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PHOTOCONDUCTIVITY IN  
SEMICONDUCTING DIAMONDS

by

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SEMICONDUCTING DIAMONDS

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## CHAPTER I

### INTRODUCTION

Diamond, ordinarily thought to be an insulator, may also occur in nature as a semiconductor. Electronic semiconductors have electrical conductivities intermediate between insulators and metals, and in general they have a negative temperature coefficient of resistance within some temperature range. The range of resistivity that is normally considered in the semiconductor range is from as low as  $5 \times 10^{-4}$  up to  $10^{10}$  ohm-centimeters.

The purpose of this investigation is to analyze the processes which give rise to photoelectrical properties in semiconducting diamond and in particular to study the nature of photoconductivity in semiconducting diamond at low temperature. Photoconductivity is the increase in conductivity of a material due to an increase in the number of current carriers available for the conduction process because of the absorption of light energy. Here "light energy" is used to mean not only the energy of photons from the visible spectrum but also of the ultraviolet and infrared regions. In this investigation, photoconductivity in the Type IIb diamond has been studied as a function of intensity of irradiation, electric field strength, temperature, and crystal orientation. Also, various aspects of the photovoltaic effect were studied.

Conducting diamonds are believed to have less impurities than non-conducting diamonds. However, it is known that imperfections assume a

major role in the conduction processes in semiconductors. Changes in conductivity such as that caused by light energy can be controlled by controlling the intensity of illumination. This leaves a very important method of changing conductivity - crystal defects which include interstitial atoms, vacant lattice sites, chemical impurities, and other lattice defects.

Robertson, Fox, and Martin (1), classified diamonds as Type I and II according to their physical properties. Type I diamonds become opaque at 0.3 microns, whereas Type II are transparent to 0.25 microns. The Type II diamond was further classified as Type IIa and Type IIb by Custers (2), the latter type having resistivities of from 25 ohm-centimeters to  $10^8$  ohm-centimeters.

In an attempt to understand the properties of semiconductors, and more especially the semiconducting diamond, difficulties are encountered. Two serious limitations encountered in the study of Type IIb diamonds are: (a) the diamonds are extremely rare, and (b) the impurity content to date has not been controllable. However, General Electric, with its method of production of synthetic diamonds may develop a solution to the latter. Another difficulty which is encountered is the problem of making a good electrical contact with the diamond.

The contacts made with a colloidal suspension of silver are fairly easy to make, but to obtain an ohmic contact is virtually impossible.



## CHAPTER II

### REVIEW OF THE LITERATURE

#### Classification

Robertson, Fox, and Martin (1) have classified diamonds into two distinct types according to their physical properties. Type I diamonds have two absorption regions in the infrared, the region from 2 to 6 microns and the region from 8 to 13 microns. The Type I absorbs below 0.3 microns while the Type II does not absorb the ultraviolet until 0.23 microns. The infrared absorption of the Type II is similar to that of the Type I in the 2 to 6 micron range, but exhibits no absorption in the 8 to 13 micron range.

#### Optical Properties

Stein and Leivo (4) observed absorption bands in Type IIb diamond at 5.07, 4.93, 4.62, 4.07, 3.56, 3.13, and 2.75 microns, with fundamental absorption occurring at 0.225 microns. They also reported (31) that the absorption peaks are temperature dependent, increasing with decreasing temperature. The ultraviolet cutoff also shifted with change in temperature. They concluded that absorption peaks were due to some impurity and were not characteristic of the lattice. From the pronounced temperature dependence of the bands, it was also concluded that the absorption was not due simply to lattice vibrations since lattice absorption is relatively temperature independent (7). Austin and Wolfe (6) also observed this temperature dependence of the absorption peaks. They also concluded that the

absorption was characteristic of Type IIb diamonds and is associated with the defect or impurity responsible for conduction.

The optical absorption characteristics of defects produced in diamond subjected to bombardment with electrons and neutrons have been studied by Ditchburn (8). They show that complex band systems arise, possibly due to interaction between electron configuration and a lattice defect.

Custers (2) further subdivided the Type II diamonds into IIa and IIb. Type IIb shows a strong phosphorescence when irradiated by short wave ultraviolet light in the region of 0.25 microns, and it also conducts electricity.

Dyer and Mathews (9) reported that the 0.365 micron group of mercury lines was found to excite fluorescence in all Type I and IIa diamonds. No precise difference in the emission of the Type I and IIa diamonds was observed except that Type I specimens exhibited a stronger fluorescence than Type IIa diamonds. No emission from Type IIb diamonds when they were illuminated with 0.365 micron light was reported by them. This has been reported by Custers (2) in 1952.

Leivo and Smoluchowski (10) found that Type IIb diamonds behave like typical impurity activated semiconductors with low concentrations of impurities having an activation energy of 0.35 electron volts.

#### Photoelectric Properties

Bell (11) found the rectification characteristics were relatively independent of the work function of the metal used for the point contact. This would occur if the rectifying barrier was formed primarily by surface states. Bell and Leivo (13) reported Type IIb diamonds developed photovoltages in the visible and near infrared extending from 0.33 to 1.3 microns

with a maximum at 0.66 microns. In the ultraviolet the photovoltage peaked at 0.23 microns. Photovoltages in other materials were first observed in 1877 by Adams and Day (12).

When ordinary diamond is illuminated by ultraviolet radiation, it has a detectable electrical conductivity, while ordinarily it is an excellent insulator. This property of diamond, which it shares with certain other highly refractive solids, was discovered by Gudden and Pohl (14) in 1920 and was the subject of extended research by them designed to explain the nature of the phenomenon. Even in these earliest studies, it was clear that not all diamonds behaved alike. Gudden and Pohl (15) found that the photoconductivity was much more predominate with one specimen which was transparent to the ultraviolet radiation up to 0.23 microns than one which was opaque to wavelengths shorter than 0.3 microns. The spectral distribution of photoconductivity was also different. In the former case the curve had a pronounced tail, the photocurrent continuously rising with shorter wavelengths, while in the latter there was a maximum at approximately 0.34 microns and a minimum at 0.3 microns followed again by a rise in the photocurrent at 0.226 microns.

Bell and Leivo (16) reported that the diamond studied showed photoconductivity in the visible and near infrared with a peak at 0.66 microns. The visible and near infrared photoconductivity is observable without previous irradiation with ultraviolet light. Maxima also occurred at 0.223 and 0.228 microns in the ultraviolet.

The ratio of the photocurrent in diamond to the intensity of the light source may show large variations over the area of a single specimen (18). The conductivity also shows variations with direction (19).

## Resistivity and Hall Measurements

Brophy (20) attempted to investigate uniformity of a Type IIb diamond by floating potential probe measurements using a tungsten point. The results were inconclusive, showing variations in potential from point to point, which were experimentally reproducible.

Resistivity measurements made on the diamond under study do not indicate the inhomogeneities which Brophy encountered. Young, of this laboratory (32), found that one end of the diamond has a resistivity of 65 ohm-centimeters, and the other end  $3.6 \times 10^5$  ohm-centimeters. This resistivity of either end is obtainable on any face of the diamond. Young also made Hall measurements on the diamond and obtained the result that the diamond is a p-type semiconductor with an activation energy of 0.35 electron volts.

## Minor Elements

In 1942 Chesley (22) investigated the emission spectra of a group of thirty-three diamonds. Of the thirty elements he tested for, thirteen were detected among the thirty-three diamonds. The elements aluminum, silicon and calcium form a persistent group which appeared as minor elements in every specimen. The elements aluminum and silicon exhibited a trend to remain in a sort of a balance with each other. Absorption spectra in the ultraviolet region revealed the presence of Type II diamond, which was found to be the purest of the thirty-three diamonds. The elements iron and titanium tended to be present in the colored diamonds. The diamond identified as the Type II had a very pale green tint. Five classifications were given as to the content of minor elements in each: large, medium, small, trace, and absent. In the Type II diamond, aluminum and silicon were listed as

small and calcium and magnesium as trace. Copper, barium, iron, strontium, sodium, silver, titanium, chromium and lead were absent. In the Type I diamond, barium was listed as large, aluminum, calcium and copper as medium, strontium and chromium as small, silicon, magnesium, iron, and sodium as trace, and silver, titanium and lead as absent.

Quantitative spectrographical analysis is never an easy procedure, and with diamond in particular, it would be even more difficult, due to the nature of the material and the fact that the trace constituents are present to the extent of a few parts per million only.

Raal recently made such a quantitative analysis (23). The main impurities in the diamonds tested are silicon, calcium, magnesium, aluminum, iron and copper, with the aluminum predominating in most cases. This result is not surprising since the first five elements are readily detectable by the spectrograph. The colored diamonds, with the exception of the Type IIa diamonds, all contain iron up to an appreciable amount in some cases. Copper also shows a tendency to be present in the colored stones with the exception of the Type IIa diamonds again. Titanium appears only when iron is present. The theory of Sutherland and co-workers (24) to the effect that Type I diamonds are more impure than Type II diamonds, seems in general to be upheld, although there are exceptions.

Raal (23) gives the following results in parts per million: Type I silicon-4, calcium-5, magnesium-4, aluminum-56, iron-20, titanium-4, copper-7, chromium-absent. Type IIa silicon-2, calcium-absent, magnesium-3, aluminum-4 and iron, titanium and copper absent. Type IIb silicon-1, calcium-absent, magnesium-3, aluminum-4, and iron, titanium, copper and chromium absent. On the whole, Type IIa and Type IIb diamonds appear to differ very little as regards to impurity content. The impurities are, almost

exclusively, silicon, magnesium and aluminum, with the latter being predominant in most cases.

One theory is that aluminum, by virtue of its being an electron-acceptor is, at least in part, responsible for the semiconducting properties of Type IIb diamonds. If this is the case, the aluminum in Type IIb diamonds may be accommodated differently in this type of diamond than that in Type IIa diamonds, since the amounts of aluminum are virtually the same in the two types. Alternatively, an excess of donor levels in Type IIa diamonds may quench the p-type semiconductivity.

It has been observed that all blue diamonds are semiconductors, but not all semiconducting diamonds are blue.

## CHAPTER III

### PHOTOCONDUCTIVITY

Photoconductivity is a structure-sensitive phenomenon. A particular substance shows a large variety of behavior as the defects are not usually a uniform thing. The impurities may be segregated as to types of impurities, or concentrated at a particular point. The one thing that semiconductors have in common is that incident radiation usually increases the conductivity. Every insulator tested thus far shows this increase in conductivity. The photocurrent produced by the radiant energy may vary as a linear function of the light intensity, as a fractional power, or as a power greater than unity. In some cases the increase of intensity decreases the lifetimes of carriers, and therefore the photocurrent increases as a fractional power of the intensity. Also simultaneous irradiation by another light source may increase, or in some cases, decrease the photocurrent. Usually the photocurrent increases linearly with the applied voltage. Sometimes the photocurrent saturates beyond a certain voltage (25).

#### Theory

If the diamond crystal is irradiated with photons of sufficient energy to excite holes from bound states into the valence band where they are free to move, we have photoconductivity. After this absorption has occurred there are no longer equilibrium conditions. Photocurrent will continue to flow until recombination occurs or until the carriers are trapped by a trapping center. This recombination takes place via bound states in the

forbidden zone or by recombination of free electrons and holes. The latter becomes significant only at very high densities of both signs of carriers. The bound states are composed of impurities, vacant lattice sites, interstitial atoms, and other crystal defects.

The most general relation characterizing photoconductivity is given by

$$n = f\tau$$

where  $n$  is the steady state increase in the density of free carriers generated by  $f$  excitations per second per unit volume, and  $\tau$  is the lifetime of these carriers in the free states. The equation of photocurrent is given by

$$J = nqv$$

where  $J$  is the current density,  $v$  the average velocity of the free carriers, and  $q$  is the electronic charge.

The mobility  $\mu$  is defined by

$$\mu = v/F$$

where  $F$  is the applied electric field. This gives us the equation of the parameters of photoconductivity as

$$J = f\tau q\mu F$$

The gain factor for a semiconductor is given by

$$G = \tau/T$$

where  $T$  is the transit time. It is seen from this that the gain can vary from values below unity to values greater than unity without any abrupt or even definable change in the physics of the process. The only implied condition for gain greater than unity is that the electrodes are able to supply carriers freely to the crystal as they are needed. This is another



way of defining an ohmic contact.

Gudden and Pohl (15) have found that for diamonds, under certain favorable conditions, the absorption of each photon of sufficient energy frees one electron for the photocurrent.

### Experimental Technique

For the monochromator and current measuring system, a Beckman DK-1 spectrophotometer was used with a tungsten lamp for the visible and near infrared source, and a hydrogen lamp as the ultraviolet source. The light was chopped at 480 cycles per second. The amplifiers are band-pass amplifiers of 480 cycles per second.

The spectrophotometer was adjusted so that the wavelength was correct to within  $3 \text{ m}\mu$  in going from long to short wavelengths. The spectral distribution of the source was determined using a Reeder Thermopile No. RHL-7C. This thermopile is a vacuum thermopile with a quartz transmission window. The curve of the spectral distribution of the light source is given in figure 1 as a plot of wavelength versus the electromotive force delivered by the thermopile. The ultraviolet spectral response curve was obtained with a General Electric FJ-76 phototube. This phototube is a specialized tube for the ultraviolet, and is equipped with a quartz window. The response curves can be reduced to photons per second per unit area so that the photocurrent curves can be corrected in terms of photons per second.

The recorder was calibrated by applying known differences in potential input to the amplifiers. In this manner the photocurrent could be read from the chart directly.

The spectrophotometer circuit was modified to eliminate the bias on

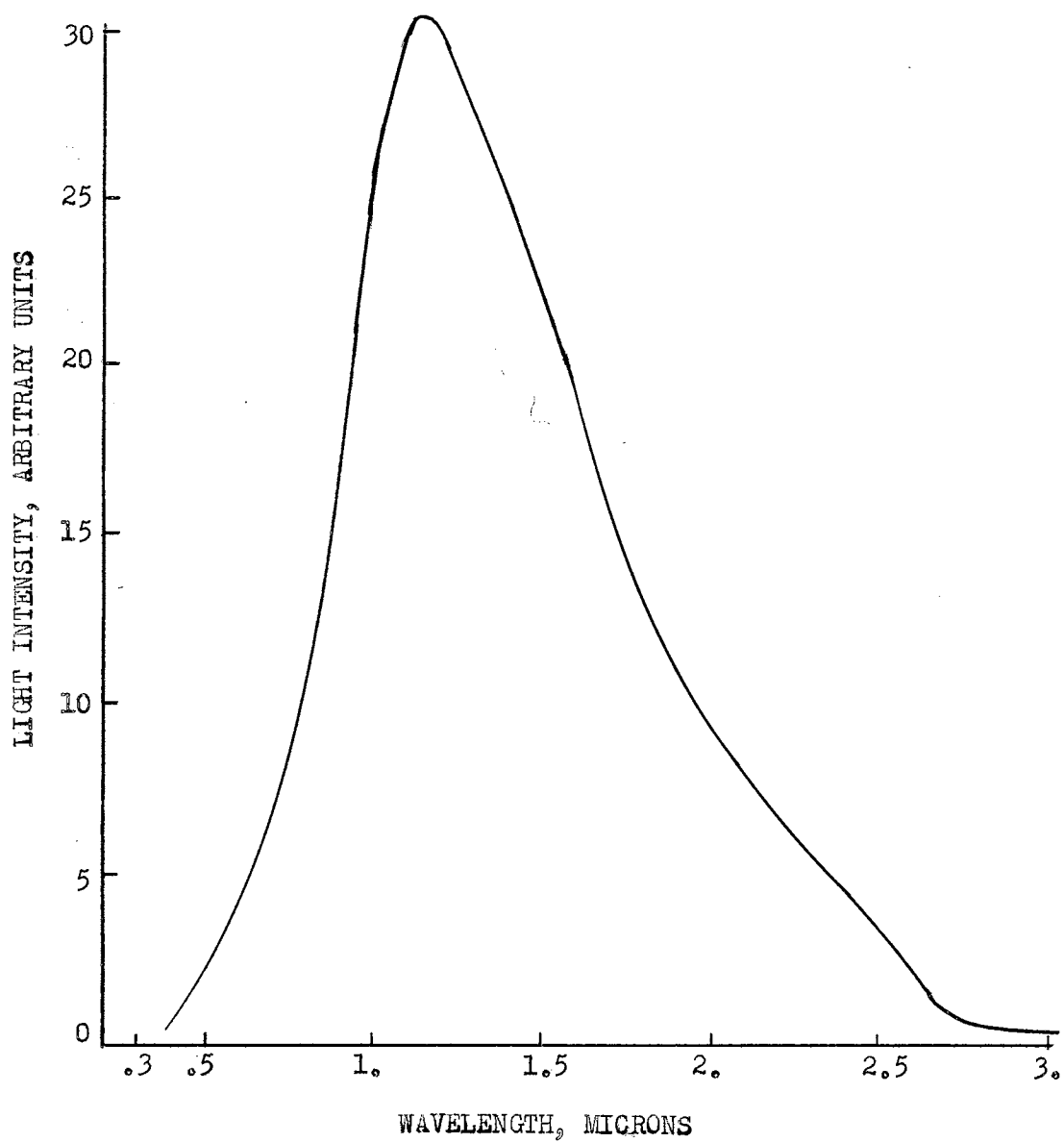


Fig. 1. Intensity Distribution of the Tungsten Light Source at the Exit Slit of the Monochromator of the Beckman DK-1 Spectrophotometer.

the lead sulfide cell, and the diamond was substituted in the circuit for the lead sulfide cell. The diamond was placed in the regular sample compartment and was shielded from stray irradiation.

A crystal holder for low temperature measurements was constructed, using an inner and outer can with a vacuum for insulation. The light was passed through quartz windows, one in each can. The windows were transparent to the limit of the instrument which was 180 millimicrons. For infrared measurements, sodium chloride windows were used. The holder has a switching mechanism for reversing bias on the diamond without disturbing the exterior circuit. The cooling for low temperature work was obtained by passing dry nitrogen through a bath of liquid nitrogen and then into the inner can. An iron-constantan thermocouple was mounted next to the specimen in the inner can in order to measure the temperature.

The circuit used for the measurement of the photocurrent is shown in figure 3. This circuit puts any ground leak of the batteries in the low potential side of the circuit, thus reducing the noise problems considerably. The currents measured in this study were of the order of  $10^{-10}$  amperes. It is easily seen that working in this range of current makes the circuit noise problem a primary problem to be overcome. This also points out the extreme sensitivity of the amplification system of the Beckman DK-1.

#### Sample Description

The diamond investigated is a rectangular parallelepiped measuring 2.25x3.51x6.48 millimeters. One end has a blue coloration which is visible to the eye. The resistivity of the blue end is 65 ohm-centimeters, and

the resistivity of the clear end is  $3.6 \times 10^5$  ohm-centimeters. The blue end appears to extend into the diamond approximately two millimeters.

#### Illumination

The intensity of the light incident upon the sample varies as the square of the exit slit width of the monochromator. The photocurrent also varies as the square of the slit width, thus giving a linear relationship between the photocurrent and the intensity of illumination (see figure 4).

Ultimately the sensitivity of a photoconductor is not measured by the number of electrons per photon, but by the signal to noise ratio for a given amount of incident radiation (25). "Signal" is the average photocurrent; "noise" is the root mean square fluctuation in current about the average. A good signal to noise ratio can be obtained in the clear end of the diamonds because the resistivity of this end is such that an appreciable field can be obtained without a very large dark current. A large dark current tends to introduce an appreciable amount of noise.

Noise in the circuit is always a major problem. Noisy contacts are the most likely source. However, other non-uniformities of a less obvious nature can contribute as well. These include non-uniform potential distribution along the photoconductor such as large potential barriers, and non-uniform photosensitivity. Obviously there is a non-uniform potential distribution due to the extreme difference in resistivity. This difference is so great, however, that we have actually considered the blue end as a contact to the clear end. Direct illumination of either or both of the contacts did not add to the noise level of the photocurrent. The

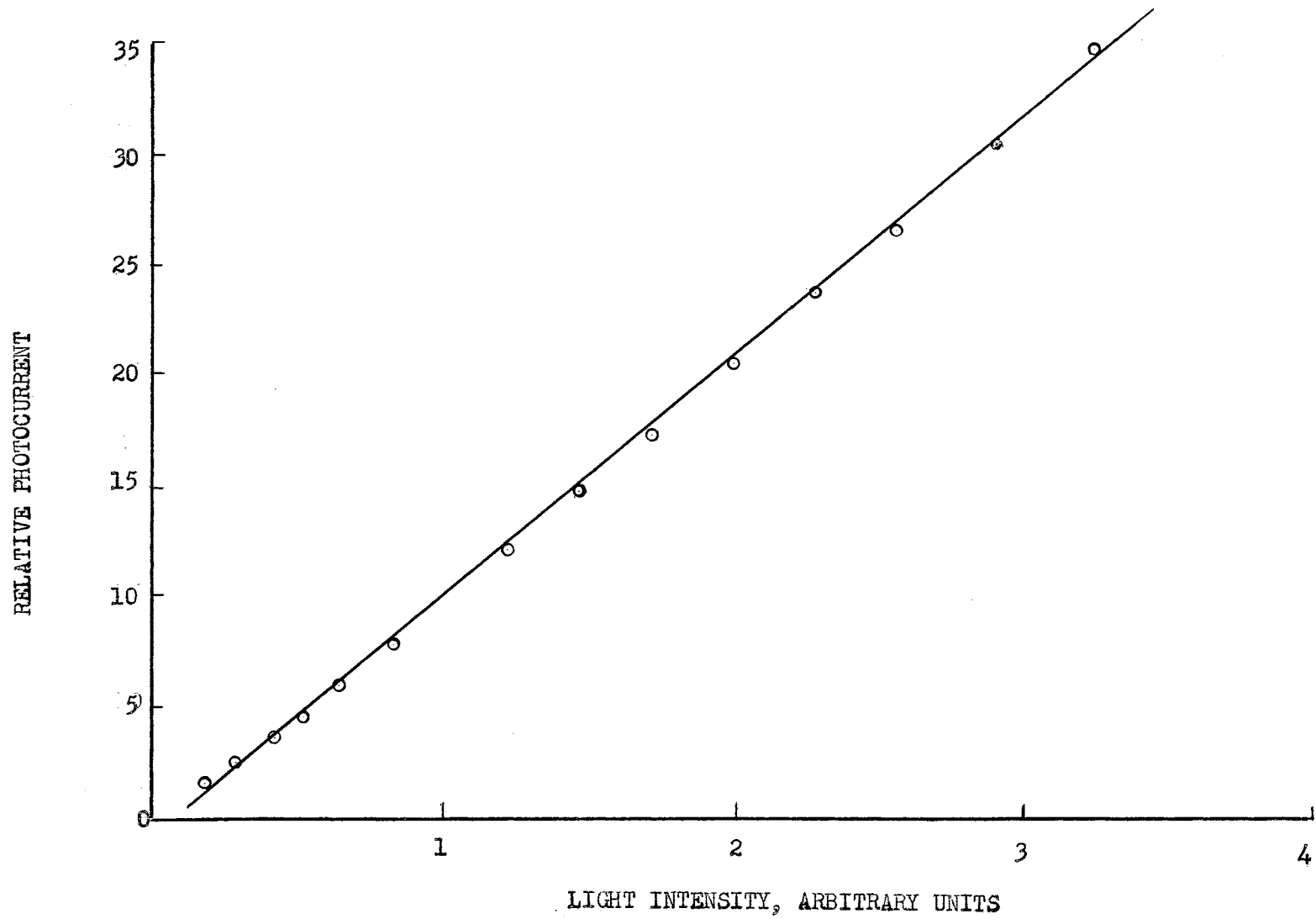


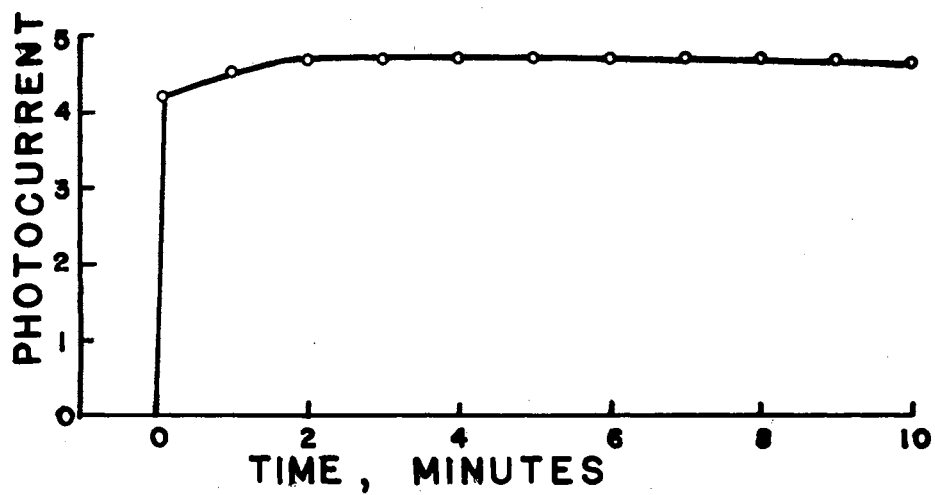
Fig. 4. Dependence of the Photocurrent Upon the Intensity of Irradiation.

reversal of current was a very different matter. Reverse bias introduced large amount of noise, which in some cases was enough to completely mask the photoconductivity. Reverse bias occurs when the blue end is negative. The reversal of the applied field also reduced the photocurrent for a fixed potential difference between the crystal electrodes. This reduction was due to the change of field brought about by the marked difference in resistance of the contacts in the reverse direction.

#### Decay Time

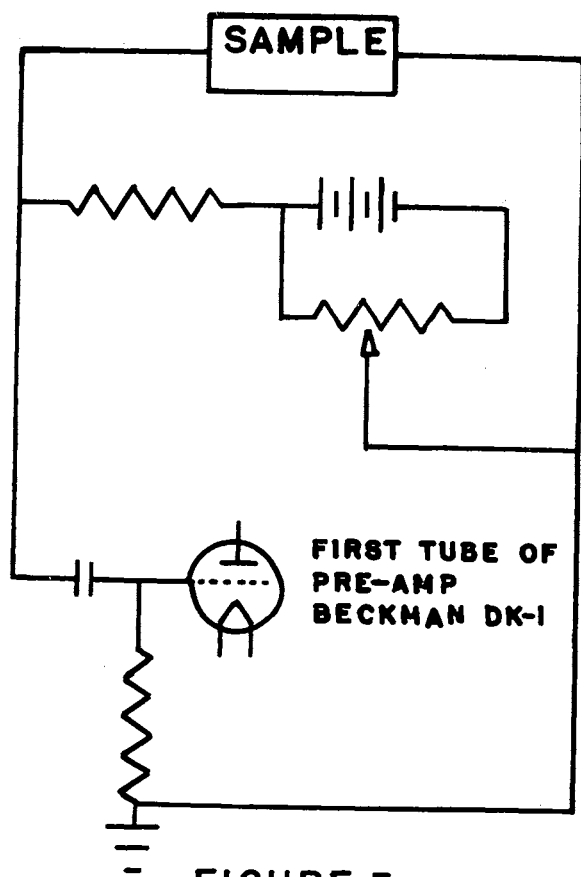
Although the shallow-trapping states do not affect the steady state photocurrents, they affect the time it takes to reach a steady state photocurrent and the time necessary for the photocurrent to decay when the light source is removed. The time necessary for the photocurrent to reach a steady state is increased as is the time for this current to decay to zero by way of emptying of the traps. In order to increase the density of the free carriers, the density of carriers in the shallow trapping states must also be increased. The rise time is then increased by the ratio of shallow-trapped to free carriers. This is also the case for the decay time.

The photocurrent in the diamond rose to 87% of the maximum in six seconds, then climbed very slowly to a maximum in 120 seconds. (see figure 2). The photocurrent remained constant until the source was removed. For direct current measurements the build-up which takes approximately ten minutes, then takes a considerable time to decay after the excitation has been removed. This indicates a large density of shallow-trapping states.



**FIGURE 2**

Fig. 2. Photocurrent vs Time, Showing the Rise Time of the Photocurrent.



**FIGURE 3**

Fig. 3. Circuit Diagram of the Circuit Used for Measurement of the Photocurrent.

### Field Dependence of Photoconductivity

Fields up to 170 volts per centimeter have been applied to the specimen in the determination of the photocurrent (see figure 5). Over this range, the photocurrent is a linear function of the field. The field was measured using potential probes, thus eliminating the potential drop across the contacts.

### Spectral Response as a Function of Temperature

This sample gives not only the normal ultraviolet photocurrents, but also a very definite visible photocurrent peak. Figures 6a, page 20, and 6b, page 21, give the spectral distribution of this visible photocurrent at room temperature. Figure 6a is the uncorrected curve, and 6b the corrected curve for the light source in terms of photons per second. The data were taken continuously, and the points shown are particular points where the light source distribution correction was made. The plots are in photocurrent per photon versus wavelength in microns. The uncorrected curve shows the peak at approximately 720 milli-microns with a slight secondary peak at approximately 850 milli-microns. The 0.72 micron peak in terms of energy is 1.72 electron volts. This curve corrected however, has no indication of the 0.85 micron peak, and the predominate peak has been shifted to 0.60 microns, which corresponds to 2.04 electron volts. The photocurrent at this peak is  $9.5 \times 10^{-9}$  amperes. The uncorrected, ultraviolet, photocurrent peak at room temperature is given in figure 7. Actually this is also essentially the corrected curve. The correction for the light source does not shift the 0.228 micron peak and shifts the 0.222 micron



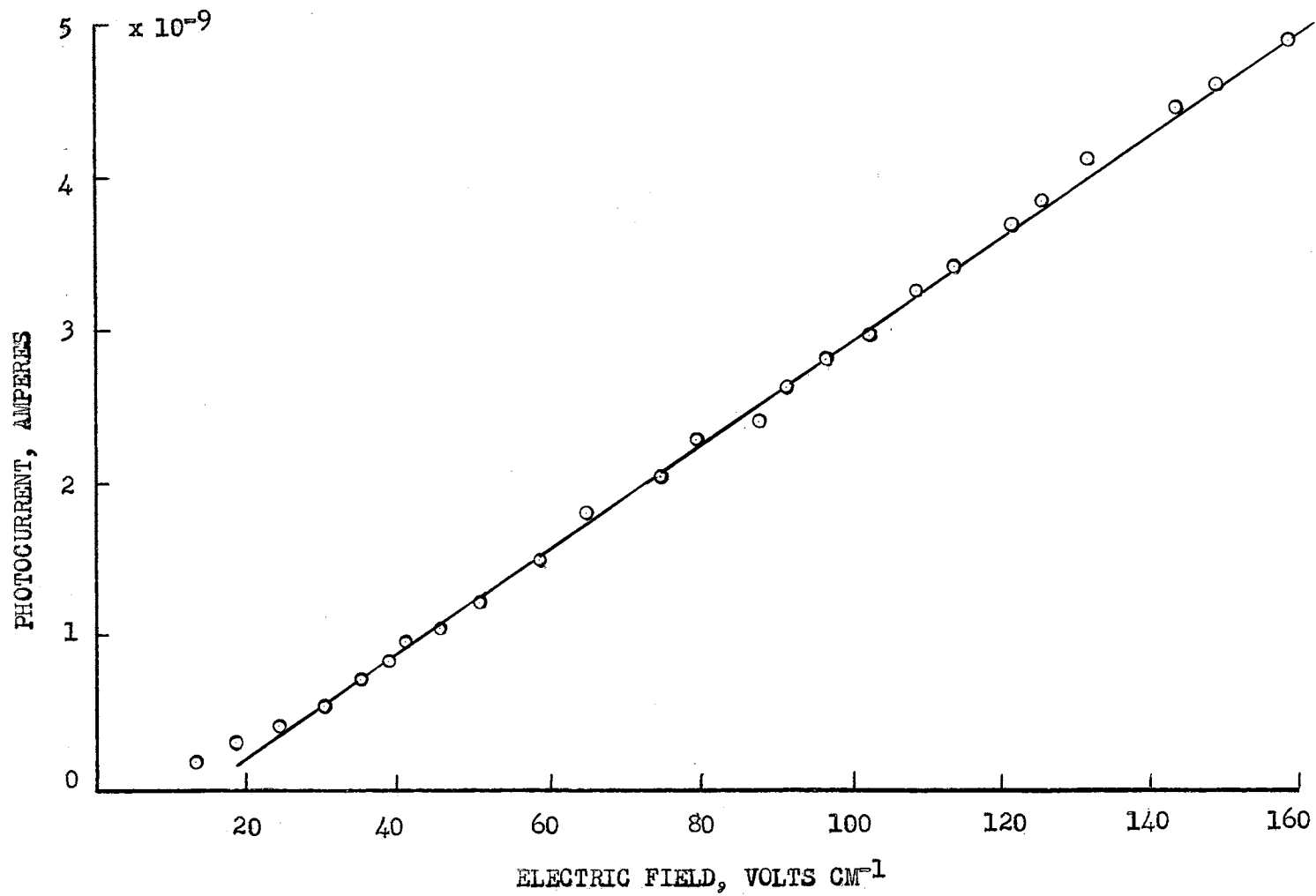


Fig. 5. Dependence of the Photocurrent Upon the Applied Electric Field.

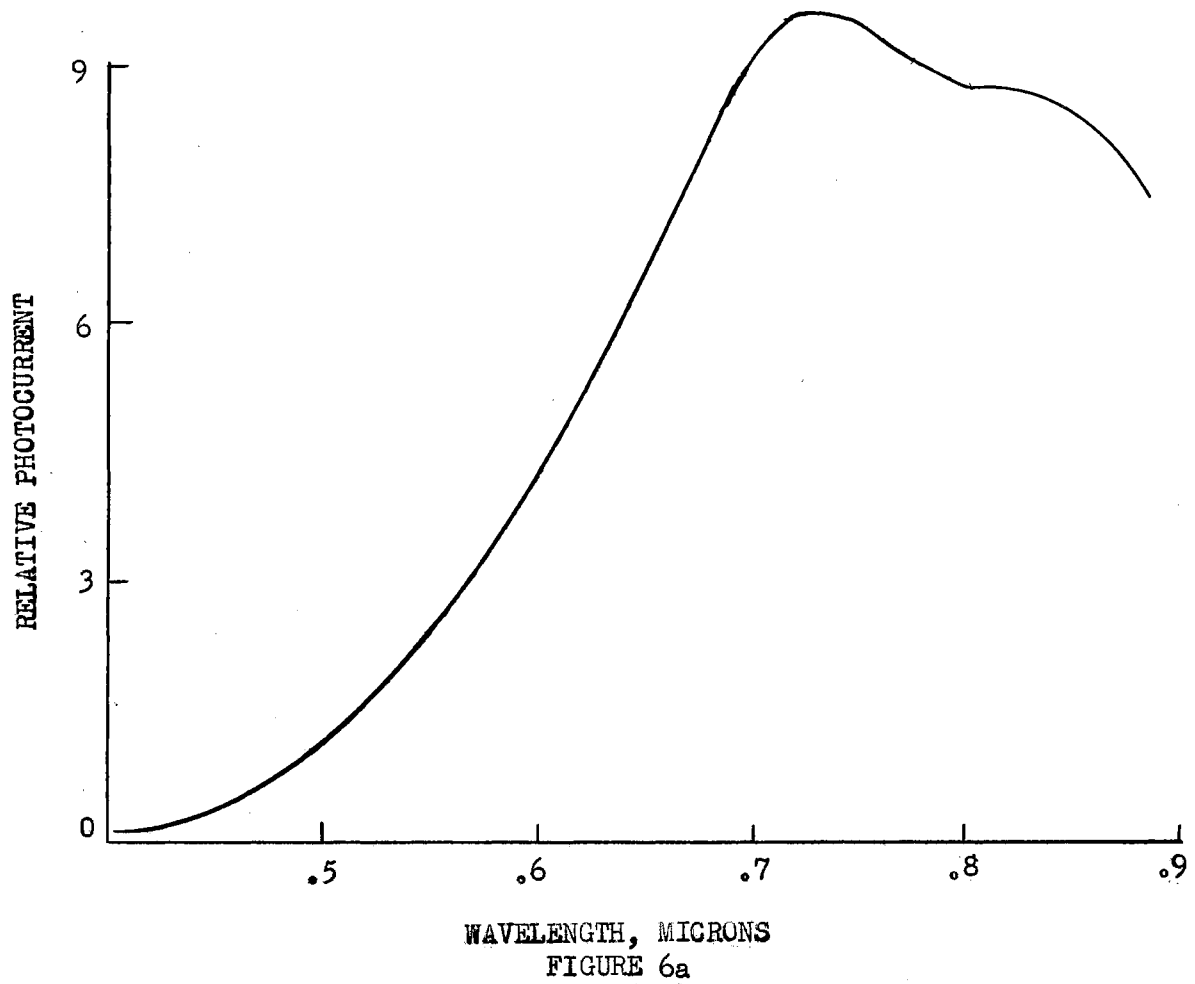


Fig. 6a. Uncorrected Spectral Distribution of the Photocurrent in the Visible and Near Infrared. The photocurrent in this plot is uncorrected for the distribution of the light source and peaks at 0.72 microns with a secondary peak at 0.85 microns.

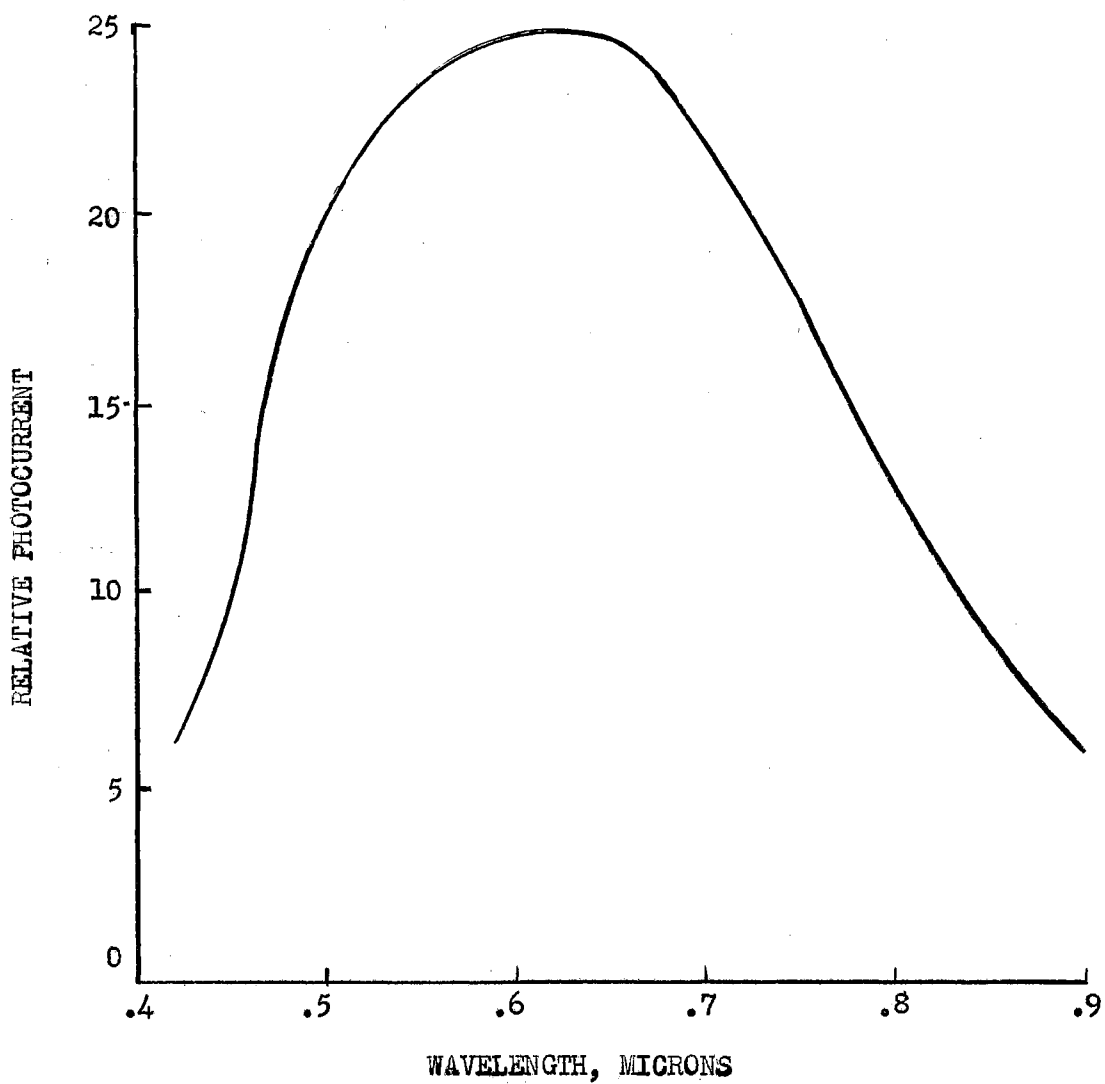


Fig. 6b. Corrected Spectral Distribution of the Photocurrent in the Visible and Near Infrared. This is the plot of 6a corrected for the light source distribution. The plot is in photocurrent per photon vs wavelength in microns.

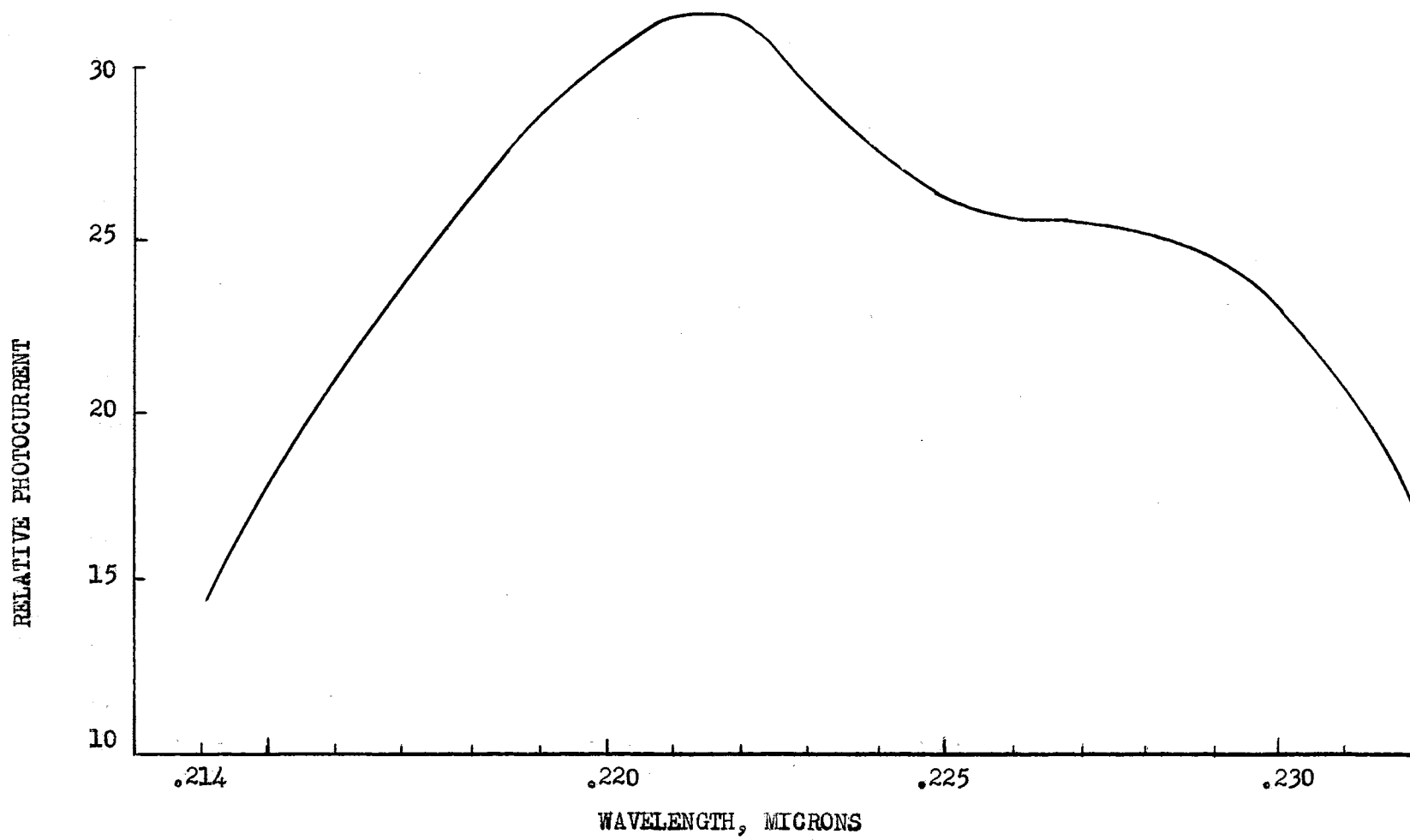


Fig. 7. Spectral Distribution of the Photocurrent in the Ultraviolet.

peak to 0.221 microns. The predominate peak appears at 0.222 microns, which corresponds to 5.58 electron volts, and a secondary peak at 0.228 microns, which corresponds to 5.45 electron volts.

Photocurrents have been observed both to increase and decrease with temperature, depending on the temperature range and the light intensity (25). The temperature can be expected to influence the lifetimes of free carriers through the capture cross sections and the number of ground states.

Since the distances of the quasi fermi levels from the valence and conduction bands depends on the temperature, the higher temperature would bring the levels closer together. If one class of bound states were predominant, then this would reduce the number of ground states and result in an increase in photocurrent with increasing temperature. On the other hand, when there is more than one class of bound states, the photocurrent can increase or decrease with change in temperature as different bound states can shift in or out of a ground state category. In general, the explanation of the temperature dependence of photocurrents in a given photoconductor is difficult because generally more than one parameter changes with temperature.

By increasing the sensitivity of the circuit to a maximum and opening the slit to two millimeters, two additional peaks were found. The peaks are very weak at room temperature, but assume a major role at a low temperature, as will be discussed later. The peaks are at 1.46 and 1.75 microns, which correspond to 0.85 and 0.71 electron volts respectively. This expanded curve shows the curve has started to rise at 2.08 microns or 0.59 electron volts. When this region is studied with an infrared monochromator, we see that photoconductivity has started at 3.0 microns or 0.41 electron

volts. The photocurrent returns to zero at approximately 0.35 microns or 3.53 electron volts. No photoconductivity was observed in the region of 5.1 to 12 microns, or in the region of 0.245 to 0.35 microns.

Increasing the temperature increases the photocurrent until approximately  $400^{\circ}$  K. At higher temperatures the photocurrent decreases as the temperature increases. It should be noted that the increase is an increase in the photocurrent of the broad region of photoconductivity from 0.35 to 3 microns, and does not appreciably increase the half width. The noise level increases sharply at  $405^{\circ}$  K and increases rapidly with increase in temperature.

The photoconductivity peak decreases in magnitude and shifts to shorter wavelengths upon decreasing the temperature below room temperature. This shift is already observable at a temperature of  $250^{\circ}$  K (figure 8). The corrected peak appears at 0.59 microns instead of 0.60 microns. At a temperature of  $223^{\circ}$  K, two additional peaks are resolved: the first appears at 1.84 and the second at 2.02 microns. The predominant peak has shifted from 0.6 at room temperature to 0.58 microns (figure 9). At this temperature there is also an indication of a peak at approximately 1.24 microns. The ultraviolet induced photocurrent is no longer measurable from approximately  $240^{\circ}$  K down. When the temperature has been reduced to  $150^{\circ}$  K the predominant peak has shifted to 0.52 microns. In addition, there are three additional significant peaks which appear. They are at 0.92, 1.6, and 2.16 microns, which correspond to 1.35, 0.78 and 0.57 electron volts respectively (figure 10). There is a slight indication of a peak at 1.24 microns in this graph which does appear at other temperatures. The photocurrent has risen from the zero point at 2.4 microns rather than the 2.08 microns at

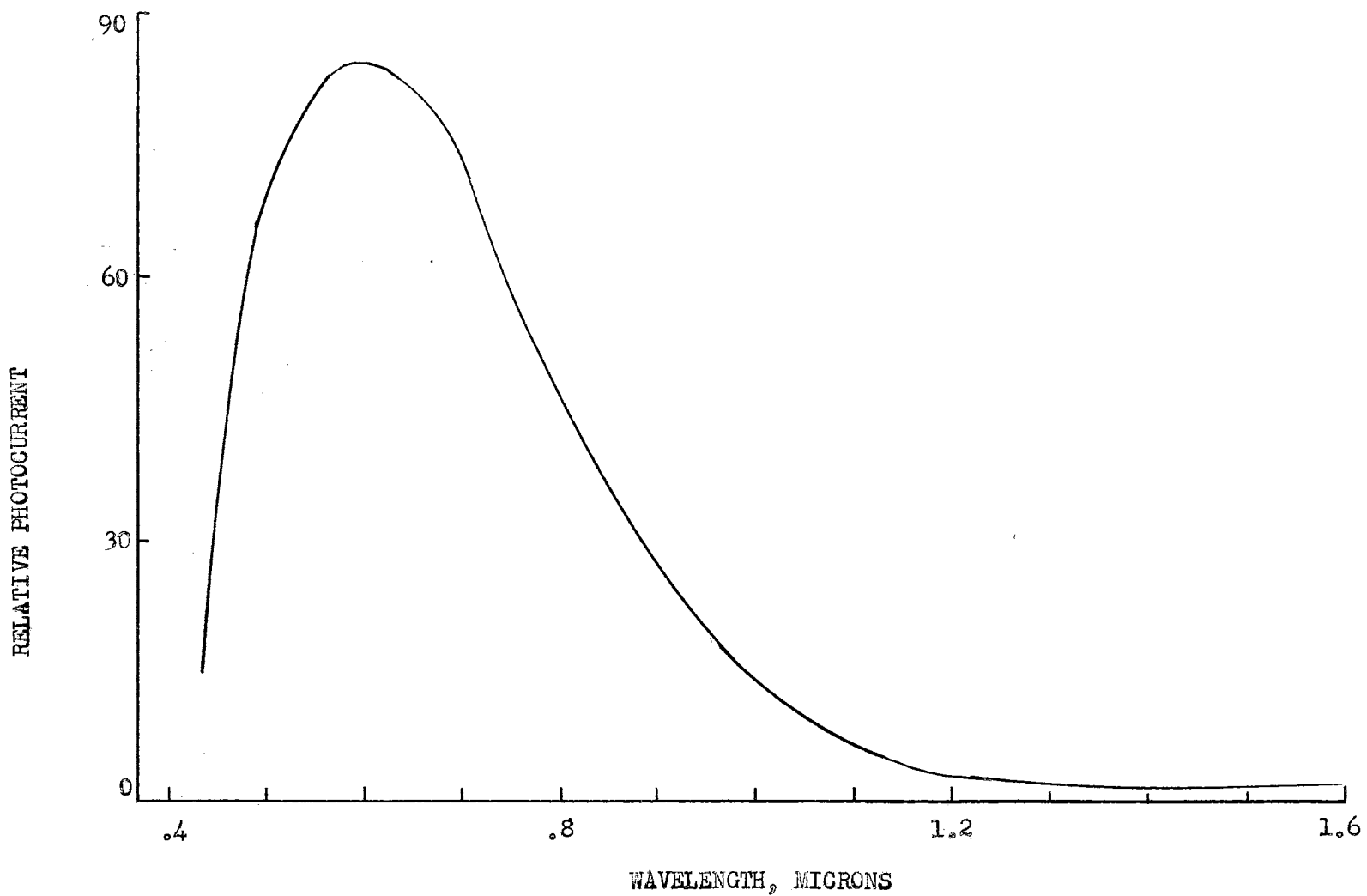


Fig. 8. Spectral Distribution of the Photocurrent in the Visible and Near Infrared at 250° K.

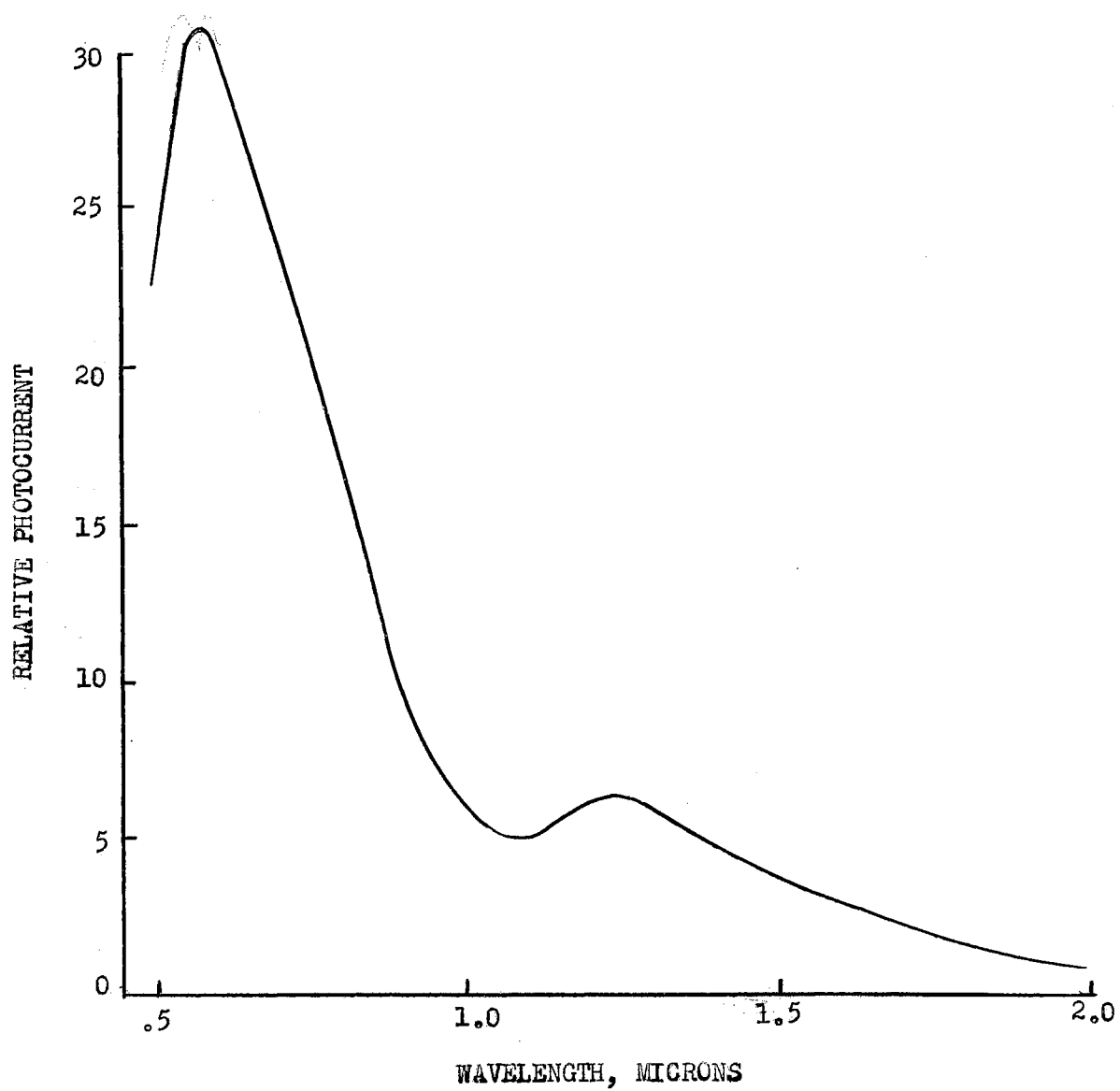


Fig. 9. Spectral Distribution of the Photocurrent in the Visible and Near Infrared at 223° K.



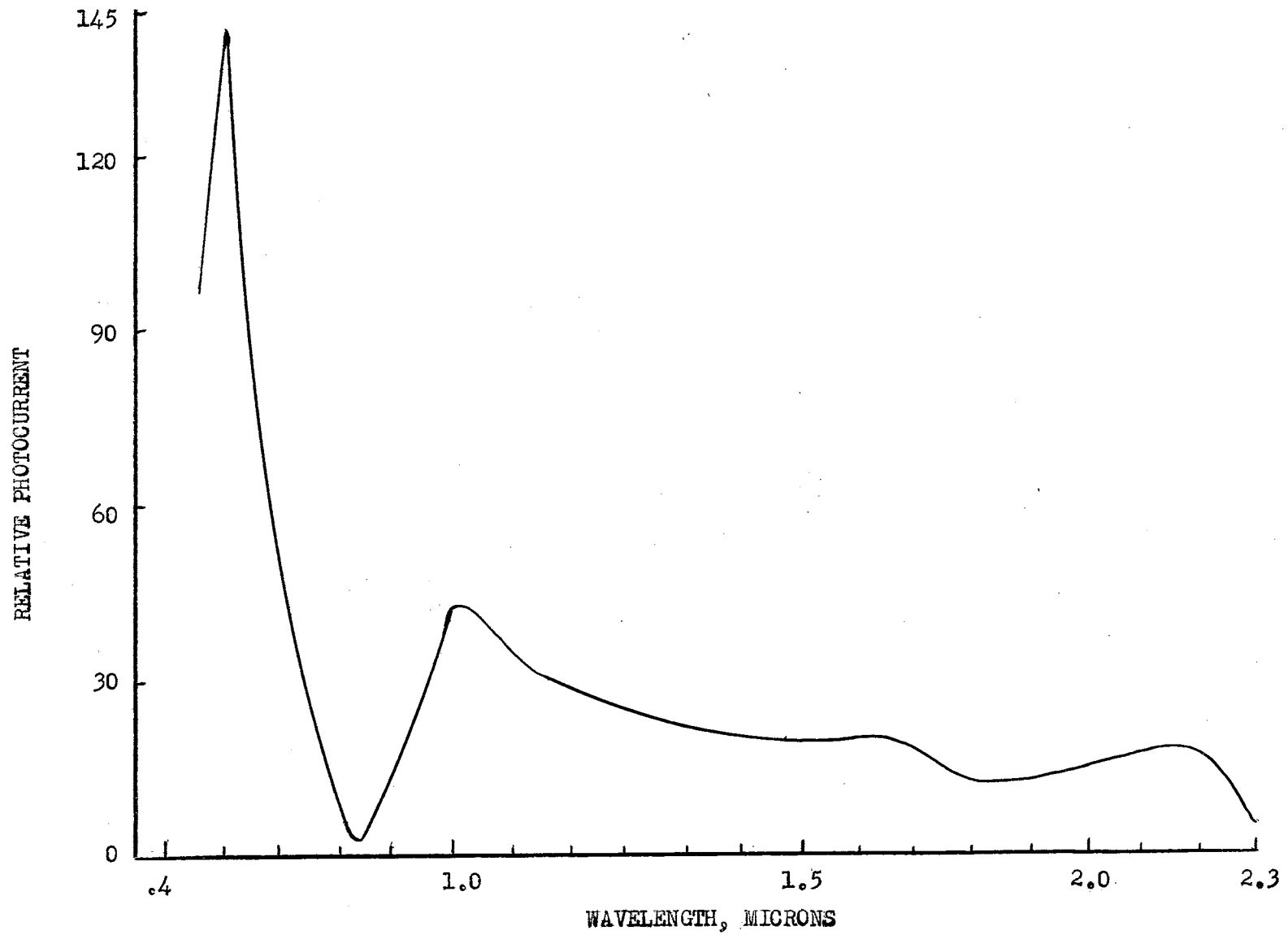


Fig. 10. Spectral Distribution of the Photocurrent in the Visible and Near Infrared at 150° K.

room temperature. At a temperature of  $127^{\circ}$  K, the lowest temperature obtained in this study of photoconductivity, the predominant peak is 0.88 microns or 1.41 electron volts. The peak which appeared at 0.6 microns at room temperature and which shifted to 0.52 and  $152^{\circ}$  K, has now disappeared and is not shown in this chart (figure 11).

#### Photoconductivity in Different Regions of the Diamond

The diamond was masked into one-sixth portions and photoconductivity measurements were made irradiating these portions. The room temperature peak, in these sections, appeared at 0.60 microns in the blue end, but was at 0.66 microns in the clear end. At a temperature of  $148^{\circ}$  K, the peak had been reduced in magnitude, and in some sections the resolved peaks in the infrared has started to appear. The blue end at this temperature gave essentially the same peak as at room temperature, and there were no infrared peaks indicated. The clear end had its peaks at 0.7, 1.28, 1.56 and 1.74 microns, so that we see that the infrared peaks have started to appear at this temperature. At a temperature of  $123^{\circ}$  K the photocurrent had reduced in magnitude to the point that it was no longer measurable in any of the sections.

#### Directional Dependence

Photoconductivity data have been taken with the largest surface area of the diamond being irradiated and contacts painted over the entire ends of the diamond. Actually it made no difference which of the four faces was irradiated. As long as the field was the same and the contacts were the same, the photocurrent was the same. When the long narrow sides of

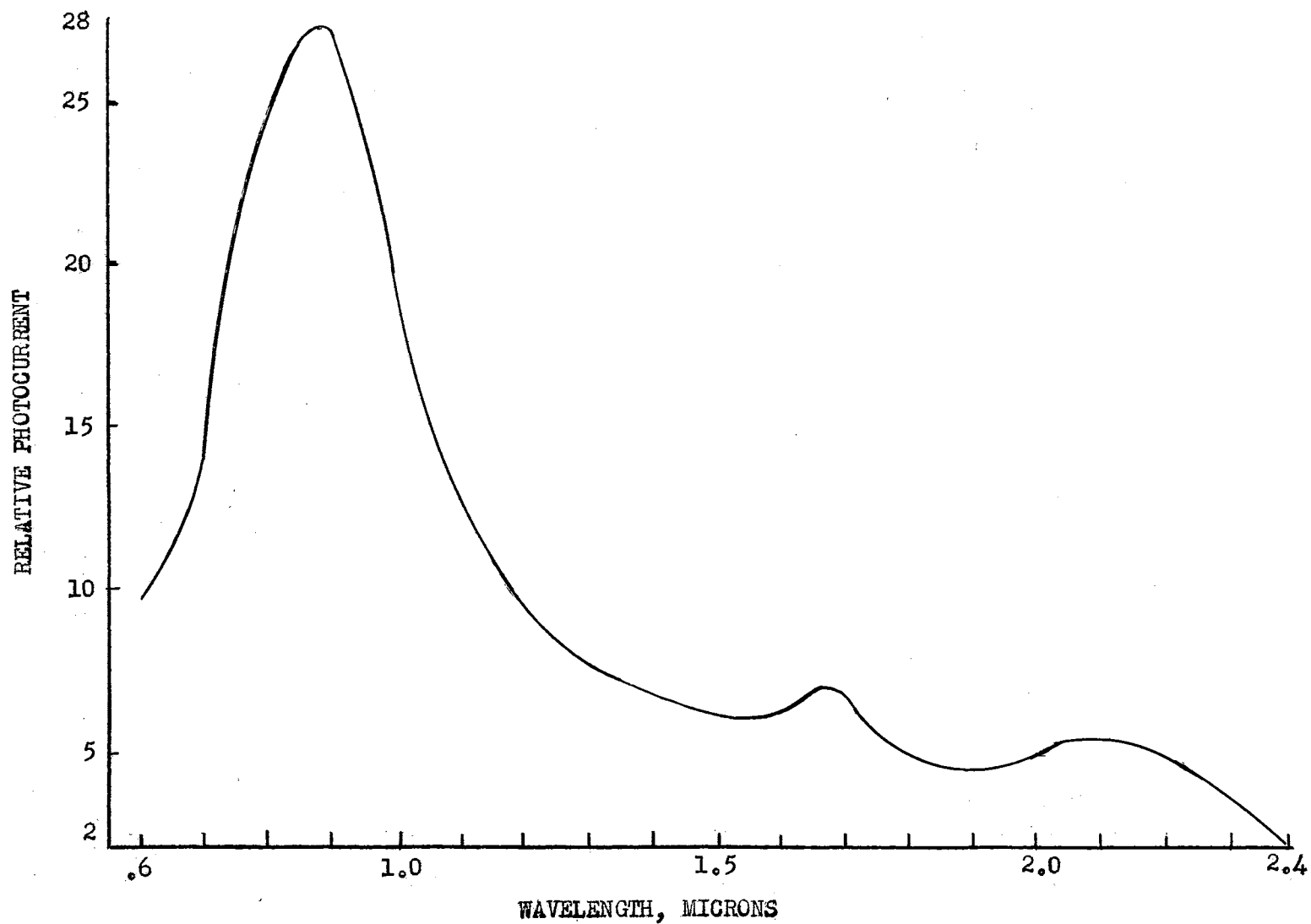


Fig. 11. Spectral Distribution of the Photocurrent in the Visible and Near Infrared at 127° K. 62

the diamond were painted, no photocurrent was observed regardless of the face that was irradiated. If the long narrow sides were painted so as to eliminate any paint on the blue end of the diamond, then photoconductivity was observed. Irradiating the largest surface areas or either end of the diamond gave a photocurrent. Upon painting the largest surface areas as contacts, no photocurrent was observed upon illuminating any face. Again, with the paint removed from the blue end, a photocurrent was observed upon irradiation of any of the other faces. This directional effect can be explained in terms of the resistivity. The resistivity of the blue end is 65 ohm-centimeters, and the clear end has a resistivity of  $3.6 \times 10^5$  ohm-centimeters. Because of the high conductivity of the blue end, the electric field in the clear end is drastically reduced for a given current if the contacts extend into the blue end. If high potentials are used, one obtains such a high dark current, and thus a very high noise level, so that the photocurrent is no longer measurable.

Measurements were made to determine whether the conduction process is a bulk or a surface phenomenon. The diamond was masked and irradiated in such a manner so that the ratio of volume to surface area was different. The photocurrent was the same regardless of which face was illuminated indicating a bulk effect. Next, the diamond was masked excepting for small areas on different faces, and these areas were irradiated. The ratio of the photocurrents was in closer agreement with the ratio of the volumes irradiated rather than the ratio of the surface areas. This again indicates a bulk effect, but the ratios were not exact. Next, the diamond was masked, excepting for thin strips along the edges. In this case the ratio of the photocurrent was in closer agreement with the ratio of the surface

areas rather than the ratio of the volumes. This can possibly be explained by internal reflections from the side surfaces. Although surface conduction cannot be ruled out, from the data taken one must consider the conduction process is primarily a bulk phenomenon.

#### Photovoltaic Effect

The photovoltaic effect was observed in the diamond at room temperature. The spectral distribution of the photovoltage is very similar to the photocurrent distribution when the metal semiconductor barrier is on the clear end. When the barrier is on the blue end, however, a very definite peak occurs at approximately 0.4 microns. This peak is not merely an indication of a rise in the regular peak at 0.6 microns, but actually will be the predominant peak when corrected to photovoltage per photon. Although measurements were not taken in the infrared, Bell (11) reports that there is no photovoltaic response in the region of 1.2 to 12 microns.

## CHAPTER IV

### RESULTS AND CONCLUSIONS

Photoconductivity in the Type IIb diamond has been studied as a function of intensity of illumination, spectral distribution, electric field strength, temperature, and crystal orientation. Also studied were various aspects of the photovoltaic effect.

Optical transitions of electrons from the valence to the conduction band will occur vertically if the wave vector is conserved (36). Absorption data would then give what one might call the optical energy gap, which would be the minimum energy necessary to excite an electron from the valence band to the conduction band in this case. Non-vertical transitions may also occur with the emission or absorption of a phonon. Stein (29) from absorption data, obtained a value of 5.5 electron volts for the energy gap of the diamond under study. Since the fundamental absorption edge may involve exciton formation rather than photoionization, this value of 5.5 electron volts is either the forbidden gap, or it represents a lower limit to the gap. In the study of impurity and lattice defects, photoconductivity may provide a better method than absorption methods. The optical absorption due to impurity and lattice defects is usually rather small because of their low concentrations. Photoconductivity measurements can be made on specimens with impurity contents that are too small to appear in optical measurements.

Alternating current measurements were made to eliminate the error induced by the dark current changing from point to point. This change in

the dark current is the result of shallow trapping. The shallow trapping does not affect the steady state photocurrent, only the time necessary to obtain this photocurrent and for it to decay. The decay time is of the order of hours so that the dark current reading will be in error unless one waits for the shallow traps to empty or the dark current is adjusted between each reading.

Ultraviolet induced photocurrent in the diamond is much greater than the photocurrent induced by visible light when corrected in terms of photocurrent per photon. However, the photocurrent in the ultraviolet is very small because no suitable high intensity ultraviolet source is available. The ultraviolet induced photocurrent decreases to a point that it is no longer measurable at a temperature of  $140^{\circ}$  K.

The reason that the photocurrent peaks instead of giving a continuum, is most probably due to transition probabilities. The valence band in diamond is approximately 22 electron volts in depth (36). Herman also introduces a model of the energy band system for diamond which includes multiple valence and conduction bands.

In regard to directional dependence the peak in the visible region appears at the same wavelength regardless of direction of the applied electric field. Also, the magnitude of the photocurrent does not appreciably change with direction. When contacts are placed on the diamond such that current can flow in the blue end, troubles are encountered. The resistivity of the blue end is 65 ohm-centimeters, whereas the clear end is  $3.6 \times 10^5$  ohm-centimeters. Therefore, when the contacts are made on the blue end, it is impossible to obtain an appreciable field without a very large dark current. A large dark current introduces noise into the circuit which

actually will overshadow the photocurrent signal. For this reason it is virtually impossible to obtain a spectral distribution of the photoconductivity if the contacts touch the blue end.

Photoconductivity measurements were also attempted in another semiconducting diamond which is on loan from the Smithsonian Institute. Although accurate resistance measurements were not made of this diamond, it has a low resistivity. The diamond is gem cut and has a blue coloration. The same problem was encountered with this diamond in regard to high dark currents, which caused too much noise before an appreciable field was obtained. The diamond is a photoconductor as shown by placing a battery and ammeter in series with it, taking a dark current reading, then turning on a desk lamp and observing the increase in current. The same argument is valid for the other semiconducting diamond which was available.

The question, "Is this a bulk or surface effect?", should be answered--both. The data which were obtained indicates a bulk property. From the very fact that Young (32) obtained the Hall Effect also points to a bulk conduction. However, Wayland (37) obtained the photoelectro-magnetic effect which is an indication of a surface effect. The bulk effect appears to be predominant, but there is some surface effect. It is known from Bell's (11) rectification data that surface states are present.

The spectral distribution of the photovoltaic effect in the visible region is very similar to the photoconductivity excepting the region is not as broad, and an additional peak appears at approximately 0.4 microns when the illuminated contact is on the blue end. The 0.4 micron peak, after correction to photovoltage per photon, is the predominant peak. Evidently this particular peak is a surface phenomenon.



Photoconductivity is a linear function of both the intensity of illumination and electric field strength. Since it is a linear function of the illumination, this implies that the lifetimes of the holes do not change with increasing light intensity.

The photoconductivity peaks shift toward shorter wavelengths and decrease in absolute magnitude with decreasing temperature. One would expect the shift toward shorter wavelengths, meaning slightly more energy was needed for the transition. The energy gap is a function of the thermal vibrations of the lattice, and the intrinsic gap increases with decreases in temperature on the order of from 2 to  $4 \times 10^{-4}$  electron volts per degree centigrade. Similarly, one might expect the activation energy for photoconductivity to increase with decreasing temperature. Another contributing factor could be non-vertical transitions. The net sum of these factors might well explain this shift toward shorter wavelengths with decrease in temperature.

At this point it would be somewhat premature to propose an energy band scheme for the diamond with the available data. The multiple valence and conduction band scheme would complicate the problem so that only after a detailed study of transition probability, and a careful analysis of data compiled, could an energy band scheme be presented. Also the temperature shift of each impurity band as well as the shift of the energy gap must be taken into account.

#### Suggestions for Further Study

A quantitative study of the relationship of surface and bulk conduction in the diamond should be made. This information would lead to a

clearer understanding of the impurity levels in Type IIb diamond.

Other possibilities include low temperature photovoltaic effect measurements, phosphorescence and fluorescence studies.

A SELECTED BIBLIOGRAPHY

1. Robertson, R., J. J. Fox, and A. E. Martin. "Two Types of Diamond." Phil. Trans. Roy. Soc., A 232 (1934), 463.
2. Custers, J. F. H. "Type IIb Diamonds." Physica, 20 (1954), 183.
3. Custers, J. F. H. and F. A. Raal. "Fundamental Absorption in Diamond." Nature, Vol. 179 (1957), 268.
4. Stein, H. J. and W. J. Leivo. "Optical Absorption in Semiconducting Diamond." Bulletin of the American Physical Society, (March, 1956), 16.
5. Blackwell, D. E. and G. B. B. M. Sutherland. "The Vibrational Spectrum of Diamond." Journal de Chemie Physique, 46 (1949), 9.
6. Austin, I. G. and R. Wolfe. "Electrical and Optical Properties of a Semiconducting Diamond." Phys. Rev., 99 (August, 1955), 1336.
7. Collins, R. J. and H. Y. Fan. "Infrared Absorption Bands in Germanium, Silicon and Diamond." Phys. Rev., 93 (February, 1954), 674.
8. Clark, C. D., R. W. Ditchburn and H. B. Dyer. "The Absorption Spectra of Natural and Irradiated Diamonds." Proc. Roy. Soc., A 234 (February, 1956), 363.
9. Dyer, H. B. and Mathews. "Fluorescence in Diamond." Proc. Roy. Soc. Vol. 243 (January, 1950), 320.
10. Leivo, W. J. and R. Smoluchowski. "A Semiconducting Diamond." Phys. Rev., 98 (1955), 1532(A).
11. Bell, M. D. "Rectification and Photoeffects in Semiconducting Diamonds." (Unpublished Master's Thesis, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, August, 1956.)
12. Adams, W. G. and R. E. Day. Proc. Roy. Soc. (London) 25, 113 (1876), cited by A. L. Hughes and L. A. Dubridge. "Photoelectric Phenomena." (McGraw-Hill Book Company, Inc., New York, 1932), p. 360.
13. Bell, M. D. and W. J. Leivo. "Photovoltaic Effect in Semiconducting Diamond." Bulletin of the American Physical Society, (April, 1957), No. 4.
14. Gudden and Pohl. Zeit f Physik, 3 (1920), 123.

15. Gudden and Pohl. Zeit f Physik, 7 (1921), 248.
16. Bell, M. D. and W. J. Leivo. "Photoconductivity in Semiconducting Diamond." Bulletin of the American Physical Society, (December, 1956), No. 8.
17. Pant, D. D. "The Photoconductivity of Diamond." Proc. Ind. Acad. Sci., A19 (May, 1944), 325.
18. Achyutan, K. "Local Variations in the Photoconductivity of Diamond." Proc. Ind. Acad. Sci., A24 (July, 1946), 162.
19. Achyutan, K. "Directional Variations of Photoconductivity in Diamond." Proc. Ind. Acad. Sci., A27 (February, 1948), 171.
20. Brophy, J. J. "Preliminary Study of the Electrical Properties of a Semiconducting Diamond." Phys. Rev., 98 (1955), 1532.
21. Dyer, H. B. and P. T. Wedepohl. "Electrical Measurements on Type IIb Diamonds." Proc. Phys. Soc., (London), B69 (March, 1956), 410.
22. Chesley, F. G. "Investigation of the Minor Elements in Diamond." Amer. Min., 27 (1942), 20.
23. Raal, F. A. "A Spectrographic Study of the Minor Element Content of Diamond." Amer. Min., 546 (1957), 309.
24. Sutherland, G. B. B. M., R. E. Blackwell and W. G. Simeral. "The Problem of the Two Types of Diamonds." Nature, 174 (November, 1954), 901.
25. Rose, A. "An Outline of Some Photoconduction Processes." R.C.A. Review, 22 (September, 1951), 362.
26. Shockley, W. Electrons and Holes in Semiconductors. (D. Van Nostrand Company, Inc., New York, 1950).
27. Moss, T. S. Photoconductivity in the Elements. (Academic Press, Inc., New York, 1952).
28. Pringsheim, P. Fluorescence and Phosphorescence. New York: Interscience Publishers, Inc. London: Interscience Publishers, Ltd., 1949.
29. Stein, H. J. "Optical Properties of a Semiconducting Diamond." (Unpublished Master's thesis, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, 1957).
30. Brattain, W. H. and J. Bardeen. "Surface Properties of Germanium". Bell System Tech. Jour., 32 (1953).

31. Leivo, W. J. and H. J. Stein. "Optical Absorption, Phosphorescence, and Birefringence in Semiconducting Diamond." Color Center Symposium at Argonne National Laboratory. (November, 1956)-f7.
32. Young, Thomas. "The Hall Effect in Semiconducting Diamond." (Unpublished Master's thesis, Oklahoma State University of Agriculture and Applied Sciences, 1958).
33. Czerny, M. "Messungen am Steinsalz im Ultraroten zur Prufung der Dispersions Theorie." Zeit fur Physik, 65 (1930), 600.
34. Burstein, E. and Paul H. Egli. "The Physics of Semiconductor Materials." Advances in Electronics and Electron Physics, Vol. VII, Ed. L. Martin, New York Academic Press Incorporated, (1955), 1-84.
35. Herman, Frank. "Electronic Structure of the Diamond Crystal." Phys. Rev., 88 (1952), 1210.
36. Herman, Frank. "Calculation of the Energy Band Structure of the Diamond and Germanium Crystals by the Method of Orthogonalized Plane Waves." Phys. Rev., 93 (1954), 1214.
37. Wayland, John. "Measurement of Carrier Lifetimes in Semiconducting Diamond." (Unpublished Master's thesis, Oklahoma State University of Agriculture and Applied Sciences, 1958).

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