DETERMINATION OF ENERGY LEVELS IN SEMICONDUCTING DIAMOND BY OPTICAL TRANSMISSION METHODS

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DETERMINATION OF ENERGY LEVELS IN SEMICONDUCTING DIAMOND BY OPTICAL TRANSMISSION METHODS

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PREFACE

The exploitation of optical phenomena yields valuable information in solid state physics, especially in the field of semiconductors. The extensive research being carried on today in this field can be traced largely to the recent impact of transistors in electronics.

When a semiconducting type of diamond was discovered, physicists began considering a mechanism that might possibly be responsible for conduction in the rare diamonds. The present study contributes to the existing knowledge of semiconducting diamond through the investigation of their optical absorption, birefringence, and phosphorescence properties.

Some limitations encountered in the present study are: (1) The natural occurrence of diamond permits no control over impurity content. (2) Diamonds are not too readily available for studies of this nature, and the type of diamond being extremely rare limited the study to two specimens. (3) In general, optical instruments available today have not been designed for quantitative work on solid materials.

I am indebted to Dr. W. J. Leivo for his valuable guidance and for making the diamonds available to me for study. I would also like to express my appreciation to Dr. J. F. H. Custers of the Diamond Research Laboratory, Johannesburg, South Africa, for the loan of the diamonds; to the Research Foundation, Oklahoma Agricultural and Mechanical College, who, through a contract with the Air Research and Development Command, has given financial aid to the study; to Dr. H. E. Harrington and other

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INTRODUCTION

In the two years since Custers (1) pointed out a type of diamond exhibiting electrical conducting properties, interest in the unusual diamonds has been mounting. Both in this country and abroad, groups have undertaken the study of these diamonds.

Diamond is normally an insulator with a resistivity in the neighborhood of 10^{14} ohm-cm. The diamonds with conducting properties have resistivities in the range from 25 to 10^{8} ohm-cm.

Some experimental data has been published on conducting diamond. The dependence of k ln r on 1/T yields a slope of .35 ev at room temperature, where k is the Boltzmann constant, r is the resistivity, and T is the absolute temperature (2, 3). A plot of the Hall coefficient vs 1/T also yields a slope of .35 ev (4). Custers (5) plotted ln r against 1/T and computed a value of .7 ev from the equation $r = A \exp \mathcal{E}_G/2kT$, where A is a constant, $\mathcal{E}_G$ is the energy gap. Dyer and Wedepohl (6) found the slope of 2k ln r against 1/T gives a slope of .77 ev. Neither of these values can be accurately stated as the activation energy without further evidence. There has been a tendency to consider .35 ev as the activation energy, especially since it so nearly coincides with the hydrogen-like model value of a group III or group V impurity in diamond. Using the value of 5.7 for the dielectric constant and knowing the majority of the carriers are holes from Hall measurements (7, 4, 3), a value of .4 ev is deduced from the hydrogen-like model for a group III impurity.

A study of the optical absorption properties of the semiconducting diamonds could yield more information on the activation energy and hence on the imperfections responsible for the high electrical conductivity in these diamonds.

An activation energy of .35 ev should give rise to an absorption in the infrared around 3.5 microns. If the activation energy is closer to 0.7 ev then the absorption should appear at approximately 1.8 microns.

A preliminary report of the present study was given at the March, 1956 meeting of the American Physical Society (8). Simultaneously Austin and Wolfe (3) at General Electric in England reported on the infrared absorption properties. Both studies list unusual infrared absorption in the semiconducting diamond. Actually there is a continuum of absorption in the infrared with peaks superimposed.

The present study covers the optical absorption properties of semiconducting diamond from fundamental cutoff in the ultraviolet to 13 microns in the infrared. The instrumentation employed in the study includes a near infrared instrument with a PbS detector. This instrument is especially valuable for study of the region between 1 and 2 microns. The study of the larger specimen used indicates the diamond is not homogeneous with regard to the absorption in the infrared. Neither is it homogeneous in color, nor in the patterns observed under a polarizing microscope. One end of the diamond is distinctly more blue than the other, and exhibits unusual absorption in the infrared. The blue end also shows a cross-hatched pattern under the polarizing microscope. The other end of the diamond is more free of color and exhibits less strain.

The fundamental absorption begins occurring at 236 millimicrons and essentially complete cutoff is reached at 225 millimicrons. This is true of both specimens, as well as both ends of the larger specimen. Both ends of the larger specimen absorb some in the ultraviolet through the visible and into the infrared. The blue end of the larger specimen exhibits a greater continuum of absorption beginning at .6 microns and extending to 4.5 microns. Peaks occur in this absorption at 2.43, 3.56, and 4.15 microns, the peak at 3.56 microns being the largest.

It is believed the extra absorption in the infrared is due to chemical impurities. The high electrical conductivity may then be a result of both chemical impurities and dislocations.

CHAPTER II

SURVEY OF LITERATURE

General Information

There are optical properties of diamond which have been observed for a number of years. The sparkling beauty of diamond was probably first revealed by Louis deBequen, a fifteenth century artist in Burgess (9). This beauty became apparent after rubbing two such materials together for an extended length of time. The brilliant, colorful flashes of diamond, when cut as a gem, are a result of its high index of refraction and its high dispersive power.

In 1797, an Englishman, Smithson Tennant, showed by experiment that diamond is an elemental form of carbon (10). By burning diamond in an atmosphere of pure oxygen he found the product to be carbon dioxide without residue. Diamond is thermodynamically a less stable form of carbon than graphite, as evidenced by the fact that it begins changing to graphite when heated to 900°C (11).

The hardness of diamond is a result of atoms sharing electrons with four neighbors in such a way to build up great stability. The diamond crystal is made up of carbon atoms lying on two equal interpenetrating face-centered cubic lattices. The unit cell contains two atoms, one in each lattice. Interatomic distance is 1.54 A. The lattice constant is 3.56 A (see Figure 1) (12). Although diamond is very dense and is the hardest substance known, its atoms are not packed in the closest possible arrangement (10).

Diamonds are somewhat slippery to handle since their surfaces seem to have the property of being slightly oily. This property is a problem to the research scientist attempting to understand the properties of diamond, but it is a property which has been capitalized upon in mining as a method of sorting diamond from the other materials coexisting with diamond in its natural location (13).

Diamonds are mined from pipes of igneous origin, where they are found in diamondiferous soil. It often takes four tons of this soil to yield one carat of diamond (13). They are also found in alluvial deposits in river beds. Some may have their origin in meteorites and are thus scattered to widely diversified areas.

The first supply of diamonds came from India, then the emphasis shifted to Brazil. In the 1860's diamond was discovered in South Africa, and at present the Premier Mine, at Cullinan, South Africa, produces about 100,000 carats per month (13). This mine is now becoming well known for the production of semiconducting diamonds. Such diamonds are rare, having an occurrence of less than one in a thousand for the Premier Mine (14). In 1954 only 21 of the rare diamonds were known to exist (1).

Diamond has the same lattice structure as germanium, silicon and grey tin. Since at present germanium and silicon are our two most valuable elemental semiconductors, it is conceivable that diamond may in the future rank with them in commercial value as a semiconductor.

Early Investigations

The observation of differences among diamonds began many years ago. Evidence taken from records maintained by early day stone setters indicates one of the first differences noted was that of laminations occurring in a few stones.

E. Becquerel (1859) and W. Crookes (1879) were among the early observers of fluorescence. Crookes observed some bright lines in the luminescence spectra of diamond. Walter (1891) studied the absorption of light by diamond and noticed a dark band at 4155 A (15). Since these early studies correlations between absorption and fluorescence have been pointed out by many authors of scientific articles (15, 16).

Miller (1862) detected a difference in ultraviolet spectra of diamonds (17). Miss Levi (1922) gave some photographs of ultraviolet spectra which indicated she was working with two types of diamond (18). Peter (1923) made similar observations (17).

In 1911 Reinkober noted that not all diamonds are alike in their absorption of long wavelength light. His observation resulted from his failure to record the intense 8 micron band which had previously been recorded by Angstrom (1892). Julius (1893) also observed the 8 micron band (18).

Gudden and Pohl (1920), experimenting in photoconductivity, showed that some diamonds had the property of having detectable electrical conductivity when irradiated with visible or ultraviolet light. They also found that in some ultraviolet irradiated diamonds additional irradiation by red light almost doubled the photocurrent (19).

A systematic study of the properties of diamond was undertaken by Robertson, Fox, and Martin and reported in 1934 (18). In their article diamonds were divided into two types, principally upon the basis of their optical properties. For example, diamonds classified as Type I are opaque to ultraviolet radiation of wavelength shorter than 3000 A, while diamonds of Type II are transparent to radiations as short as

2250 A. Many diamonds do, however, show characteristics of an intermediate nature. Type I and Type II diamonds are also distinguished by their infrared absorption spectra, their birefringence, luminescence, and photoconductivity (see Table I). It has been found since the publication of their article that Type II diamonds should be further classified as Type IIa and Type IIb (20). Some authors have attacked this arbitrary division of diamonds into types (21). Perhaps it is not a concrete method of division, but it is one that has facilitated an orderly method of investigating diamond.

After the work of Robertson, Fox, and Martin, the problem was attacked by x-ray techniques. Raman and Nilakantan reported that many diamonds had extra spots or streaks in their x-ray diffraction patterns (22). Similar observations were made by Lonsdale and Smith, who reported that extra streaks were more characteristic of Type I diamonds and also that, in general, Type II diamonds appear to be much more mosaic than Type I diamonds (23).

It may be convenient at this point to summarize in table form the characteristic features of diamond as they were then known.

Using the information tabulated in Table I as a basis, further investigations of the physical properties of diamond have been conducted.

Fluorescence and Absorption

In general Type I diamonds fluoresce with varying intensity of blue, greenish-blue, green, or greenish-yellow when irradiated by 3650 A light. Type II diamonds do not fluoresce when exposed to this radiation.

Nayar (16) studied the fluorescence and absorption spectra of

TABLE I

Knowledge of Types of Diamond in 1940

Property	Type I	Type II
Occurrence	Common type	Rare
Form	Derivatives of cubic system	Derivatives of cubic system, but with fine parallel laminations
Isotropy	Considerable anisotropy between crossed nicols	Nearly isotropic
Infrared absorption persisting at -170°C	At 3, 4.1, 4.8, and 8 μ	At 3, 4.1, 4.8 μ, no band at 8 μ.
Ultraviolet absorption	Not complete until 3000 Å, sequences of bands near this λ increasing in intensity down to -170°C.	Not complete until 2250 Å, faint absorption and diffuse bands near cutoff, disappearing at -100°C.
Photoconductivity*	Small even with high voltages	Present with small or no voltage
X-ray diffraction	Shows extra spots and streaks	Normal

* Response to ultraviolet and visible light.

Type I diamond at liquid air temperature. More than 25 discrete frequencies were listed in the ultraviolet spectrum beyond 3447 A. The 25 lines were in addition to the 4152 A line which was found to be a doublet in absorption.

Anderson (17) repeated some of the work done by Nayar and reported finding a correlation between the intensity of the 4155 A band and the color of the diamond. Anderson stated some yellow diamonds do not show a strong development of the 4155 A band. He further stated that certain brown diamonds portrayed a pale green fluorescence with bands at 5370, 5120, 5040, and 4980 A. But, according to Pringsheim (24), color producing impurities are not responsible for luminescence.

Raman (25) believed the spectroscopic evidence suggested the luminescence to be a property of diamond itself and not due to any extraneous impurities. Rendall (26) revealed the luminescence showed a pattern effect in a single diamond and a definite correlation exists between transparency to the 2536 A line of Mercury and the luminescence of diamond. Mani (15) made a low temperature study of diamond. The Type II diamonds of that study were colorless as seen in daylight and showed no trace of absorption lines in the visible spectrum.

Bishui (27) examined the fluorescence of six specimens, one of which was transparent in the ultraviolet. A feeble line was observed at 4156 A in the luminescence of the ultraviolet transparent diamond, but no bands were observed in the absorption around this region. Bishui also observed that the 4156 A absorption line disappeared in Type I diamond when heated to 275°C but the birefringence is not altered. He therefore suggested the birefringence is not directly related to the luminescence and the impurity causing fluorescence could be of a chemical nature. In Bishui's work on ultraviolet absorption spectra he observed that the transparency of the crystals cannot be correlated with the intensity of the 4156 A fluorescence band. He further observed the intensity of the 4156 A line to be greater when diamonds which were transparent up to 2240 A showed two absorption bands at 2360 A and 2363.5 A (28).

According to Blackwell and Sutherland (29) many yellow fluorescent diamonds are Type II when classed according to their infrared absorption spectrum. Also, in some specimens they found a relation between a sharp line at 4155 A and a 10 micron band.

Raman and Jayaraman (21) found a few diamonds showed neither blue nor greenish-yellow luminescence. Such diamonds exhibited a characteristic type of birefringence consisting of a set of fine streaks parallel to each other, or sets of such parallel streaks intersecting each other. They also reported diamonds which exhibited no visible birefringence were free from laminations.

In 1952 Custers (20) found a diamond with unusual phosphorescence, showing maxima at 4665, 5310, and 5720 A. The same diamond was also found to be a conductor of electricity. It was transparent in the ultraviolet region and was thus classed a Type II. However, since the diamond proved to be a conductor and did phosphoresce when exposed to 2536 A light, Custers proposed a further classification of Type IIb. The Type IIa is a good insulator and does not phosphoresce when irradiated by 2536 A light.

The line which divides Type I diamond from Type IIa and Type IIb on the basis of luminescence and absorption in the visible and ultraviolet would now seem rather distinct. Yet it is found that thin sheets of Type I diamond will actually transmit to the cut-off value listed for Type II diamond (30) and one need not search far in the literature to find values given for cutoff anywhere in the range between that normally accepted for Type I and that of Type II.

Minor Elements

The minor elements of diamond were investigated by Chesley (31). Of the specimens studied, one from Brazil and one from the Premier Mine may have been Type II. These two diamonds contained Al, Si, Ca, and Mg. In all specimens Al and Si exhibited "sympathetic" variation in each diamond. Chesley's method would not have detected some elements, such as boron, hydrogen, nitrogen, phosphorus, oxygen, sulphur, or the halogens (32).

Custers' natural blue conducting diamonds contained only Si as a minor element and sometimes a trace of Mg (1). Silicon may be expected to yield a level at the center of the gap and the same could be true for magnesium (33).

Infrared Absorption

The work of Robertson, Fox, and Martin regarding the infrared spectrum has not been questioned. Only the reasons for the differences they observed have been debated and still are. Raman (34) attempted to explain the differences on the basis of tetrahedral and octahedral symmetry of diamond. The tetrahedral variety lacks a center of symmetry which would give rise to the 8 micron absorption band in the infrared. According to this theory the octahedral diamond has a center of symmetry and therefore does not show absorption in the infrared at 8 microns. Diamonds were considered to have portions of both tetrahedral and octahedral types to account for the varying intensity of the 8 micron band. To further defend his theory, Raman ruled out the possibility that neighboring atoms have different charges by noting the absence of the piezo electric property. He concluded the differences lay essentially in the orientations of the orbital and spin moments of the electrons.

Ramanathan (35) reported finding patterns of infrared transparency in individual cleavage plates of diamond closely analogous to the patterns of luminescence and ultraviolet transparency observed by other investigators. Other observations worthy of notice are: (1) The diamonds which absorb most in the 8 micron region show a weak blue fluorescence. (2) Yellow luminescent diamonds are more transparent in the 8 micron region than the blue luminescent diamonds. (3) The nonluminescent (to 3650 A light) diamonds are highly transparent in the 8 micron region. (4) As the ultraviolet transmission limit of a diamond progresses further into the ultraviolet, the transparency becomes greater in the infrared.

Blackwell and Sutherland (29) advanced the infrared study of diamond when they found some of the Type II diamonds from the Premier Mine showed extra bands in the 3 micron region. (See Figures 2, 3, 4).

A 21 micron band, observed in Type I diamond by Willardson and Danielson (36), was found to vary directly with the 8 micron band. They suggest there is a relation between the 8 micron absorption region and the traps at 0.1 to 0.2 ev below the conduction band.

In 1954 Collins and Fan (37) reported the 8 micron absorption band to be a result of impurities or lattice imperfections. Also in 1954, Sutherland, Blackwell, and Simeral (38) published an article regarding the two types of diamond. In their article they concluded Type IIS (spectroscopically classed) diamonds are normal in their infrared absorption while Type IS diamonds have their infrared spectrum disturbed by the occurrence of impurity centers which destroy the center of symmetry.

Other Studies

Photoconductivity has been investigated by the use of ultraviolet and visible radiation (19). Essentially the same information is obtained from photoconductivity measurements as from optical absorption measurements (39).

Other properties of diamond have been studied and attempts made to correlate the various properties. For instance, the subject of counting properties of diamond is far from a closed matter. The selection of counters on the basis of ultraviolet cutoff has not proved successful. Selection according to birefringence patterns has been somewhat better (40) but is still not the answer.

Since the discovery by Custers of a type of diamond with electrical conducting properties investigations of a specialized nature have been made. Leivo and Smoluchowski (2) measured the dark resistivity of a Type IIb diamond. The diamond appeared to behave like an impurity activated semiconductor, with a low concentration of impurities. The dependence of k ln r on 1/T yields a slope of about 0.35 ev.

Brophy (4) investigated the rectifying properties of Type IIb diamond. He reported the entire surface to be p-type with considerable conductivity inhomogeneity. From a plot of the Hall constant versus 1/T, he established an activation energy of 0.35 ev. Dyer and Wedepohl

(6) have made electrical measurements on a Type IIb diamond and found the specimen to be reasonably homogeneous with regard to resistivity.

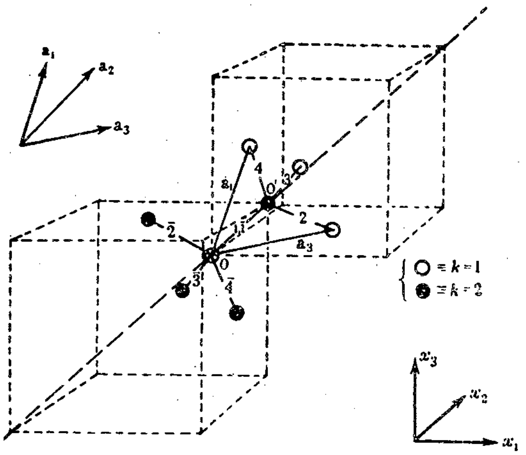
Mr. Bell (41) of Oklahoma Agricultural and Mechanical College is currently investigating the electrical properties of Type IIb diamond, especially rectification, photovoltaic effect, and photoconductivity. His observations are very interesting and may be an aid to understanding the mechanism of conduction in diamond.

The electrical and optical properties of diamond can be summed up, in table form, as follows on page 15.

TABLE II

Knowledge of Types of Diamond at the Beginning of the Present Study

Property	Type I	Type IIa	Type IIb
Resistivity	Approximately 10^{16} ohm-cm	Approximately 10^{16} ohm-cm	25 to 10^{8} ohm-cm
Ultraviolet transparency	Extensive absorption beyond 3000 A	Transparent to 2250 A	Transparent to 2250 A
Nature of conductivity at room temperature	None present	None present	Holes (p-type)
Luminescence	Fluorescence excited by 3650 A light	Neither fluoresces or phosphoresces	Phosphoresces when excited by 2500 A light
Infrared absorption	Varying intensity band at 8 microns not present in other two types	No unusual bands observed	Not yet known to be different from Type IIa



re 1. First Neighbors of the Two Carbon Atoms in the Unit Cell of Diamond. *

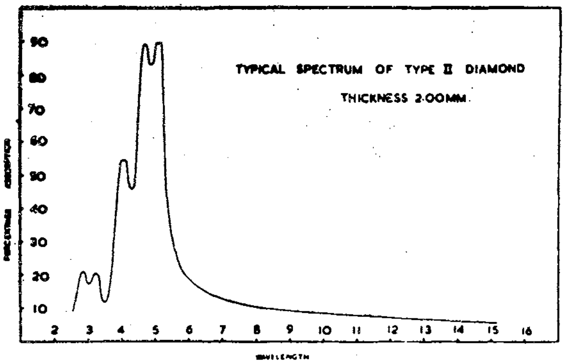
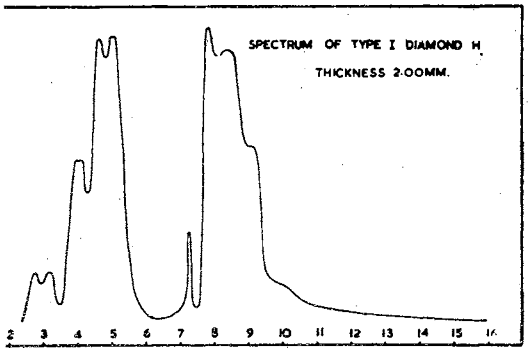


Figure 3. Typical Absorption Spectrum of a Type II Diamond. **



e 2. Typical Infrared Absorption Spectrum of a Type I Diamond. **

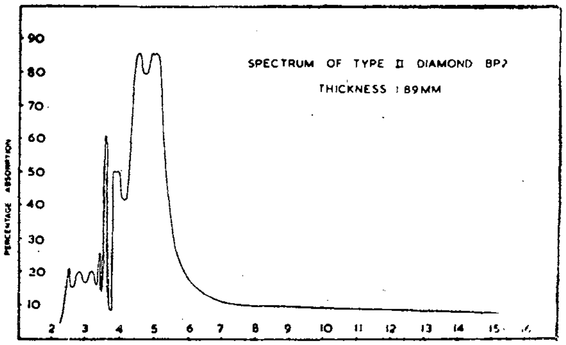


Figure 4. Infrared Absorption Spectrum of a Blue Type II Diamond from the Premier Mine in South Africa. **

* Reproduced from Smith (12)
** Reproduced from Blackwell and Sutherland (29)

CHAPTER III

EXPERIMENTAL

Specimens

The larger diamond (Figure 5) is a Type IIb stone from the Premier Mine in South Africa. It has rectangular dimensions of 2.5 x 3.5 x 6.5 mm^3. The flat surfaces and comparatively large size make it well suited for optical studies. One end of the diamond has a distinct blue color while the other end is nearly free from coloration. The minimum of resistivity was found by Leivo and Smoluchowski (2) to occur near 360°C. In the preliminary Hall measurements conducted, the majority carriers were shown to be holes (7). Mr. Bell (41) examined the rectification properties of the diamond and found inhomogeneities over the surface. In general, however, it appeared p-type. Patterns can be observed in the diamond when viewed on a polarizing microscope, indicating strain exists within the diamond.

The smaller diamond, also a Type IIb stone from the Premier Mine, is a rather cigar shaped chip. It is blue tinted and is a better conductor than the larger stone.

Both stones phosphoresce with a bluish-white color after irradiation with a full spectrum Mercury arc lamp. The phosphorescence of the smaller diamond and the blue portion of the larger diamond appears to decay more rapidly than the phosphorescence of the clear portion of the larger diamond. When placed on a monochromator the blue end of the larger diamond exhibits phosphorescence when excited by wavelengths of 2345 A and shorter. An exciting wavelength of 2260 A is required in the clear region, and the resulting phosphorescence persists for a much longer time than that in the blue portion.

Apparatus

A Beckman Model DK-2, double beam, ratio recording spectrophotometer was the principal instrument used in the study of the ultraviolet, visible, and near infrared regions. It is a very versatile instrument which covers the range from 185 millimicrons to 3500 millimicrons with provisions for reading percent transmission, absorbance, and energy vs wavelength. The optics of this instrument are more extensive than those of single beam instruments, five additional mirrors having been incorporated into the instrument to provide the double beam function. The prism material is natural quartz which extends the range of the instrument into the infrared without change of prisms. Hydrogen and tungsten lamps are employed as sources. The instrument utilizes two detectors: a photomultiplier which has a usable range from 185 to 600 millimicrons and a lead sulfide cell with a usable range from 400 to 3500 millimicrons. The PbS cell is a semiconductor which has recently found application as an infrared detector. Use of the cell permits better resolution in the near infrared than could be gained with a thermocouple detector. The alignment of this instrument is a critical factor when used to study small solid materials.

A preliminary study of the ultraviolet and visible regions was made with a Beckman Model DU Spectrophotometer. The range of the instrument is from 200 to 1000 millimicrons. It reads directly in percent transmission or optical density on point settings of wavelength. Hydrogen and tungsten lamps are used for sources. A photomultiplier and red phototube are employed as detectors. The prism material is fused quartz.

Three instruments were used in the infrared study: a Perkin-Elmer Model 12-C, a Perkin-Elmer Model 21, and a Baird Recording Spectrophotometer Model B. The Perkin-Elmer Model 12-C Spectrometer is a single beam instrument employing an electrically heated carborundum rod for a source, a rocksalt prism and a thermocouple detector. The output of the thermocouple is amplified and applied to a Leeds and Northrup recorder. The light is chopped at 7 cps, making ac operation possible in the remainder of the detection system. A single beam instrument is not entirely satisfactory for the work undertaken in this study since conditions may not remain the same from the recording of the reference energy to the recording of the energy passed through the diamond. The instrument also has a slight shift of wavelength between two successive recordings.

The Perkin-Elmer Model 21 is similar in many respects to the Model 12-C. It has provisions for ratio recording, adding greatly to its value as a research instrument.

The Baird Recording Infrared Spectrophotometer also employs a rocksalt prism and an electrically heated carborundum rod for a source. The detector on the Baird instrument is a bolometer.

The birefringence of the larger diamond was observed on a Unitron MPS Polarizing Microscope. Pictures were taken using a Unitron Model ACA Photomicrography set, an Argus C3 camera, and 200 exposure index film.

It was necessary to make special mounts for all the instruments used in obtaining optical transmission data (Figure 6). A clamp type mount was first utilized on the Perkin-Elmer Model 12-C and Model 21 instruments.

However, when it was learned from the survey of literature that Type II diamonds sometimes chipped during normal handling, the clamp was abandoned and a permatex cement was used to secure the diamond to the mounts.

To minimize the effect of surface contamination, the diamonds were cleaned with alcohol before each spectral run. As a further precaution the diamonds were frequently cleaned with concentrated nitric acid.

Presentation of Data

The optical spectra of two semiconducting diamonds have been examined between the fundamental absorption in the ultraviolet and 13 microns, with the instruments listed in the previous section.

By using a diamond with nearly parallel faces and instruments with appropriate sources and detectors, it was possible to work with comparatively small slit widths throughout the region.

The spectra of the larger diamond are shown in figures (7, 8, 9, 10). The continuous line represents a portion of the diamond which is nearly free from coloration. The dashed line represents the portion of the diamond characterized by a blue coloration. The spectrum of the blue portion is similar to that of Blackwell and Sutherland's Premier Overblues (29), while the spectrum of the clear portion more nearly resembles that of ordinary Type II diamonds.

Although in fair agreement with transmission values expected when computing reflectivity, the exact values of transmission cannot be definitely established by the methods of the present study. This fact was realized when it was found that changing the focus of the light source changed the percent transmission; also, changing detectors may give different values of transmission for the same incident wavelength and the

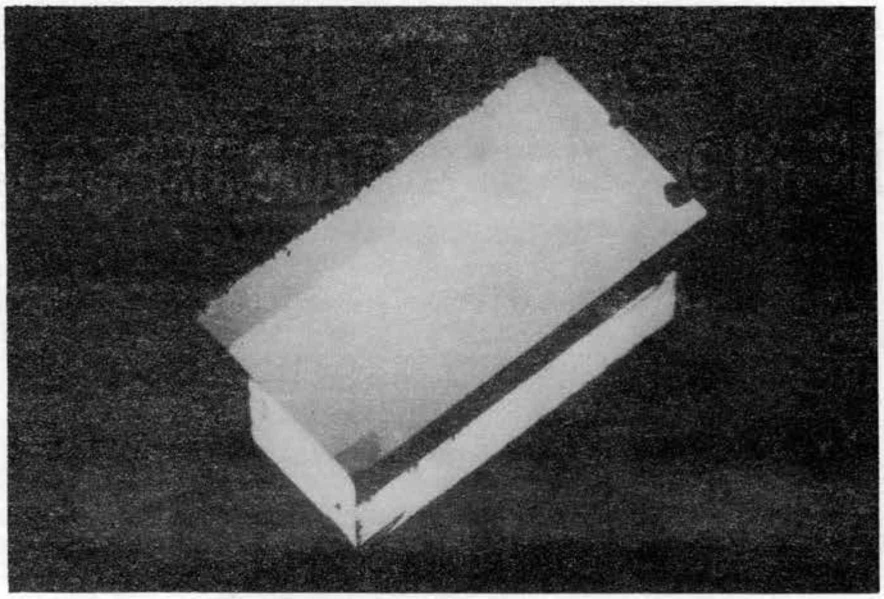


Figure 5. The Larger Type IIb Diamond ($2.5 \times 3.5 \times 6.5$ mm^3) Used in the Study. Supplied by J. F. H. Custers of the Diamond Research Laboratory, Johannesburg, South Africa.

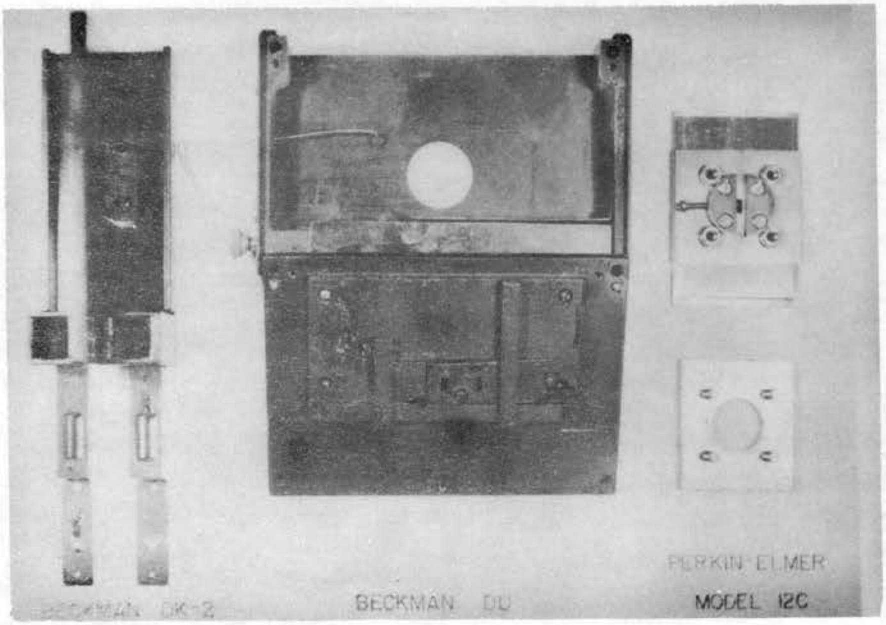


Figure 6. Special Mounts and Adapters Employed in the Study.

same slit width. The difficulties may have two or more possible causes. First, the beam is not uniform in intensity and adjusting the focus shifts the region of maximum intensity over the diamond which is not homogeneous with regard to optical absorption. Second, the detectors may not give uniform response over their surfaces. If the diamond did not have exactly parallel faces, the energy may be incident on a different area of the detector after passing through the diamond than the area used in establishing 100% transmission, thus giving erroneous values of percent transmission. By adjusting for maximum transmission on the DK-2 Spectrophotometer a reasonable match was achieved between the different detectors and different sources; however, a difference of 6% between the thermocouple detector and the lead sulfide detector could not be eliminated. The bolometer also gave different values of transmission than the thermocouple. Considering the difficulties it can be appreciated that only relative magnitudes of absorption are significant.

A pronounced difference between the spectrum of the two portions of the larger diamond can be observed in the region between .6 to 4.5 microns. Peaks in this continuum of absorption occur at 2.43, 3.56, and 4.15 microns. Small increases in absorption occur at 1.6, 1.87, 2.35, and 3.45 microns. Besides the continuum of absorption, the blue portion seems to exhibit a small amount of absorption throughout the region examined as compared with the clear portion. It is conceivable that some of the difference could arise from a change in reflectivity if the faces of the diamond are not exactly parallel. Yet there is undoubtedly some absorption since passing light through the longer dimension of the diamond results in a decreased amount of transmitted energy.

The contour of the curve in the fundamental absorption region is very similar for the two portions and for the two specimens. It is also similar to that of silicon and germanium in the fundamental absorption region.

The gradual decrease in transmission from 1 micron to the fundamental absorption may be expected from the changing values of reflectivity. Using the values given by Moss (42) for the index of refraction, a decrease in transmission of 2.5% should occur between 1 micron and .4 micron due to changing reflectivity.

The diamond chip does not transmit light nearly so well as the larger diamond; however, by using the 0 to 10% transmittance scale of the DK-2 Spectrophotometer and high gain on the Perkin-Elmer 12-C Spectrometer it was possible to obtain the cutoff value for the specimen and to observe the extra absorption in the region from .6 to 4.5 microns. (See Figure 11).

When viewed under a polarizing microscope patterns were observed in the larger diamond (Figure 12). A difference was noticed for the blue and clear portions of the diamond, the blue portion showing a cross-hatched pattern.

Equal areas of the larger diamond were painted with DuPont conducting paint to facilitate resistivity measurements. Resistivity of the blue region is 10^4 ohm-cm while the clear region has a resistivity of 10^6 ohm-cm.

The monochromator of the DK-2 Spectrophotometer was used to determine the wavelengths responsible for excitation of phosphorescence. The blue region of the larger diamond was excited by 2345 A and phosphorescence decayed rather rapidly, while in the clear region 2260 A was necessary for excitation and the resulting phosphorescence persisted for several minutes.

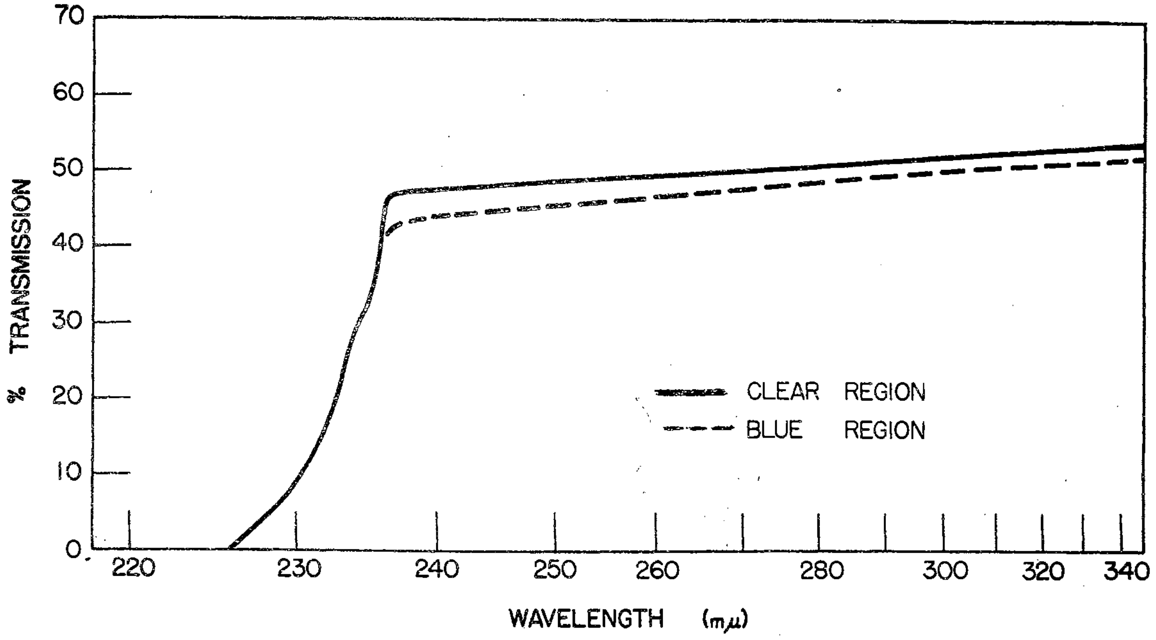


Figure 7. Ultraviolet Absorption Spectrum of the Larger Type IIb Diamond.

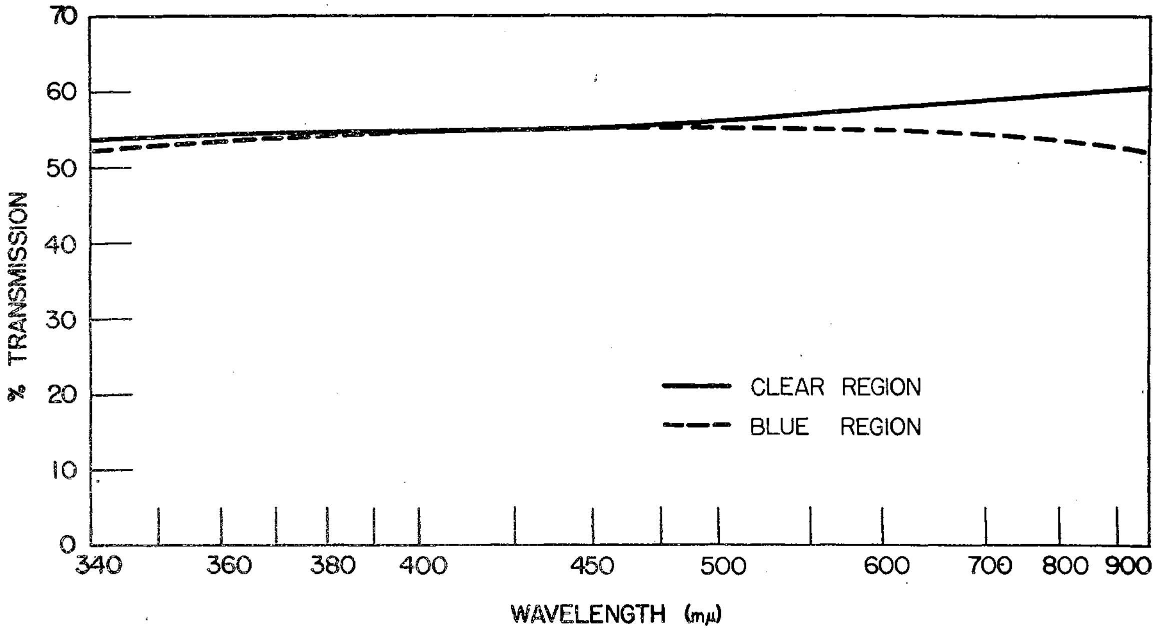


Figure 8. Visible Absorption Spectrum of the Larger Type IIb Diamond.

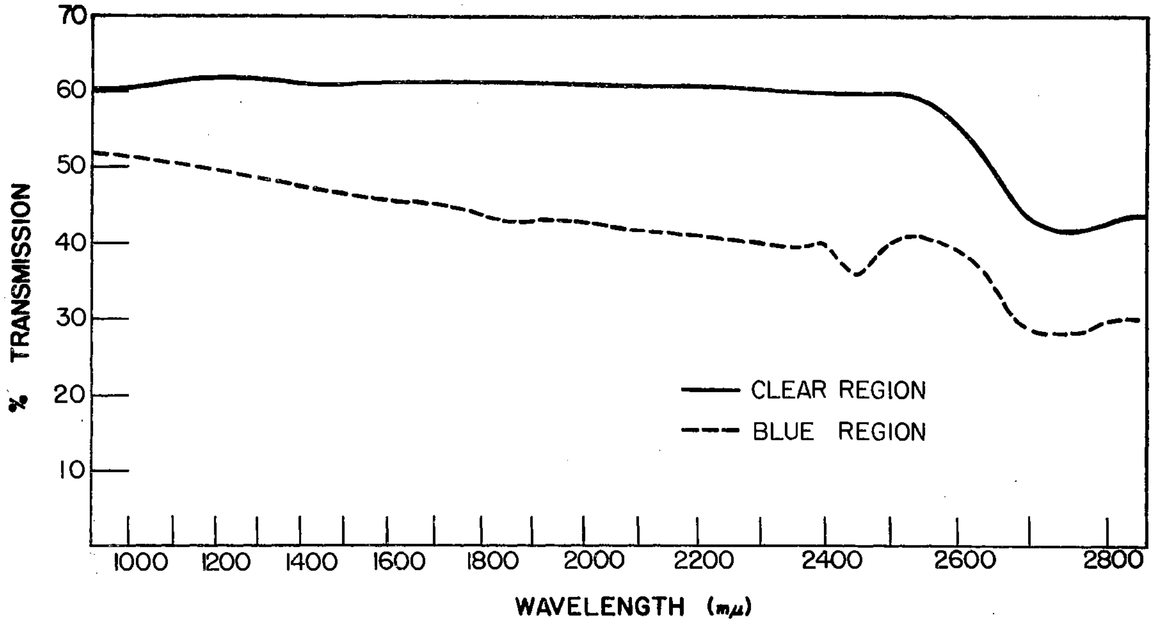


Figure 9. Near Infrared Absorption Spectrum of the Larger Type IIb Diamond.

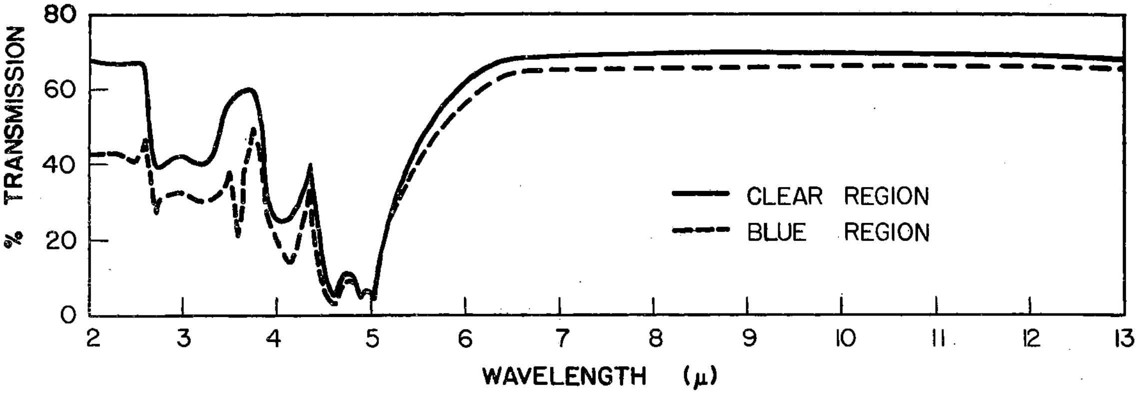


Figure 10. Infrared Absorption Spectrum of the Larger Type IIb Diamond.

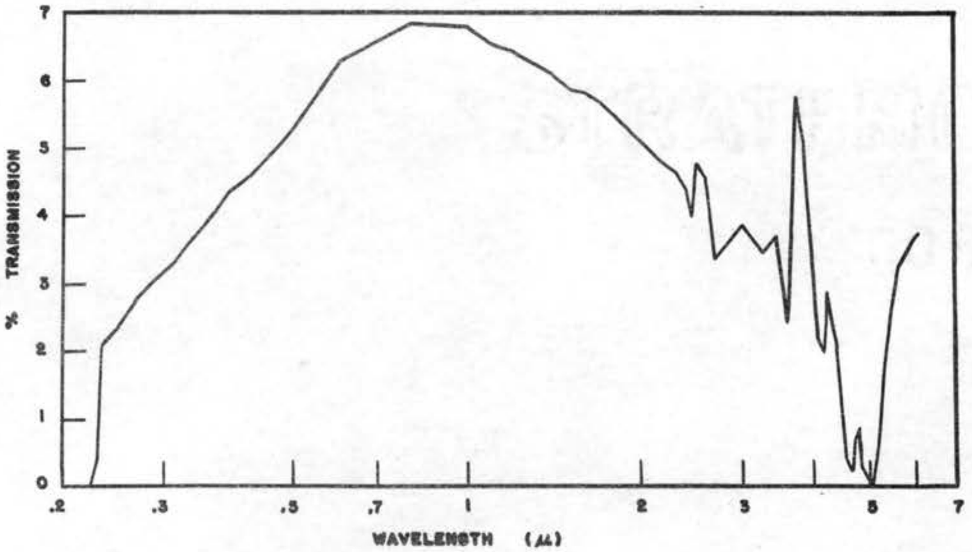


Figure 11. Absorption Spectrum of the Smaller Type IIb Diamond.

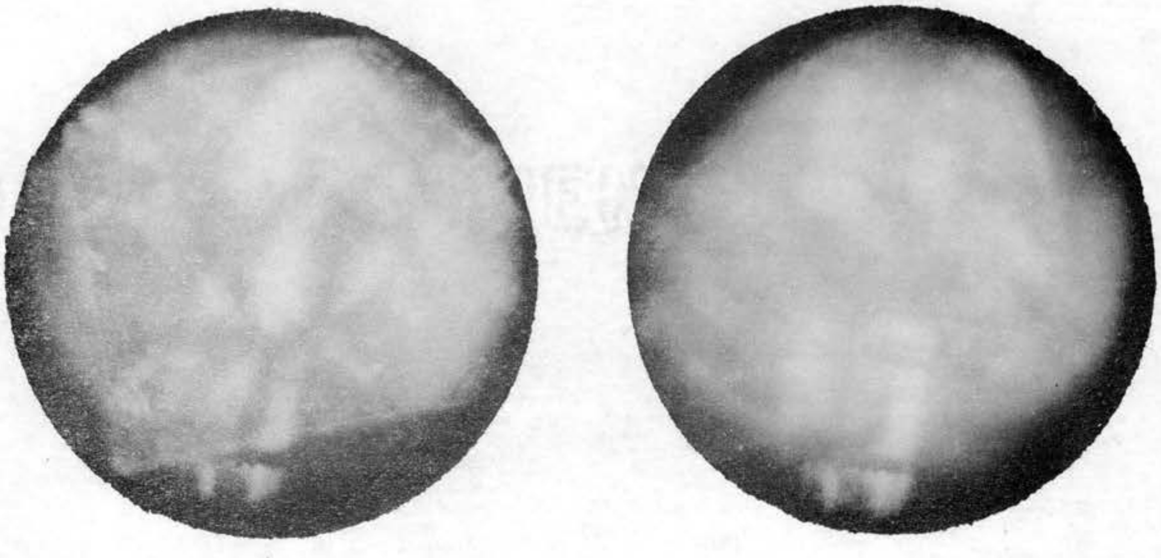


Figure 12a. Blue Region Through 2.5 mm Dimension.

Figure 12b. Clear Region Through 2.5 mm Dimension.

BIREFRINGENCE PATTERNS OF THE LARGER TYPE IIb DIAMOND

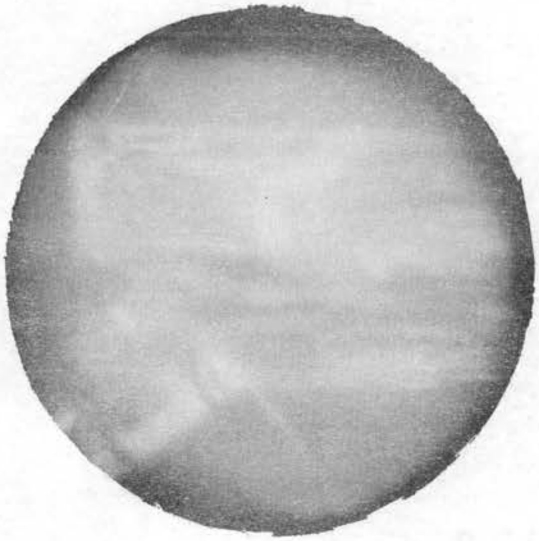


Figure 12c. Blue Region Through 3.5 mm Dimension.

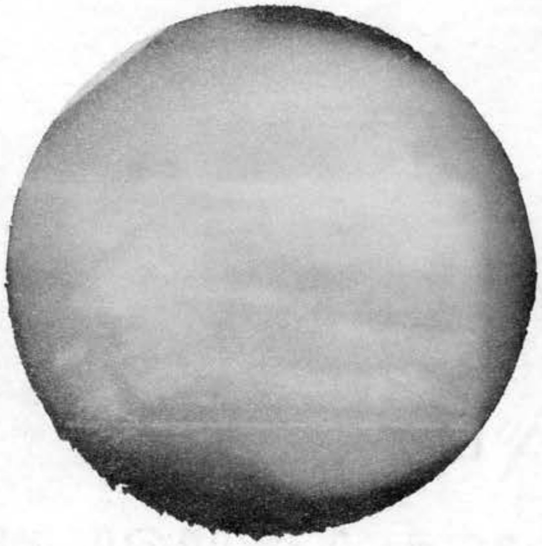
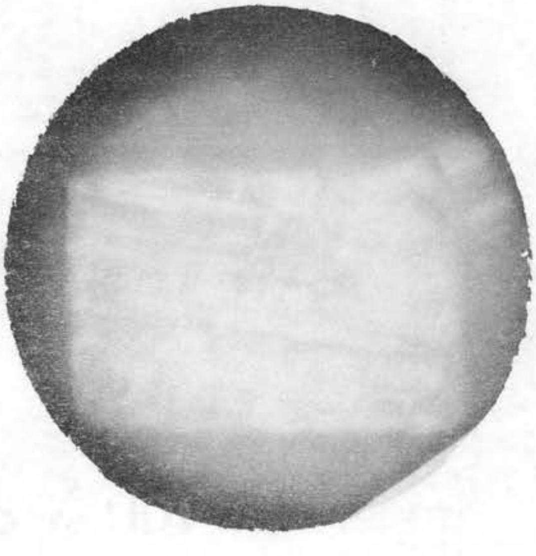


Figure 12d. Clear Region Through 3.5 mm Dimension.



re 12e. Through 6.5 mm Dimension with Blue Region Nearest Objective Lens.

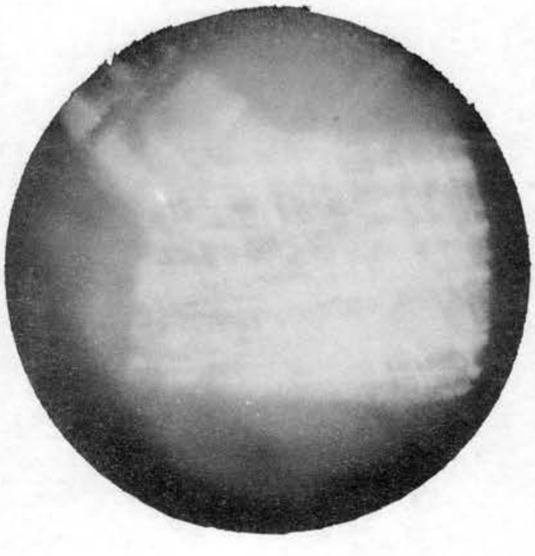


Figure 12f. Through 6.5 mm Dimension with Clear Region Nearest Objective Lens.

BIREFRINGENCE PATTERNS OF THE LARGER TYPE IIb DIAMOND

CHAPTER IV

SIMULTANEOUS STUDIES

Almost simultaneously with the preliminary report on the present study (8), other groups reported similar observations on the optical properties of Type IIb diamonds (3, 43).

Clark, Ditchburn, and Dyer (43) examined the optical absorption spectra of many diamonds. They gave a comparison of the data obtained from Type I, Type IIa, and Type IIb diamonds. Their Type IIb diamonds appeared more transparent than either of the other types in the region between 3500 to 2500 A. A Type IIa diamond was reported to have a gradually increasing absorption beginning about 7000 A and extending to cutoff in the ultraviolet. They also observed a fluorescent spectrum in Type IIa diamonds which could arise from two emission systems, one system having a principal emission line at 4149 A (2.989 ev), the other at 5030 A (2.465 ev). No corresponding absorption lines have been observed.

The findings of Clark, Ditchburn, and Dyer are not in complete accord with data taken in the present study. The blue end of the larger diamond, which shows more of the Type IIb properties (see Chapter III), was found to exhibit slightly greater absorption in the region between 3500 to 2500 A than the clear region of the diamond.

In their study of the infrared Clark, Ditchburn, and Dyer found that Type IIb diamonds absorbed in a region where the Type IIa diamonds did not absorb. They reported peaks in the extra absorption occurred at

1.85, 2.35, 2.44, 3.33, 3.60, 4.05, and 4.23 microns.

Some of these peaks appear very definite in the blue region of the larger diamond studied and there is some indication of peaks corresponding to other values they have listed, except their 4.23 micron peak which would be rather difficult to establish since it is so near the CO_2 absorption peak. In certain regions of the blue portion nearly as much indication of a peak was found at 1.6 microns as at 1.85 microns. Clark, Ditchburn, and Dyer worked with several specimens, which makes their data a little difficult to interpret. For instance, the infrared data was taken from different specimens than the visible and ultraviolet data.

A Type IIb diamond with low resistivity was examined by Austin and Wolfe (3). A continuum of absorption was observed in the near infrared. Peaks in the absorption occurred at 2.5, 3.4, 3.5, and 4.1 microns. Absorption through the region of the peaks increased about 30% when the diamond was cooled to -155°C and became indistinguishable from the background when the temperature was elevated to 300°C. They suggest the behavior indicates chemical impurities.

The observations made on the peaks in extra absorption by Austin and Wolfe are very similar to the observations of the present study; however, their study was limited to the infrared region. The two studies differ widely with regard to the homogeneity of the respective specimens. Austin and Wolfe's diamond exhibited the same absorption in all portions of the specimen. Just the opposite observations were made on the larger specimen used in the present study.

Austin and Wolfe also reported photoconductivity was detectable between 0.9 and 3.6 microns when the Type IIb diamond was cooled to -155°C. They concluded the absorption of light in this wavelength range leads to the production of free holes.

CHAPTER V

DISCUSSION AND CONCLUSIONS

Discussion

The role of impurity and defect centers in solids is one area which has been advanced by optical and other studies. Impurity and lattice defects affect the electrical and optical properties in a number of ways. They act as the source of majority carriers under thermal, impact, and optical ionization. They may also act as radiative or nonradiative trapping centers and as recombination centers (39).

Energy levels within the forbidden gap may arise from the introduction of impurities into the crystal. For example, the introduction of a group V impurity into the diamond lattice may give rise to an energy level just below the conduction band. An electron near the bottom of this band behaves in much the same way as an electron behaves in free space, except it may have an effective mass different from that of an electron in free space. The electron has modes of motion around the impurity atom much like the motion of the electron around the proton in a hydrogen atom. However, the charge is embedded in a dielectric medium; therefore, the charge carriers are bound to the impurity atom by a coulomb potential which is reduced by the dielectric constant of the medium. A similar situation would hold true for the group III impurity atoms except the valence band would be involved rather than the conduction band and it would be a hole in motion rather than an electron.

Low temperature optical studies have demonstrated optical absorption and photoconductivity due to un-ionized group III and group V impurities in both germanium and silicon (39). The same phenomena may be expected in diamond, but should be apparent at higher temperatures.

There are small but reproducible differences in ionization energy among the group III and group V elements in silicon (44, 45). On the basis of the simple hydrogen model, the differences are not expected. A more detailed model is obviously needed which takes into account the nature of the impurity atom and its interaction with neighboring atoms (39).

Since a peak in optical absorption does occur at 3.56 microns experimental data indicates diamond may owe its semiconducting properties to a group III element, which would not have been detected in the experiments on minor elements. One is tempted to assume this cause of conduction since, on the basis of the hydrogen model, the group III elements in diamond should have an ionization energy of approximately .4 ev and it is near .4 ev that one of the peaks in absorption occurs. The 3.56 micron peak which can be associated with the activation energy is actually one of a series and in a continuum of absorption which occurs only in Type IIb diamond. Furthermore this peak is near the long wavelength limit of the continuum of absorption. Leivo and Smoluchowski (2) found the slope of k ln r vs 1/T to be .35 ev. Brophy (4) further supports the assumption by stating an activation energy of .35 ev from Hall measurements. Austin and Wolfe (3) obtained similar values for the activation energy.

Some qualifying statements should be made regarding the determination of an activation energy from a plot of k ln r vs 1/T. The expression is deduced from $p = 2\left[\frac{2\pi mkT}{h^2}\right]^{3/2} \exp - (\varepsilon_f - \varepsilon_v)/kT$.

p = number of holes in the valence band
m = effective mass of the holes
k = the Boltzmann constant
T = absolute temperature
h = Planck's constant
$\mathcal{E}_F$ = energy at the Fermi level
$\mathcal{E}_V$ = energy at the top of the valence band

The equation for holes has been obtained by assuming spherical distribution of states. Further assumptions are: the value $2\left[\frac{2\pi mkT}{h^2}\right]^{3/2}$ remains essentially constant over the temperature range, the mobility (μ_p) is not affected by a temperature change, and the Fermi level lies at the acceptor level.

Using the simplifying assumptions and the relation $1/r = pe\mu_p$, the previous equation for holes can be rewritten in the form $1/r = A \exp - \mathcal{E}_G/KT$, or $r = B \exp \mathcal{E}_G/KT$, where A and B are constants. Taking the natural logrithm of each side yields the expression $k \ln r = \mathcal{E}_G/T + C$. If $k \ln r$ is plotted on one axis against $1/T$ on the other axis, then $\mathcal{E}_G$ becomes the slope and the constant C is the intercept.

Another interpretation of $k \ln r$ vs $1/T$ gives a slope of $\mathcal{E}_G/2$. This interpretation results from a derivation for an intrinsic case and requires the Fermi level to lie midway between the top of the valence band and the acceptor level.

On the basis of the conductivity measurements there is no justification for selecting one interpretation over the other and the activation energy could be either .35 ev or .7 ev.

The author undertook the optical absorption studies with the thought that a corresponding absorption may determine which value is actually the activation energy. The results of the optical study show absorption corresponding to the .35 ev (3.56μ) and also absorption in the region corresponding to .7 ev (1.8μ). Although the optical study did not point out the activation energy specifically it yields important facts which must be considered in postulating a mechanism of conduction.

The simple energy band model has been quite helpful in visualizing methods of conduction. In this model the top of the valence and the bottom of the conduction band are assumed to occur at a crystal momentum, $k = 0$, and the surfaces of constant energy are assumed to be spherical (39).

The optical transition of electrons from the valence band to the conduction band takes place vertically in order to conserve momentum (46). Non-vertical transitions may also occur, accompanied by the absorption or emission of phonons to satisfy momentum conservation. The contour of the absorption curve in the cut-off region of diamond is highly suggestive of non-vertical transitions (see Figure 7). The optical energy gap corresponds to the minimum photon energy required to transfer an electron from the valence band to the conduction band and should equal the forbidden energy gap. For homopolar materials, where the static dielectric constant is essentially equal to the optical dielectric constant, the optical energy gap and the thermal energy gap are nearly equal (39).

Optical processes which may occur for donor and acceptor centers include (a) photoionization absorption involving transitions from the valence band to the ground state of the acceptor level and (b) optical excitation absorption involving transitions from the ground state to excited states of the acceptor center, which would appear as narrow bands beyond the long wavelength photoionization limit (39). The presence of elements having a small amount of solubility could not be observed directly by optical absorption (39). These transitions are then best observed through the photoconductivity produced. It is therefore advisable to carry out both optical absorption and photoconductivity measurements. Mr. Bell (41) found a peak in photoresponse around .6 microns which is near the short wavelength limit of the extra absorption in Type IIb diamond.

Elements whose valence differs from that of the diamond lattice by more than one generally introduce more than one energy level into the forbidden band and cannot be explained in terms of a simple atomic model (39). It may be possible that such an element is responsible for the conductivity observed in diamond, yet Custers (14) found only silicon in a Type IIb diamond. Silicon would not behave as an impurity center when introduced substitutionally as a foreign element, but could create energy levels near the center if introduced interstitially (33).

Isolated impurities constitute only one of the many types of imperfections which may occur in semiconductors as well as metals. Other types include lattice vacancies and interstitials, dislocations, and surface imperfections such as grain boundaries or, possibly, free surfaces. All such imperfections can give rise to localized states with energy levels in the forbidden gap. A few facts may be listed for consideration (47):

1. Germanium can be made to flow plastically by a slip mechanism above about 500°C. Dislocations put into germanium by bending give rise to acceptor levels whose total number is of the order of magnitude of the number of atomic sites along the dislocations (48, 49). Slips have been observed in diamond parallel to a (111) plane making an angle of 70½° with the surface, and an angle of 60° to the growth direction (50). If this slip is due to a dislocation, the angle implies a displacement of one atomic lattice in 10^5 lattices.

2. The free surface of germanium probably possesses surface traps which behave essentially like acceptor levels below the center of the forbidden gap (51, 52). The acceptor levels may be due to adsorption of oxygen (53). An adsorbed atom or molecule of oxygen can accept an electron either from donor impurity levels in the semiconductor or from massive metal in proximity. The oily surface of diamond has been attributed to the adsorption of elements such as oxygen (54). Possibly some of the conductivity in diamond is due to surface states. That surface states exist is evidenced by Mr. Bell's (41) work on rectification properties.

3. Grain boundaries in germanium give rise to acceptor levels most of which lie very close to the top of the valence band (47). Grain boundaries act as short-circuit paths of p-type layers. Achyuthan (55) found photoconductivity was not uniform over the entire area of an ultraviolet transparent diamond. He found conductivity to be a maximum in the direction of the lamina observed in Type II diamond (56).

4. Vacancies and interstitials generated by radiation bombardment or heat treatment give rise to acceptor levels in germanium, one near the valence band and one near the center, and to paired donor and acceptor levels in the middle of the forbidden gap in silicon (47). The electrical properties of silicon depend markedly on the thermal and growth history (39). It is also possible in silicon to get irreversible increases in conductivity at high temperatures (57). Lark-Horovitz (58) suggests that lattice defects created by neutron and electron bombardment of silicon and germanium give rise to donor and acceptor centers. The lattice vacancies behave as acceptor centers with relatively deep levels and the interstitial atoms behave as donor centers. Custers (14)

has suggested the diamonds from the Premier Mine may have been brought to the surface rather rapidly and this may in some way account for the unusual Type II diamonds. The possibility of carbon atoms in different electronic states from that normally expected in diamond would give rise to discrete lines superimposed on a continuous absorption in the infrared (38). Absorption caused by dislocated carbon atoms would not change the ultraviolet cutoff, while absorption due to impurities and missing carbon atoms would be expected to shift the cutoff. (38).

Very little is known about the nature or origin of recombination traps. We do know the recombination rate can be increased in germanium by certain elements dissolved in the germanium, also by quenching from high temperatures (47). It is very possible that Type I diamonds have a greater density of the traps than Type II, which could account for the weak photoconductivity observed in Type I diamonds.

Robertson, Fox, and Martin (18) reported the ultraviolet cutoff shifted with temperature on their diamond D-2. They observed a shift of 143 A for a temperature change of $400^{o}C$, thus implying a shift similar to germanium and silicon which is about 10^{-4} ev/C^{o}. Clark, Ditchburn, and Dyer (43) report a shift of cutoff with temperature but do not give values.

The selection of counting diamonds may be aided by the distinction between Type IIa and Type IIb diamonds. In general, Type II diamonds most nearly free from strain have proved to be the best counters (59). The diamond (D-22) of Robertson, Fox, and Martin, which was probably a Type IIb, failed to count alpha particles (59). Benny and Champion (60) observed a sharp absorption line at 2400 A in their Type II diamonds which were poor counters. It may well be the Type IIa diamonds are the best counters.

Much of the experimental data gathered by Robertson, Fox, and Martin can be pieced into the data now being obtained on Type IIb diamonds. They found the maximum response to red light occurred at 5850 A and this is close to the values observed recently by Mr. Bell (41) in photovoltaic and photoconductivity measurements. They also reported two faint absorption lines at 2330 and 2350 A which disappeared at low temperatures. The 2350 A line may be the same as the 2356 A line observed by Clark, Ditchburn, and Dyer (43). The 2350 and 2330 A lines could represent transitions from the acceptor levels near the valence band to the conduction band. At lower temperatures the probability for the acceptor levels to be occupied by electrons would become less, hence the 2330 and 2350 A absorption lines would diminish.

Summary and Conclusions

The optical properties of two semiconducting diamonds have been investigated to obtain information on the nature of the imperfections responsible for the anomalous behavior of these rare diamonds. Optical absorption properties were examined from the fundamental cut-off in the ultraviolet to 13 microns. Particular effort was made to gain resolution in the wavelength range which could be associated with the activation energies determined by other methods (2, 4, 5). Observations of phosphorescence were conducted to gain further knowledge of the energy levels and trapping levels in the forbidden energy gap. Birefringence of one diamond was investigated to obtain additional information relating to the nature of the imperfections.

Results of the study suggest the following energy level schemes:

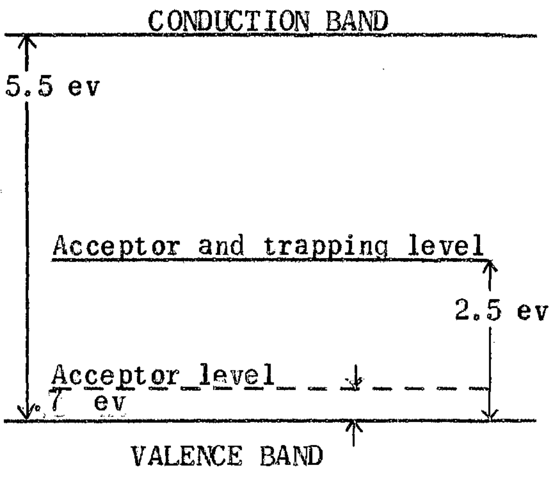


diagram 1

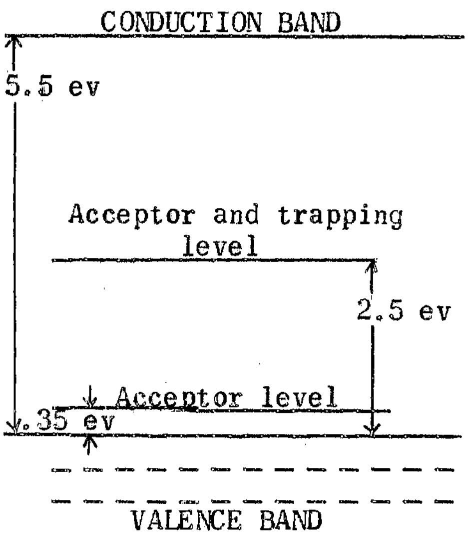


diagram 2

The ultraviolet cut-off value of 225 millimicrons indicates the forbidden energy gap is about 5.5 ev. The color of the phosphorescence suggests a trapping level near the center of the forbidden gap. Observations of the phosphorescence by Custers (20) and photoconductivity studies by Bell (41) position the level near 2.5 ev above the valence band. The observations of birefringence suggest the level may be introduced by a slip condition in the diamond.

It was thought at the beginning of the study that the optical absorption in the infrared would give the necessary information to definitely state the impurity activation energy; however, absorption occurs in a continuum which includes the wavelength associated with both interpretations of the activation energy (.35 and .7 ev) which have been stated in other studies. (2, 4, 5). A peak in absorption occurs at 3.56 microns (.35 ev). Slight indications of peaks also occur near 1.87 microns (.66 ev) and 1.6 microns (.77 ev). Other definite absorption peaks occur at 2.43 microns (.51 ev) and 4.15 microns (.3 ev). Minor increases in absorption also occur near 3.45 microns (.36 ev) and 2.35

microns (.53 ev). There is some indication the absorption at 1.6 microns is not directly related to the other absorption peaks just discussed.

From the optical studies two possible mechanisms of conduction can be formulated. One mechanism, illustrated in diagram 1, requires the Fermi level to lie on the acceptor level nearest the valence band. The activation energy corresponds with the 1.87 micron region and all other peaks occurring at longer wavelengths may be associated with excited states of the impurity atom. Another mechanism, suggested in diagram 2, requires the Fermi level to lie about half way between the valence band and the acceptor level. The activation energy is then associated with the 3.56 micron peak and the absorption at shorter wavelengths in the continuum may represent structure in the valence band.

The decay times of phosphorescence observed in the larger diamond indicate the portion of the diamond which exhibits the blue color and the better conducting properties also possesses the larger amount of impurity.

Birefringence patterns observed in the larger diamond suggest the level near the center of the forbidden gap is a consequence of a slip condition in the diamond. The cross-hatched pattern in the blue portion of the diamond indicates secondary slip may be present. Peculiar growth conditions for Type IIb diamonds may have aided the entrance of chemical impurities into the diamonds. It is believed that chemical impurities are responsible for the high electrical conductivity observed in Type IIb diamonds.

Plans are currently being made to extend the study of optical absorption properties by going to low temperatures which would sharpen the absorption peaks and possibly locate peaks in absorption which are not apparent at room temperature. Low temperature studies will also give the temperature dependence of the extra absorption in the infrared and the change in ultraviolet cutoff with temperature.

Other studies which may be suggested and are in fact under consideration by Dr. W. J. Leivo, Oklahoma Agricultural and Mechanical College, are: photoconductivity at low temperatures, spectrographic analysis, Hall measurements as a function of temperature, and x-ray patterns.

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Master of Science

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