

uncertain estimates of electron capture counting efficiencies or on guesses of cross sections and are not of sufficient accuracy to warrant presentation at this time. In several of these cases the alpha-branching fraction and thereby the alpha-decay rate can be obtained more rigorously by calibrating the electron capture counting

efficiency against another alpha-decay process, such as of an astatine parent of a related bismuth radioactivity. Such experiments are in progress in this laboratory.

We are indebted to Mr. J. T. Vale, Mr. G. B. Rossi, and the cyclotron crews who carried out the irradiations on the 184-inch and 60-inch cyclotrons.

A Comparative Study of Photoconductivity and Luminescence

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Measurements of luminescence emission and photoconductivity as a function of (1) operating temperature during excitation, (2) time during decay, and (3) temperature during thermostimulation were made for a zinc sulfide crystal. The results indicate that the processes of luminescence and photoconductivity are dissimilar. Evidence is presented for the presence of surface conductivity, especially important in measurements made with acicular crystals.

INTRODUCTION

EVER since it was realized that some semiconductors exhibit both luminescence and photoconductivity, there has been an attempt to find whether or not a correlation exists between the two processes. The task of establishing a unified picture of photoconductivity and luminescence has not met with success. Investigations of possible correlations between the two processes, such as have been conducted by Parker,¹ Hardy,² Bergmann and Ronge,³ Randall and Wilkins,⁴ Herman and Hofstadter,⁵ Frerichs,⁶ Garlick and Gibson⁷ and Broser and Warminsky,⁸ present a composite picture indicating that luminescence and photoconductivity may be related, but probably are not manifestations of the same process. This indication is supported by measurements with zinc sulfide in the present paper.

EXPERIMENTAL

The crystal used for the comparative measurements of luminescence and photoconductivity was a ZnS crystal deposited from an atmosphere containing H₂S gas and Zn vapor in a temperature gradient ranging up to 1150°C which was maintained for 2 hours.⁹ The crystal had a low intensity green luminescence emission

under 3650A ultraviolet excitation and a phosphorescence emission at room temperature which suggested the possibility of copper impurity in a very small proportion. The crystal was 4 mm long and 0.5 mm in diameter; x-rays showed that the crystal structure was cubic and that, therefore, the crystal had actually been formed at a temperature below 1020°C.¹⁰ It was not a perfect single crystal, but should be described rather as an acicular polycrystal.

Photoconductivity measurements were made under direct current conditions. This method makes necessary a consideration of the potential barriers which exist at the contacts between the crystal and the electrodes. The metal electrodes used on the ZnS crystal described in this paper were formed by applying silver paste (E. I. duPont de Nemours and Company) and drying. In general, it is necessary to resort to probe measurements of potential in order to determine the true potential applied across the main body of the crystal. For this ZnS crystal, however, barriers at the ends of the crystal were almost completely removed by heating with silver paste contacts at the ends, at 650°C, for five minutes. There was a reasonably uniform potential distribution along the crystal, and the same fraction of the applied potential was across the main body of the crystal during excitation and in the dark.

Measurements as a function of temperature were made by placing the crystal in the specially insulated apparatus, which had been used in a previous investigation.¹¹ The crystal was excited by 3650A ultraviolet from a 100-watt C-H4 mercury projector spot lamp with appropriate filters. Luminescence emission was observed by a multiplier phototube (RCA 1P21).

¹ W. L. Parker, as cited in H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., 1950), pp. 302-304.

² A. E. Hardy, *Trans. Electrochem. Soc.* **87**, 355 (1945).

³ L. Bergmann and F. Ronge, *Physik. Z.* **41**, 349 (1940).

⁴ J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **184**, 347 (1945).

⁵ R. C. Herman and R. Hofstadter, *Phys. Rev.* **57**, 936 (1940).

⁶ R. Frerichs, *Phys. Rev.* **76**, 1869 (1949).

⁷ G. F. J. Garlick and A. F. Gibson, *Proc. Roy. Soc. (London)* **188**, 485 (1947).

⁸ I. Broser and R. Warminsky, *Ann. d. Physik* **7**, 288 (1950).

⁹ Crystal prepared by S. M. Thomsen.

¹⁰ X-ray analysis by I. J. Hegyi.

¹¹ R. H. Bube, *Phys. Rev.* **80**, 655 (1950).

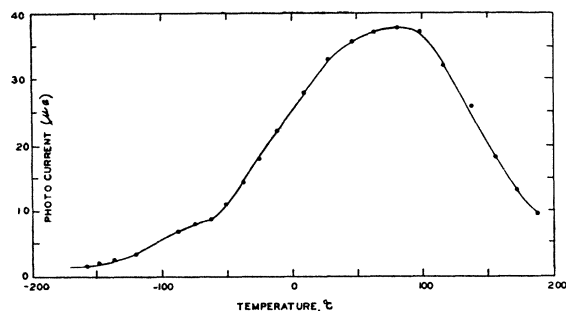


FIG. 1. The photocurrent of the ZnS crystal during excitation by 3650A ultraviolet as a function of operating temperature.

The following comparisons between photocurrent and luminescence emission are made: (1) variation with operating temperature during excitation; (2) variation with time during decay; and (3) variation with temperature during thermostimulation.

RESULTS

The variation of the photocurrent and the green luminescence emission intensity with operating tem-

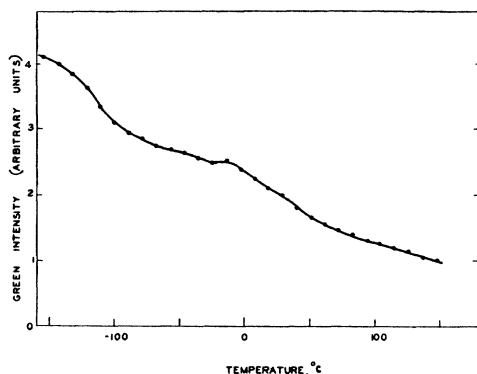


FIG. 2. The green luminescence emission, as excited by 3650A ultraviolet, as a function of operating temperature, for the ZnS crystal.

perature during excitation between -150° and 200°C is shown in Figs. 1 and 2. The photocurrent is found to exhibit a definite maximum, whereas the emission intensity decreases continuously.

The variation of the current and the green phos-

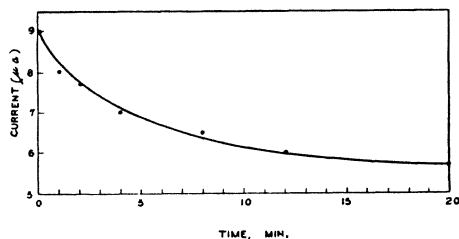


FIG. 3. The decay of current for the ZnS crystal after excitation at room temperature by 3650A ultraviolet.

phorescence emission intensity with decay time at room temperature is shown in Figs. 3 and 4. In the first minute of decay, the current decays to 90 percent of its initial value, whereas the phosphorescence emission decays to less than 10 percent of its initial value. At all temperatures between -150° and 200°C , the decay of the phosphorescence emission was found to be more rapid than the decay of the current. The application of potentials up to 100 volts did not produce any measurable changes in the decay of phosphorescence emission.

The rate of decay of the current in the first minute of decay varied markedly with the temperature of the crystal. The decay is characterized generally by a rapid drop followed by a much slower decay. Table I gives the percent of the initial current which still remained after 1 minute decay at various temperatures.

Figures 5 and 6 give the curves of thermostimulated current and thermostimulated phosphorescence emission as a function of temperature for a heating rate of $0.18^{\circ}/\text{sec}$. To obtain the curve of thermostimulated current, the crystal was heated in the dark to 200°C to empty all traps, cooled in the dark to -165°C , excited by 3650A ultraviolet, allowed to decay for a short time in the dark, and then heated in the dark at a linear rate. The thermostimulated current is taken as the difference between the current at a given temperature as read during the cooling from 200° to -165°C and the current at the same temperature during the linear heating.

The glow curve of Fig. 6 was not obtained with the identical crystal of the previous measurements, but was obtained with a larger polycrystal taken from the same batch and with the same apparent emission spectrum, phosphorescence decay, and thermostimulated phosphorescence characteristics.

When the crystal is excited at -165°C , electrons are trapped in traps of various depths. As the temperature is raised during the linear heating, electrons are released from traps by thermal energy. The radiative transition of these electrons to the ground states of luminescence centers is the cause of the thermostimulated emission. If the electrons which participate in the luminescence process enter the conduction band in passing from traps to luminescence centers, there should be a close correspondence between the thermostimulated emission and the thermostimulated current.

The thermostimulated phosphorescence emission is contributed mainly by the emptying of traps below 0°C , whereas the thermostimulated current arises principally from the emptying of traps above 0°C . In both curves, however, there are peaks or indications of peaks at approximately -100° , -40° , and 80°C . The peaks at -100° and 80°C can be easily detected from Figs. 5 and 6, and there is a definite indication of a bulge in the curve of Fig. 5 near -40°C such as would be caused by a peak in this region corresponding to the peak of Fig. 6. It is found, however, that the three peaks in the glow

curve are in exactly opposite ratio to one another as are the three peaks in the thermostimulated current curve. At the same time, it is seen from comparing Figs. 1 and 5 that the photocurrent follows the same variation with temperature as does the thermostimulated current, whereas comparison of Figs. 2 and 6 indicates that the general rate of decrease of the luminescence emission intensity with temperature becomes less in those temperature regions where peaks in the glow curve are found. This lessening of the decrease rate, which results in a shallow secondary maximum, is explainable in terms of an increase in the number of centers available for repetitive excitation as the traps are emptied by increasing the operating temperature.^{12,13}

A comparison of Table I and Fig. 5 shows that the percent of the initial current remaining after 1 minute

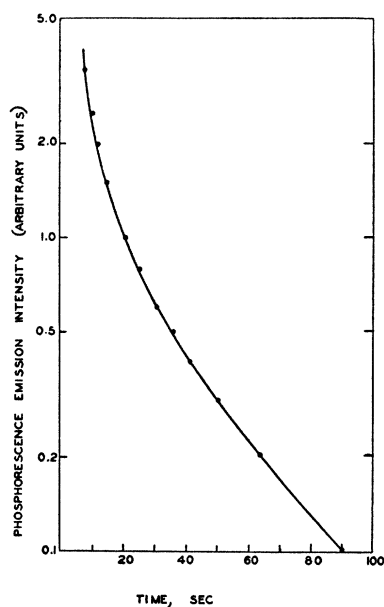


FIG. 4. The decay of the phosphorescence emission at room temperature after excitation by 3650A ultraviolet for the ZnS crystal.

decay at various temperatures is closely comparable to the magnitude of the thermostimulated current at those temperatures, i.e., to the number of conduction electrons available from traps.

As far as other measurements of photoconductivity are concerned, the photocurrent was found to vary linearly with the applied potential, and the photocurrent was found to vary as a power of the excitation intensity. This power was equal to 0.50 at 97°C and higher temperatures, and varied between 0.50 and 1.00 for lower temperatures.

DISCUSSION

One explanation for the differences and similarities between the observed photoconductivity and lumi-

¹² F. A. Kroeger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York, 1948), p. 251.

¹³ R. H. Bube, *J. Opt. Soc. Am.* **39**, 681 (1949).

TABLE I. Decay of current as a function of temperature.

Crystal temperature, °C	Percent of current remaining after 1 minute decay
193	58
97	90
23	89
-65	40
-165	3

nescence effects might be that the surface of the crystal is principally responsible for the conductivity effects, whereas a major fraction of the luminescence effects are contributed by regions of the crystal away from the surface.

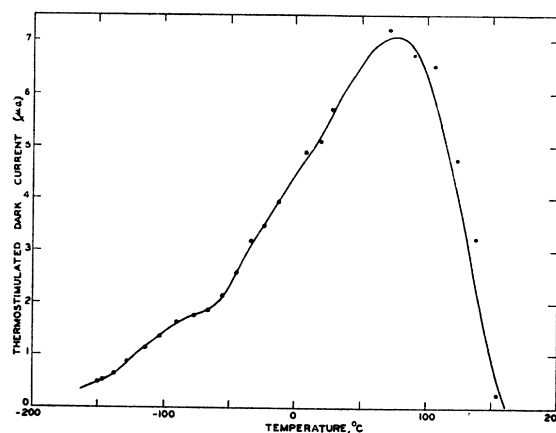


FIG. 5. The thermostimulated current of the ZnS crystal as a function of temperature, after excitation at -165°C with 3650A ultraviolet, at a heating rate of 0.18°/sec.

The presence of surface effects on conductivity have been detected by noting changes in photoconductivity for the same crystal under tests in air and in vacuum. For all ZnS (and CdS) crystals tested, it has invariably been found that the photosensitivity is *increased* by changing from an air to a vacuum surround.¹⁴ Measure-

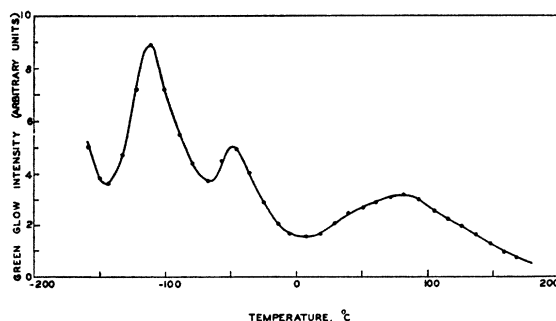


FIG. 6. The thermostimulated phosphorescence emission of a larger ZnS crystal, from the same batch as the ZnS crystal used in the other measurements, after excitation at -165°C with 3650A ultraviolet, at a heating rate of 0.18°/sec.

¹⁴ The opposite effect has been reported for phosphorescent sulfide and fluoride *powders* by E. Voyatzakis, *Compt. rend.* **209**, 31 (1939).

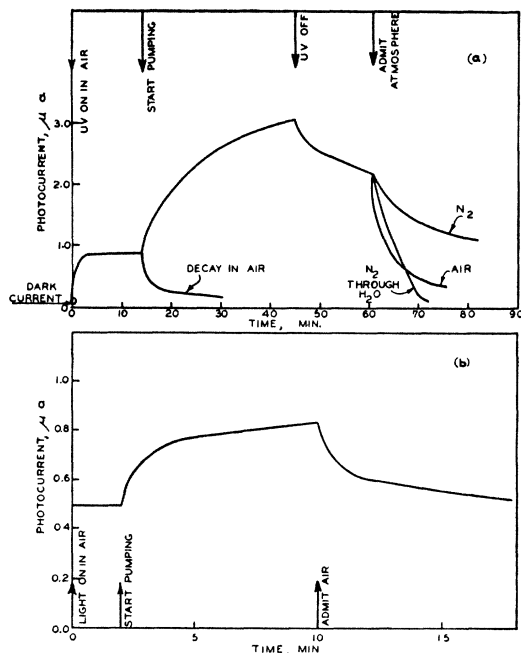


FIG. 7. (a) The effect of atmosphere variation on the photocurrent and the decay of current for a ZnS crystal. The atmospheres used were dry tank N₂ admitted through tubing containing a small amount of moisture, room air, and tank N₂ bubbled through water. (b) The effect of atmosphere on the photocurrent of a CdS crystal.

ments of photocurrent as a function of temperature show that the first heating through which a crystal passes in vacuum, after having been exposed to air, causes an irreversible change in the photocurrent. Upon returning the crystal to room temperature after the heating, the photocurrent is found to have increased over its original value, and the variation of photocurrent with temperature thereafter is completely reversible. The current decreases again upon exposure to air.

Figure 7 shows the effects of atmosphere variation on the photocurrent for a ZnS and a CdS crystal.¹⁵ Both crystals used for these tests were acicular in shape. It may be noted from Fig. 7 that the presence of moisture *decreases* the sensitivity and *increases* the rate of decay. Placing the crystal in vacuum increases the photocurrent by over 300 percent for the ZnS crystal and by over 60 percent for the CdS crystal.

If the total conductivity can be varied by such a large factor by changes which can occur only at the surface of the crystal, it follows that a large fraction of the conductivity must occur in surface regions.

¹⁵ Prepared by K. F. Stripp.

At the present time, it does not seem possible to make precise quantitative measurements of pure volume conductivity. Acicular crystals can be used to obtain nearly barrierless contacts and are suitable for potential distribution studies, but a major portion of their observed photoconductivity is caused by surface effects; flat crystal plates can be used to obtain nearly complete volume conductivity as opposed to surface conductivity, but no study can be made of the potential distribution inside the crystal. Although these difficulties cause one to be cautious about placing too much significance on the numerical results, an insight into the physics of the process may still be obtained. A program aiming at as full an understanding of the photoconductive process as possible under the aforementioned difficulties is being carried out at present by A. Rose and R. W. Smith of these Laboratories.

The measurements on the ZnS crystal used for the comparison of photoconductivity and luminescence were made for highest photosensitivity, i.e., in vacuum and after an initial heating to drive off moisture. If it is assumed that the surface is less conducting than the volume in the absence of moisture, the addition of moisture, which makes the surface conductivity more nearly equal to the volume conductivity, would act to decrease sensitivity and increase rate of decay, in agreement with the observed experimental results.

If the luminescence effects and the photoconductivity occur in essentially the same region of the crystal, however, the data are evidence that only a fraction, if any, of the electrons excited from luminescence centers contribute to the photocurrent. The very slow decay of current at room temperature, compared with the much more rapid decay of the phosphorescence emission, indicates that a large portion of conduction electrons are not returning to luminescence centers. Two possible explanations suggest themselves: (1) a large portion of the conduction electrons are initially excited from the filled band or from nonluminescence centers, rather than from luminescence centers (holes in the filled band or in nonluminescence centers having a much smaller capture cross section for excited electrons than holes in luminescence centers), or (2) a large portion of excited luminescence centers transfer their holes to the filled band or to nonluminescence centers (by some type of hole migration), so that most of the conduction electrons must return to holes in the filled band or in nonluminescence centers.

The author wishes to express his sincere appreciation to Dr. A. Rose for many helpful and interesting discussions.