive peaks and the phosphorescence spectral distribution also seem to indicate that a nonradiative recombination process is predominant in these diamonds.

Triboluminescence was found in each of the investigated semiconducting diamonds. Electroluminescence studies gave further indication of inhomogeneous surface states, this condition having been observed previously by Bell and Leivo (12) in photovoltaic studies. The electroluminescence is blue and may be obtained by using a metal probe or painted contact but always in forward bias, and it therefore corresponds to carrier injection electroluminescence.

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