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**PHOTOCONDUCTIVITY OF THE SULFIDE,
SELENIDE, AND TELLURIDE OF ZINC OR CADMIUM**

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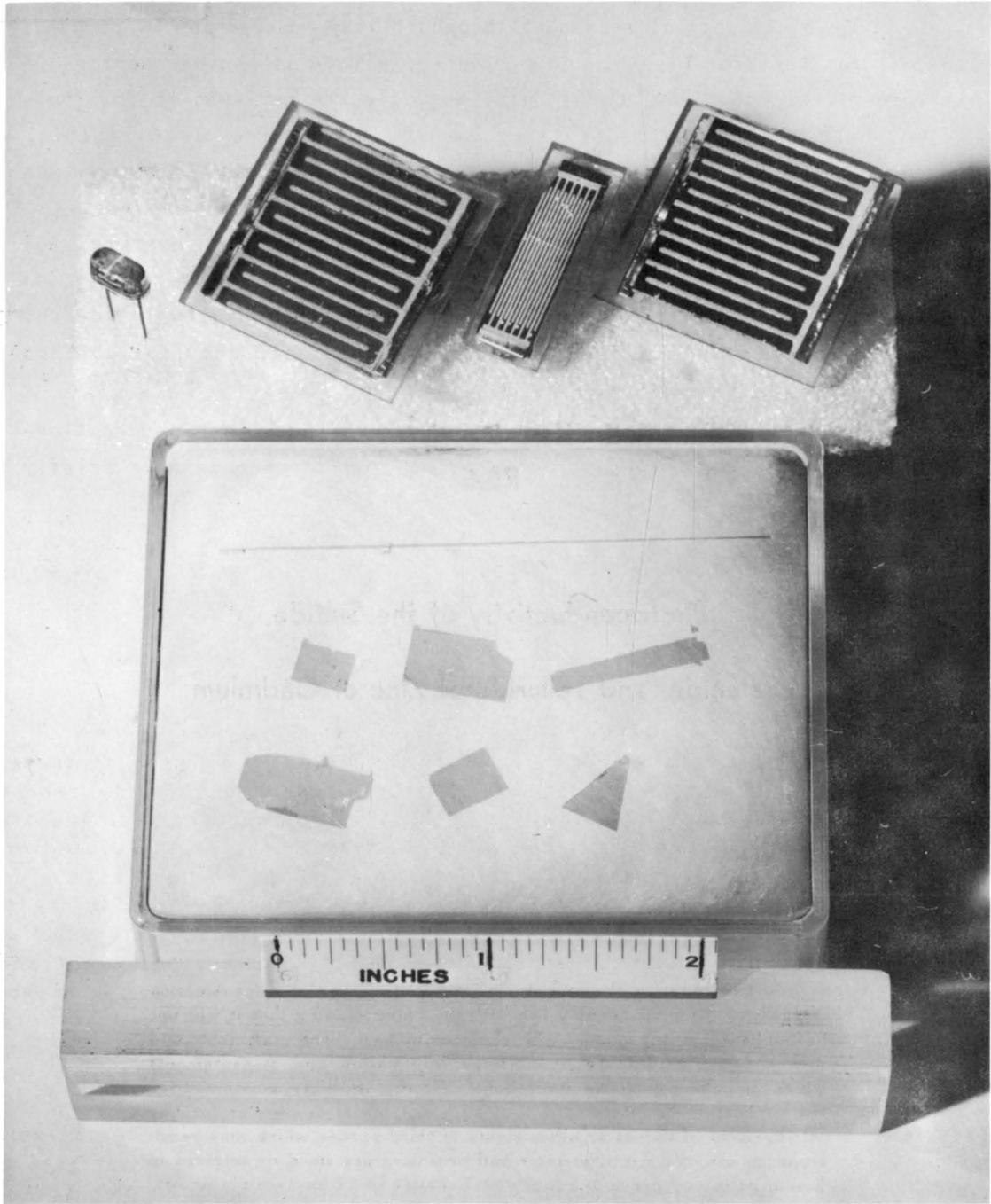


Fig. 1 - Photograph of large plate-like CdS crystals and of commercial crystal and sintered-layer photocells.

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The highlights of recent photoconductivity research on evaporated, powder, and sintered layers, and on single crystals of photoconductors in the group ZnS, CdS, ZnSe, CdSe, ZnTe, and CdTe are reviewed in this bulletin. The following aspects of photoconductivity are discussed: (1) spectral response, (2) impurity sensitization, (3) electrode contact problems, (4) conductivity, (5) mobility, (6) speed of response, (7) photocurrent vs light intensity, (8) photocurrent vs temperature, (9) infrared quenching, (10) thermally stimulated current and trapping, (11) space-charge limited current, (12) photoconductivity and luminescence, (13) photovoltaic effect, (14) photoemissive effect, and (15) surface photoconductivity.

The utility of the concepts of the Fermi-level and demarcation-level in the description of many photoconductivity phenomena is briefly discussed.

Introduction

The use of photoconductors for the performance of various tasks in research and industry is undergoing a broad expansion at the present time¹⁻⁶. Photoconductors from the group discussed in this bulletin are currently in use, or being considered and developed for use, in such widely diverse applications as (1) direct photocells for measurement of light intensity, (2) detectors for x-rays, alpha- and beta-particles, and gamma rays, (3) automatic automobile headlight dimmers, (4) streetlight control, (5) oximeters, (6) "noiseless" switches, (7) smoke and fire control, (8) solar generators, (9) detectors in computers, and (10) miscellaneous toys and novelties. Fig. 1 shows several large CdS crystals and typical crystal and sintered-layer commercial cells.

Photoconductivity in these materials is characterized by the fact that the "gain" may be much larger than unity. The term "gain" is used to mean the ratio between the number of charges passed through the crystal per unit time and the number of photons absorbed per unit time. Excitation produces a free electron

and a free hole; in most of these materials, electrons are the majority carriers and the holes are rapidly trapped. The free electron moves through the crystal under the influence of the field to the positive electrode, and hence out of the crystal. At the time that an electron moves out of the crystal at the positive electrode, another electron enters the crystal at the negative electrode. Charge continues to flow through the crystal until recombination occurs between the trapped hole and a free electron. Values of the "gain" as high as 10^4 have been observed in CdS. Note that if the negative electrode were of such a type that electrons were not free to enter the crystal from it, then the "gain" would be limited to a value of unity or less. The gain may be simply expressed in terms of the lifetime of a free electron, τ , and the transit time of an electron between electrodes, t :

$$\text{Gain} = \tau/t \quad (1)$$

When t is expressed in terms of the mobility,

μ , the applied voltage, V , and the distance between electrodes, L , Eq. (1) for the gain may be converted to:

$$\text{Gain} = (\tau\mu V)/L^2 \quad (2)$$

Research in the photoconductivity of zinc sulfide holds an historic position in the field, dating back at least to the work of Gudden and Pohl⁷ in 1920. It is only in the last decade or two, however, that appreciable advances have been made in the understanding of the photoconductivity processes involving quantum gains larger than unity in such materials. The development of the techniques for the growth of single crystals, given impetus by the publication of Frerichs⁸ in 1946 on the vapor-phase growth of cadmium sulfide crystals, has played an important role in obtaining this understanding. This bulletin will review the highlights of research in the past ten years on photoconductivity in the sulfide, selenide, and telluride of zinc or cadmium: six materials with many similar properties. No attempt has been made to provide an exhaustive bibliography of the subject, but rather instead to mention key publications, references to which will lead the reader into the heart of the recent photoconductivity literature.

The topics to be discussed have been divided into two main categories. The first concerns the preparation of photoconductors by the different methods which have been used: as evaporated, powder, or sintered layers, and as single crystals. The second concerns a number of photoconductivity phenomena, a comprehension of which is essential for an understanding of the nature of the photon and electron processes in these photoconductors.

I. Preparation of Photoconductors

I-1. Evaporated Layers

The use of evaporation in vacuum for the preparation of photoconductor layers has received wide use, principally because of the relative ease with which uniform layers of fairly large area can be produced without the presence of graininess. Evaporation methods are

usually not difficult to develop using the normal vacuum techniques, and usually may be sufficiently controlled to yield reproducible results. The major disadvantage of evaporated layers is that the crystallinity of the layer is much less perfect than that of a single crystal; effects associated with crystal imperfections (such as trapping) may determine the performance of the layer. It is also difficult with evaporated layers to make a systematic study of impurity effects under controlled conditions.

Evaporated layers of CdS have been prepared by many investigators⁹⁻¹³. It is generally reported that choice of an optimum pressure and rate of evaporation enables the preparation of CdS evaporated layers with properties which approach those of single crystals. In particular, the optical properties of the evaporated layer are very similar to those of the single crystal, whereas the electrical properties are much more sensitive to the exact method of preparation and to the type of post-preparation treatment. The optical properties of thin evaporated layers of CdS (1200-6000 Å thick) are described by Gottesman¹⁴.

Schwarz^{15,16} describes several variations in the evaporation procedure which have proven useful for the preparation of layers of CdS, CdSe, and CdTe; such variations include cathode sputtering and the use of a low-voltage arc to achieve evaporation.

Görlich and Heyne¹⁷ have prepared evaporated layers of CdSe and CdTe, the latter being formed by vaporizing Cd and Te together in vacuum. Braithwaite¹⁸ obtained layers of ZnTe by evaporating the material formed by fusing Zn and Te.

I-2. Powder Layers

In the years before the techniques for the growth of single crystals had become well developed, many measurements of photoconductivity were made on powder samples. Powders have been useful for the gross detection of the existence of photoconductivity¹⁹, the spectral response of photoconductivity²⁰, and phenomenological observations of such photoconductivity phenomena as growth and decay of photocurrent and infrared quenching²¹; such measurements, however, cannot be generally used to establish

quantitatively reliable data on conductivities of materials because of the effect of the particle-to-particle contacts on the relationship between current and voltage.

Kuwabara²² has measured the optical properties of very small particles of CdS in glass. He found that the absorption edge lies at shorter wavelengths than that for single crystals, and shifts to longer wavelength with heat treatment of the glass.

The photosensitivity which could be obtained from such powders has until recently generally been much lower than that which could be obtained from properly prepared single crystals. Kolomiets²⁹ reported an increase in the photosensitivity of a CdS powder when the powder was heated in an atmosphere of oxygen; it was believed that the oxygen converted some of the CdS at the surface of the powder particles to CdO, thus increasing the conductivity and improving the particle-to-particle contact.

Thomsen and Bube²⁴ have found it possible to prepare CdS powder photoconductors which exhibit many of the desirable properties of single crystals. Powder layers of large area may be prepared by spreading onto a suitable surface a prepared mixture of microcrystalline photoconductor powder (prepared by a special phosphor-technique, involving the incorporation of chlorine and copper impurity), in a plastic solution, and allowing the layer to harden. A two-inch square cell of such a powder layer can pass an ampere for an illumination of a few foot-candles. Photocells made from powder layers are described by Nicoll and Kazan²⁵.

I-3. Sintered Layers

A variation of the powder layer which approaches even closer to having the same characteristics as single crystals, is the sintered layer²⁴. Sintered layers of CdS or CdSe are made by spraying a "paint" of CdS or CdSe (a water mixture of sulfide or selenide with chloride and copper) onto a suitable surface, and firing the surface with its dried layer to form a polycrystalline sintered layer. This method is very useful in producing large-area photoconductors with crystal-like characteristics without involving the difficulties met in growing large-area single crystals or in

producing large-area photoconductor layers by evaporation in vacuum.

I-4. Single Crystals

There are three essentially different methods for the preparation of single crystals of photoconductors: (1) vapor phase reaction of the elements, (2) sublimation of the powder and recrystallization, and (3) growth from the melt.

The report by Frerichs^{9,26} of the growth of single crystals of CdS, CdSe, and CdTe by the vapor phase reaction of Cd and H₂S, H₂Se, and H₂Te provided considerable impetus to the development of this technique for the growth of single crystals. Many other investigators have elaborated on this basic method to grow crystals of CdS²⁷⁻³⁰, and crystals of ZnS³¹⁻³³.

The sublimation of ZnS powder with subsequent recrystallization from the vapor phase has been used for the growth of single crystals of ZnS by Kremheller³³ and Piper³⁴. Sublimation of ZnS and CdS powder under a low pressure of a few psi of H₂S for periods of the order of days has been used by Reynolds and Czyzak³⁵⁻³⁷ to grow crystals of CdS and ZnS as large as 13x8x5 mm³.

CdTe has the lowest melting point of all the photoconductors under consideration in this bulletin (1041°C) and therefore is suitable for growing crystals from the melt as well as from the vapor phase^{38,39}.

II. Photoconductivity Phenomena

II-1. Phenomenological Photoconductivity Theory

An absolute theory of photoconductivity does not exist; although it is possible to predict the approximate spectral response of a material from a knowledge of its absorption characteristics, it is not possible to predict the "gain", usually called the photosensitivity, from a knowledge of the constituent elements only. The sensitivity, the temperature dependence, the speed of response, and many other characteristics of the photoconductivity of a material depend on the capture cross-sections

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for electrons and holes of imperfections in the crystal. Recombination of electrons and holes takes place predominantly through these imperfections; hence the location, the concentration, and the nature of these imperfections determine most of the photoconductivity properties of the crystal. Such imperfections may be associated with crystal defects or with incorporated impurities; in CdS and CdSe it seems that crystal defects play a major role in determining the photoconductivity properties and in determining what effects are caused by incorporated impurities*.

To prepare a sensitive photoconductor, therefore, it is necessary to make certain that centers with large recombination cross-section are absent, and that whatever recombination centers are present have as small a cross-section as possible. For CdS and CdSe crystals, and for other n-type photoconductors in the group under consideration, the free hole formed by excitation across the band-gap is captured quickly at an imperfection; the "sensitizing" centers must therefore be of the type that have a small capture cross-section for free electrons, once they have captured a hole. Values for this capture cross-section for a free electron have been derived from measurements of photoconductivity for ZnS and CdS by Smith⁴⁰, Bube^{20, 41}, Fassbender^{42, 43}, Schoen⁴⁷, and Broser and Warminsky⁴⁴; the values lie between 10^{-20} and 10^{-24} cm². Such cross-sections are some five to nine orders of magnitude smaller than atomic dimensions, and indicate that the high photosensitivity of these materials is associated with the presence of centers which are effectively surrounded by a potential barrier for the capture of an electron.

In attempting the theoretical description of photoconductivity, there have been essentially two modes of approach. The first method of approach consists in setting up a fairly simple model: simple in the sense that only a small number of different types of discrete levels are assumed present in the forbidden gap. Then a system of differential equations is set up for the rates of change of

the concentration of the various filled and empty states. The solution of these equations, usually in severely complicated form, is applied to the experimental data, a fit being attempted by the adjustment of suitable parameters. Examples of such calculations are given by Broser and Warminsky^{44, 45}, Frerichs⁴⁶, Schoen⁴⁷, and Kallmann and Kramer⁴⁸. In many cases such calculations are useful, but in general they are sufficiently far from reflecting the actual complexity of affairs in the photoconductor so that they provide only a partial and approximate analysis of the phenomena.

The second method of approach consists in attempting to treat the photoconductivity properties of a material in a collective and somewhat statistical way to obtain a semi-quantitative description of phenomena and to retain a direct concept of the physical nature of the processes involved. This method has been largely developed by Rose⁵¹⁻⁵³ and is characterized by the use of the quasi or steady-state Fermi-level, and by the general assumption that there is usually a fairly high concentration of levels with a broad energy distribution in the forbidden gap. It will prove convenient in the discussion of the photoconductivity phenomena in the following sections to use the method of Rose; at this point we shall briefly present its more important features.

The distance of the steady-state electron Fermi-level from the conduction band, E_{fn} , (see Fig. 2) may be calculated from the conductivity and the temperature according to the equation:

$$E_{fn} = k T \ln(N_C e \mu / \sigma) \quad (3)$$

where T is the absolute temperature, N_C is the concentration of states in the lowest kT -wide part of the conduction band, e is the electronic charge, μ is the mobility, and σ the measured conductivity. A similar hole Fermi-level can be defined in terms of the concentration of free holes. In describing electronic phenomena, it is convenient to consider these Fermi-levels as indicating the approximate boundary between shallow trapping levels, lying above the electron Fermi-level or below the hole Fermi-level, and recombination levels, lying between the two Fermi-levels. If a level does not lie between the two Fermi-levels, it is assumed that it is in thermal equilibrium with the nearest allowed

*A model may be constructed to explain photoconductivity with quantum gain greater than unity in terms of distributed barriers in the crystal which are reduced by irradiation by light⁴⁹⁻⁵⁰. Although such barriers may be present and give rise to such effects, they are not necessary for the occurrence of photoconductivity with gain greater than unity.

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V_c represents a cation vacancy and V_a an anion vacancy. The sign inside the bracket represents the number of trapped electrons or holes; the sign outside the bracket represents the effective charge of the defect with respect to the rest of the crystal.

We shall see in more detail in the following sections how these concepts can be applied to describe photoconductivity phenomena in CdS and CdSe crystals. Fig. 3 illustrates the dependence of photosensitivity on the location of the demarcation levels in schematic fashion. The crystal is in a desensitized state when only Class I centers are able to function as recombination centers; the crystal becomes sensitized as Class II centers become able to function as recombination centers because of a shift in the demarcation level. Holes formed by excitation become concentrated in small capture cross-section* Class II centers, and electrons formerly in Class II centers are transferred via the conduction and valence bands to fill and hence make unavailable for recombination the large capture cross-section Class I centers.

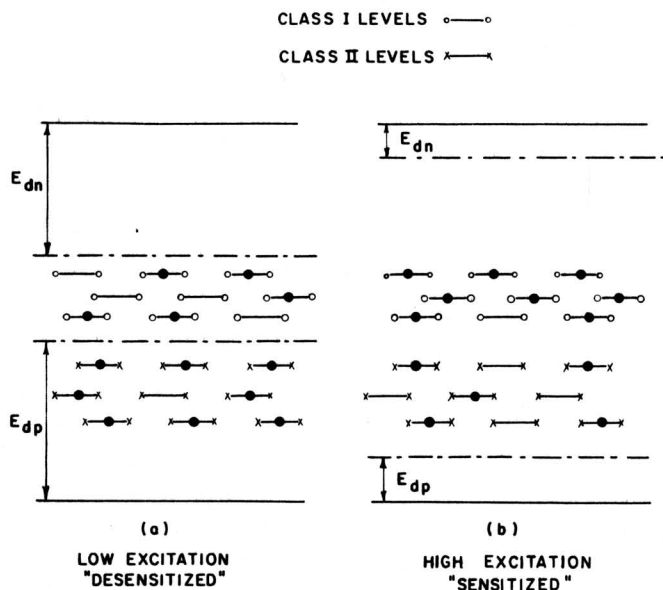


Fig. 3 - Schematic representation of sensitization of a crystal with increasing excitation intensity.

*In the remainder of the bulletin, the term "capture cross-section" will mean the capture cross-section for free electrons by a center which has previously captured a hole.

II-2. Band Gap and Spectral Response

For a pure photoconductor crystal, the dependence of photosensitivity on wavelength will be very similar to the dependence of the absorption on wavelength. The photosensitivity will be high and fairly constant for irradiation with photons with energy greater than the forbidden gap (for exceptions caused by surface effects, see section II-16), and the photosensitivity will decrease very rapidly as the energy of the photons irradiating the crystal is made less than the forbidden gap.

The most common methods for determining the width of the band gap involve measurements of (1) absorption, (2) excitation spectrum for photoconductivity, (3) excitation spectrum for luminescence, (4) luminescence edge emission spectrum, and (5) dark conductivity as a function of temperature. Small but definite differences exist between the values of band gap determined by different methods; this is largely because the theoretical concepts of the band edges in relation to these various measurements have not been clearly established.

Table I presents a summary of the results of measurements of band gaps by many investigators. Table II presents a summary of the results of measurements of the temperature variation of the band gap.

Hoehler⁵⁴ has measured the variation in the band gap of CdS as a function of pressure between 1 and 330 atmospheres; he reports a change in the absorption edge of about $-0.01\text{\AA}/\text{atmosphere}$. From a comparison between the pressure-caused and the temperature-caused shift in the absorption edge, Hoehler concludes that the shift in the edge caused simply by thermal dilatation of the crystal accounts for only about 20 per cent of the total shift in the edge found with changing temperature.

Moss⁵⁵ has discovered that for many photoconductors the ratio of the fourth power of the index of refraction to the wavelength corresponding to the absorption edge is approximately a constant; this constant is about 77 if the wavelength is expressed in microns. If, for example, a value of 2.45 is taken for the index of refraction of CdS, and a value of 0.51 micron for the edge wavelength, the ratio is 71.

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TABLE I

WIDTH OF THE BAND GAP, EV (AT ROOM TEMPERATURE EXCEPT WHERE SPECIFIED)

Material	Absorption Spectrum	Photocon. Exc. Spectrum	Lum. Exc. Spectrum	Lum. Edge Emission	Cond. vs. Temp.	References
cub-ZnS	3.64			3.60		56 57
hex-ZnS	3.64 3.70 3.70 3.55 3.65 3.60	3.68	3.70		3.77	20 35, 58 56 59 60 61
cub-ZnSe		2.58		2.66		63 57
cub-ZnTe	2.15					63
hex-CdS	2.38 2.42 2.44	2.41 2.38 2.47 2.44 2.42-2.48	2.52(77°K)	2.45		62 64 57 59 65 66 67 68
hex-CdSe		1.74				62
cub-CdTe	1.42	1.41 1.47			1.43-1.57	62 38 39 69

TABLE II

TEMPERATURE DEPENDENCE OF THE BAND GAP, (EV/DEGREE) X 10⁻⁵
(BAND GAP DECREASES WITH INCREASING TEMP.)

Material	Absorption Spectrum	Temperature Range	Photocon. Ex. Spectrum	Temperature Range	References
hex-Zns	46 85	At 77°K At 800°K			61 61
cub-ZnSe			72	90°-400°K	62
hex-CdS	41 49 50	4°-77°K 77°-300°K 290°-980°K	52 46-58 26-37 42-58	90°-400°K 300°-425° At 115°K At 265°K	64 64 66 62 67 68 68
hex-CdSe			46	90°-400°K	62
cub-CdTe			36	90°-400°K	62

II-3. Impurity Sensitization

The incorporation of impurities in these photoconductors may (1) increase the dark conductivity and the photosensitivity, (2) decrease the dark conductivity and photosensitivity, or (3) provide a new photosensitivity for photons with energy less than the width of the band gap, corresponding to direct excitation from the impurity centers.

In ZnS, for example, the incorporation of silver impurity extends the spectral response to longer wavelengths by providing an absorption at about 3.42 eV, and copper extends the response even further by providing an absorption at about 3.30 eV.²⁰

In CdS, the incorporation of a halide or a trivalent cation increases both the dark conductivity and the photosensitivity without appreciably affecting the spectral response.^{24, 28, 29, 70} The incorporation of silver or copper decreases the dark conductivity and the photosensitivity, and also adds considerable new photosensitivity in the red portion of the spectrum.^{10, 11, 24, 28} The effect of these impurities on CdSe is very similar to that for CdS; in this case, the new spectral response associated with the incorporation of copper is in the near infrared.

The mechanism by which the incorporation of a halide, chloride for example (or of a trivalent cation), increases the photosensitivity of CdS merits further consideration²⁰. When chloride ions are incorporated in CdS, they may have two effects: (1) they may alter the effective valence of the ions of the host crystal, or (2) they may cause crystal defects. The relative importance of these two effects will be determined by the atmosphere present during the growth of the crystals²⁰. When a chloride ion substitutes for a sulfur ion in the crystal in accordance with the first of these effects, the result may be expressed by saying either that: (1) for each chloride incorporated, a monovalent cadmium ion is formed; or (2) for each chloride incorporated, a loosely bound electron exists in an orbit about the chloride ion.

Pure cadmium sulfide crystals have a very low dark conductivity (about 10^{-12} mho/cm) and a low photosensitivity. The incorporation of only about 2 parts per million of chloride

increases the dark conductivity to about 1 mho/cm. This is because the extra electron which is loosely bound when chloride substitutes for sulfide has a binding energy of about 0.04 eV⁴¹; the electron is therefore free at room temperature. But as the conductivity is increased from 10^{-12} mho/cm to 1 mho/cm by the incorporation of chloride, the photosensitivity is also increased by a factor between 10^8 and 10^6 .²⁸ It is this increase in photosensitivity in spite of the fact that the incorporation of impurities potentially provides more recombination centers, which is easily explained by the concepts of Rose, previously discussed in section II-1.

As the electrons provided by the incorporation of chloride increase the dark conductivity, they will also shift the Fermi-level and bring new centers into the role of recombination centers. These new recombination centers will be filled in the dark and hence, if their nature is appropriate, they will be able to function as the small capture cross-section centers of Class II type, described in section II-1. Holes formed by excitation will aggregate in the small capture cross-section Class II centers and the electrons formerly in Class II centers will be transferred to the large capture cross-section Class I centers which were responsible for the low sensitivity of the pure crystals. Thus the sensitization process decreases the rate of capture of electrons by Class I centers, and hence increases the lifetime of free electrons.

The effect of copper (and silver) in decreasing the dark conductivity and photosensitivity can be explained by considering the copper to play the role of a low-lying acceptor center; the copper centers accept the electrons provided by the incorporation of the chloride or other donor impurities, decrease the conductivity, and hence remove the sensitization by removing Class II centers from their role of recombination centers. In addition the copper centers now provide an additional sensitivity in the red caused by direct excitation from the copper centers to the conduction band. When high proportions of copper are incorporated in evaporated, powder, or sintered layers, the spectral response may remain high out to 9000 Å.^{10, 11, 24}

Bube and Thomsen²⁸ have reported specific-

ally on the effects of Cl, Br, I, Al, Ga, In, Cu, and Ag impurity on the conductivity and photosensitivity in CdS and CdSe. Veith¹⁰ and Goercke¹¹ have reported on the effects of excess Cd, and Cu and Ag impurity in CdS. Kroeger et. al.²⁹ have described the effects of Ga, In, Sb, Cl, and Ag impurity on the conductivity of CdS.

A number of authors have reported on the effect of oxygen impurity in CdS, CdSe, and CdTe, particularly on the properties of evaporated layers. Oxygen impurity has been reported to have the following effects: (1) decrease in dark conductivity and slight decrease in photosensitivity of CdS after exposure to oxygen at room temperature (reversible in vacuum), but a permanent increase in dark conductivity by prolonged heating in oxygen⁷¹; (2) improved sensitivity, particularly for CdSe, if prepared in an atmosphere containing oxygen¹⁵⁻¹⁷; (3) extension of the spectral response of CdS to longer wavelengths for up to 2 per cent oxygen impurity⁹⁷; and (4) increase in the concentration of trapping centers in CdS.^{72,74}

II-4. Electrode Contact Problems

For most applications, both practical and theoretical, it is desirable that the current through a photoconductor be proportional to the voltage applied to the photoconductor, i.e., that the material obey Ohm's law. An ohmic contact is one made with an electrode which is able to supply to the crystal an excess or a reservoir of carriers ready to enter the photoconductor as needed. Such an ohmic contact to an n-type insulating crystal is obtained by using a metal with work function smaller than that of the insulator. The nature of the effects of electrode material on the electrical properties of CdS has been investigated by Broser and Warminsky⁷⁵ and by Buttler and Muscheid.⁷⁶ By various treatments, Buttler and Muscheid were able to make ohmic contacts to CdS using both gold and aluminum electrodes; they found that by providing ohmic contacts to the crystals, undesirable effects such as rectification, instability, irreversible "forming" changes, and noise, were either eliminated or greatly reduced.

Following the approach of using materials with low work function for the electrodes, Smith and Rose^{77,78} have shown that ohmic

contacts to CdS can be made with indium or gallium electrodes (either melted or evaporated). In such crystals, the photovoltaic effect is absent, and Shulman et. al.⁷⁹ have shown that the noise is much less than for crystals with silver electrodes.

Sintered layers of CdS or CdSe give a photocurrent which obeys Ohm's law for applied fields as small as 2 millivolt/cm, even when silver electrodes are used.²⁴

II-5. Conductivity

The photoconductors discussed in this bulletin are all n-type conductors, with the exception of CdTe which may exhibit either n-type or p-type conductivity.

The experiments of Smith⁸⁰ on electroluminescence in pure CdS crystals suggest that the emission is the result of the recombination of electrons and holes after injection of both charge carriers from the electrodes; in such pure crystals, hole conductivity may play a role in the electronic processes, but in most sensitive photoconducting crystals, it is almost certain that hole conductivity is completely negligible. Sommers⁸¹ has shown from measurements of the photo-electro-magnetic effect on the CdS crystals used by Smith that the hole lifetime in these crystals is about 0.1 microsec., about 1/10 of that of the electron lifetime. In sensitive crystals, where the electron lifetime is 10^4 times or more longer than this, it is likely that the hole lifetime is considerably shorter than in pure crystals.

Impurities from Groups III and VII of the periodic table act as n-type impurities in CdS, CdSe, and CdTe; impurities from Groups I and V act as p-type impurities. The activation energies for n-type impurities vary from a few hundredths of a volt in CdS^{41,70} to a few thousandths of a volt in CdTe.⁸⁸ Activation energies for p-type impurities have been obtained only for CdTe; they lie between 0.3 and 0.5 ev. It is probable that the activation energies of p-type impurities are even larger in CdS or CdSe, for which the band gap is larger than in CdTe. The failure to detect any p-type CdS or CdSe when these same impurities are used may possibly be explained therefore by the large activation energies of p-type impurities which would be involved.

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For high concentrations of Cl and Ga impurity in CdS, Kroeger et. al.⁷⁰ have reported that the activation energy becomes negligible for impurity concentrations of $10^{18}/\text{cm}^3$ and higher, and that conduction then takes place in an impurity band.

Hauffe⁸² has measured the conductivity of CdSe layers in a partial pressure of Cd or Se as a function of temperature. For pressures greater than 10^{-1} mm Hg, he found that the conductivity increased as the 0.2 power of the pressure of the Cd vapor, or decreased as the 0.5 power of the pressure of the Se vapor.

Appel^{89, 93} has reported on measurements of the temperature dependence of the conductivity of CdTe between 25 degrees and 600 degrees C.

II-6. Mobility

Values for the mobility of electrons in CdS have been reported by many investigators;^{40, 41, 43, 44, 70, 84} they lie between about 1 and 200 $\text{cm}^2/\text{volt sec.}$, with a probable average value of about 100 $\text{cm}^2/\text{volt sec.}$ The mobility in CdSe is of the same order of magnitude.

Jenny and Bube⁸⁸ have reported that the electron mobility in CdTe is about 300 $\text{cm}^2/\text{volt sec}$ and that the hole mobility in CdTe is about 30 $\text{cm}^2/\text{volt sec.}$

Measurements of the temperature variation of the electron mobility in CdS have been reported by Kroeger et. al.⁷⁰

II-7. Speed of Response

The growth and decay of both photoconductivity and luminescence are easy to measure but difficult to interpret. Detailed measurements on the growth and decay of photoconductivity in ZnS and CdS have been made by many investigators^{21, 73, 85-87}, but the relative simplicity in fitting such curves with equations derived from many different theoretical models makes such fittings usually of little value.

It is generally true that the decay of photoconductivity consists of two parts: (1) an initial rapid portion corresponding to the direct recombination of free electrons and (2) a subsequent much slower portion corresponding to the recombination of electrons which have been thermally freed from traps. If high intensity excitation is used to give a high con-

centration of free electrons, the major portion of the decay curve will be of the first type and the observed decay time will be equal to the true lifetime of a free electron needed to satisfy Eq. (2). If a low intensity excitation is used, the decay curve will be mainly of the second type and the observed decay time will be longer than the true lifetime of a free electron. The complex distribution of trapping levels and recombination levels in a real crystal makes theoretical calculations based in detail on a model containing only one or two sets of discrete levels of limited value only. Decay times vary from a few micro-seconds for insensitive crystals at high excitation intensity to a few seconds for sensitive crystals at low excitation intensity. CdSe photoconductors have a generally faster speed of response than CdS photoconductors.

The performance of a photoconductor can conveniently be described in terms of Eq. (2) by a comparison between the observed decay time and the calculated lifetime using the measured values of applied field and gain. For measurements on single crystals at high light intensities, the observed decay time will be equal to the calculated lifetime, but at low light intensities, the observed decay time is frequently found to be as much as a hundred or a thousand times longer than the calculated lifetime. Under normal operating conditions, the observed decay times for powder layers are between 10^3 and 10^5 times longer than the lifetime calculated from Eq. (2), and for sintered layers, the observed decay times are about 10 to 10^8 times longer than the calculated lifetimes. The comparison of decay time with calculated lifetime for powder layers is strongly dependent on the applied field, because of the non-ohmic current-voltage relationship found with powder layers.

There is a phenomenon involved in the growth of photoconductivity in CdS and CdSe which merits further brief consideration. The growth of photoconductivity in CdS crystals at room temperature depends strongly on the length of time which has elapsed since the previous excitation. After periods of darkness of several days, a pronounced S-shaped growth curve is obtained, more than 20 seconds being required in one case, for example, for the photocurrent to rise the first 1 per cent of its equilibrium

value. It has been shown by Bube⁸⁸ that such slow S-shape growth curves occur only when the electron Fermi-level passes through that portion of the forbidden gap which is between 0.6 and 0.8 eV from the conduction band in CdS, and between 0.3 and 0.6 eV from the conduction band in CdSe. The slow growth corresponds to the time required for readjustment of the occupancy of recombination levels, holes becoming located at centers with small recombination cross-section (Class II centers), and electrons being transferred from Class II centers to decrease the rate of recombination at large recombination cross-section Class I centers.

The Class II levels postulated in this process probably lie slightly below the middle of the forbidden gap in both CdS and CdSe, and, as will be shown in the following sections, play an important role in many of the photoconductivity phenomena found in these materials. When the electron Fermi-level is raised by the application of light through the critical range, the hole demarcation level corresponding to this electron Fermi-level is lowered through that part of the forbidden gap over which these Class II levels are distributed. The crystal, therefore, is undergoing a process of sensitization in the growth of photoconductivity, and it is the time required to achieve the equilibrium sensitization that gives the slow S-shape growth observed.

II-8. Photocurrent vs Light Intensity

Most simple considerations involving one class of recombination centers predict that the photocurrent should vary with a power of the light intensity, n , between 0.5 and 1.0, depending on the particular conditions assumed. Rose⁵¹, for example, has shown how particular values of n of 0.5 and 1.0 can be obtained by considering a uniform distribution of trapping levels, and how any value between 0.5 and 1.0 can be obtained by considering an exponential distribution of trapping levels. Values of n in the range between 0.7 and 0.9 are very common in measurements on CdS crystals at room temperature.

In CdSe at room temperature, however, the photocurrent usually varies with a power of the light intensity greater than unity^{40, 89}; this phenomenon is called superlinear photocon-

ductivity. Extensive measurements of superlinear photoconductivity in CdSe and also in CdS have been made as a function of temperature by Bube.⁹⁰ Fig. 4 gives the photocurrent vs light intensity data for a crystal of CdSe. A slope equal to or less than unity, S_1 , is found at low temperatures, and at intermediate temperatures for high excitation intensity. A slope greater than unity, S_2 , is found at intermediate temperatures for low excitation intensity, and at high temperatures for high excitation intensity. A slope equal to or less than unity, S_3 , is again found at high temperatures for low excitation intensity. An analysis of such data for many crystals of CdSe (all of which showed superlinearity, except for a very few crystals with very low sensitivity), shows that superlinearity occurs when and only when the electron Fermi-level varies between 0.3 and 0.6 eV below the conduction band. Similar measurements on CdS at elevated temperatures show that superlinearity in CdS occurs when the electron Fermi-level varies between 0.6 and 0.8 eV from the conduction band.

According to Rose, superlinearity occurs when the hole demarcation level, the location of which is associated with the location of the electron Fermi-level, moves down to include Class II crystal defect centers as recombination centers with small recombination cross-section. Sensitization of the crystal - manifesting itself in the occurrence of superlinearity - occurs as long as the hole demarcation level moves down to include more centers of Class II type. When the Class II centers are not functioning as recombination centers, a linear or sublinear variation of photocurrent vs light intensity for the crystal in a desensitized state is found; when all of the Class II centers are acting as recombination centers, a linear or sublinear variation of photocurrent vs light intensity is again found, but this time for the crystal in a sensitized state. The location of the Class II levels is such that superlinear photoconductivity, for a normal range of excitation intensities (10^{-3} to 10^8 ft-candles), is found for CdSe between -40 degrees and 120 degrees C, and for CdS between about 100 degrees and 200 degrees C.

In a practical sense, this means that, although CdS and CdSe may have equal sensitivi-

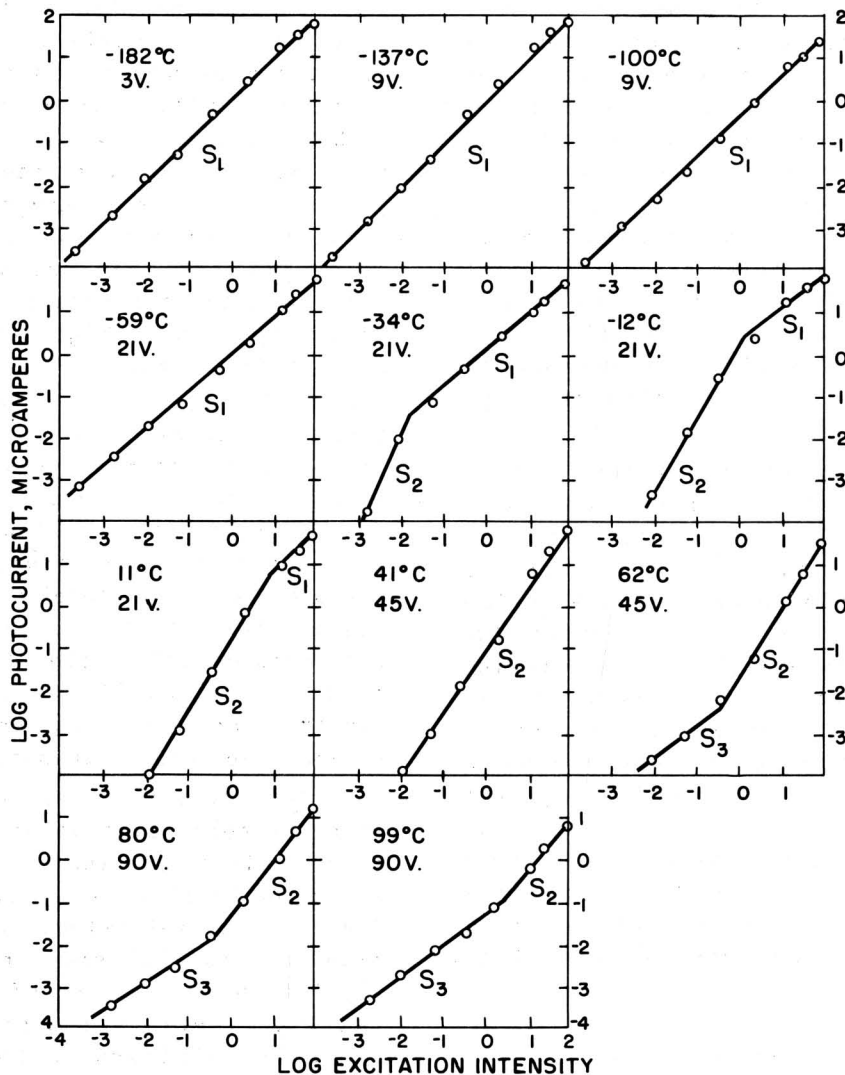


Fig. 4 - Photocurrent of a crystal of CdSe as a function of excitation intensity for several different temperatures. The temperatures and the applied voltages are indicated on the figure. An excitation intensity of 100 is equivalent to 900 ft-candles.

ties for high excitation intensities at room temperature, CdS will be considerably more sensitive than CdSe at low excitation intensities.

In evaporated, powder, or sintered layers in which high proportions of Cu are incorporated (up to 1000 parts per million), superlinear photoconductivity is found for CdS at room temperature, probably associated in this case with levels caused by the Cu rather than with crystal defect levels.^{10, 24}

II-9. Photocurrent vs Temperature

Relatively small variations in photo-sensitivity with temperature can and do occur because of changes in the density and nature of levels in the neighborhood of the Fermi-levels as they move with changing temperature. Such variations occur for most crystals below room temperature, and vary greatly with the preparation and treatment of the crystals.^{9, 1} Fig. 5 presents the normalized photocurrent vs temperature for four crystals of CdSe prepared by

different techniques and subjected to different treatments.⁹⁰ The variation of photocurrent with temperature below room temperature is dependent on the past history of the crystal.

The important thing to note, however, is that Fig. 5 also shows that all of these crystals of CdSe show a large and rapid decrease in photosensitivity when the temperature is raised above room temperature. Other measurements demonstrate that crystals of CdS show such a decrease in photosensitivity when the temperature is raised above about 100 degrees C.

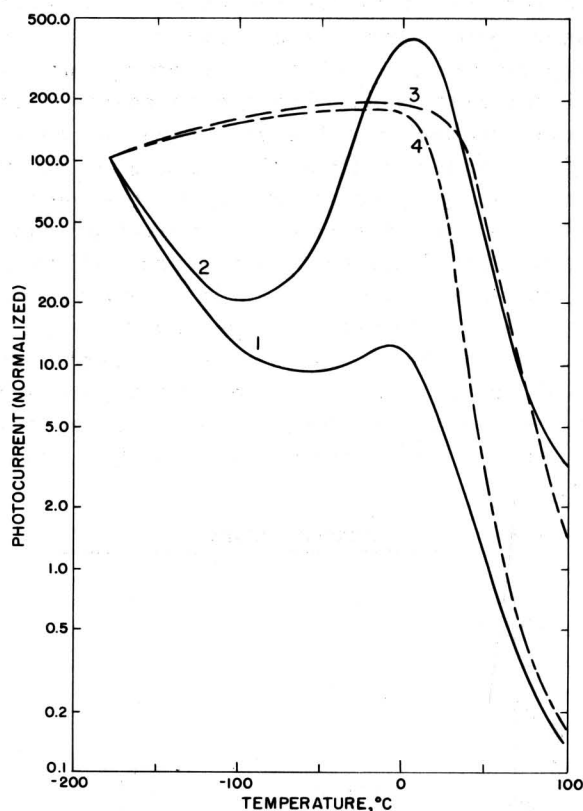


Fig. 5 - Photocurrent as a function of temperature, normalized at -180 degrees C, for an excitation intensity of 130 ft-candles, for (1) a crystal of CdSe prepared from vapor reaction of Cd and Se, (2) a crystal of CdSe prepared from sublimation of CdSe powder, (3) crystal of type (1) annealed 16 hours at 400 degrees C under 20,000 psi argon, and (4) crystal of type (1) heated for 5 minutes at 900 degrees C in Se vapor and quenched.

An analysis of measurements on the temperature breakpoint for the photosensitivity of

CdSe and CdS crystals⁹⁰ indicates that the photosensitivity breakpoint is associated with a location of the Fermi-level of 0.6 ev below the conduction band in CdS and of 0.3 ev below the conduction band in CdSe. A rapid decrease in photosensitivity occurs when the Fermi-level drops further from the conduction band than this value. The actual temperature breakpoint for the photosensitivity is very sensitive to the excitation intensity, lying at lower temperatures for lower excitation intensities, in such a way as to give a constant location of the Fermi-level for the breakpoint. Such a decrease in the photosensitivity occurs with increasing temperature, when the lowering of the electron Fermi-level and the raising of the associated hole demarcation level start to remove Class II centers from acting as recombination centers and hence cause the crystal to revert to its desensitized condition.

A confirmation of the fact that the same Class II centers are responsible for both the temperature dependence and the superlinearity of photoconductivity is given by an examination of those few crystals of CdSe which do not show superlinear photoconductivity at room temperature. The photosensitivity of such crystals does not decrease even when the temperature is raised to 100 degrees C.

The observation that certain photochemical reactions occur in CdS at temperatures over 100 degrees C, caused by atomic displacements and rearrangements, has been reported by Boer⁹².

II-10. Infrared Quenching

The occurrence of infrared quenching of photoconductivity in CdS and ZnS has been reported by several investigators.^{9, 21, 48, 93, 94} Taft and Hebb⁹⁵ found two quenching bands at 0.9 and 1.5 ev, which they associated with excitation of trapped holes in two different types of centers.

A more recent investigation of infrared quenching in CdS⁹⁶ has revealed the following details: (1) three quenching "bands" with maxima at 0.89, 1.35, and 1.65 ev are found; (2) insensitive crystals show only the 1.65 ev quenching; (3) the 0.89 and 1.35 ev quenching "bands" are intimately connected, a linear relationship existing between their magnitudes in different crystals; (4) quenching in the 0.89 ev "band" disappears for temperatures

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below about -50 degrees C; (5) all quenching disappears for temperatures greater than about 100 degrees C. Fig. 6 shows infrared quenching spectra for several typical CdS crystals. Similar investigation of infrared quenching in CdSe crystals^{9,8} reveals that (1) infrared quenching in CdSe occurs only below -50 degrees C; (2) three quenching maxima, not well resolved, are found at 1.20 , 1.05 and 0.79 ev.

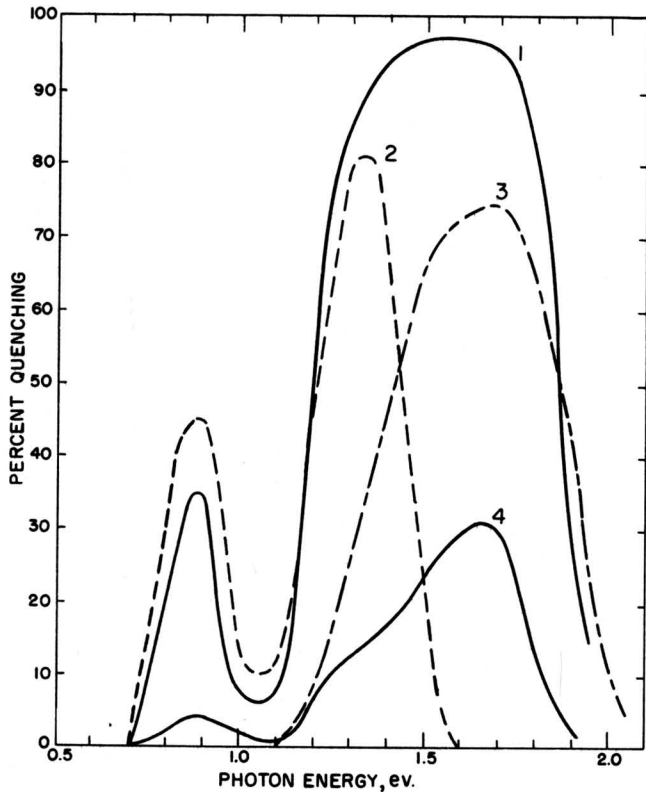


Fig. 6 - Infrared quenching spectra at room temperature for four typical selected crystals of CdS. Relative sensitivities of the crystals are (1) 2, (2) 54, (3) 0.2 and (4) 0.8.

An analysis of these data shows that infrared quenching in CdS and CdSe can occur only when the Class II centers are acting as recombination centers, i.e., when the electron Fermi-level lies above 0.6 ev from the conduction band in CdSe, and above 0.8 ev in CdS, and when the hole demarcation level therefore lies below the Class II levels. Infrared quenching, then, occurs when electrons are raised from the filled band to Class II centers, freeing a hole from a Class II center to be transferred to a Class I center where re-

combination is much more probable. Apparently two different types of Class II centers exist; in CdS, for example, one type is associated with the 1.65 ev quenching in insensitive crystals, and the other type is associated with the 1.35 and 0.89 ev quenching in sensitive crystals. A schematic representation of the transitions involved in the infrared quenching of CdS is given in Fig. 7. This transition scheme is based on the assumption that the "band-shape" of the high-photon-energy quenching spectrum is not intrinsic to the process of quenching but is really caused by a competition between excitation and quenching by the high-energy photons, excitation becoming much more prominent with increasing photon energy. Such a competition does exist over a range of energies slightly smaller than the band gap. On this basis, the significant energy in the quenching spectrum is not the energy for maximum quenching, but the lowest photon energy which will give any quenching at all. This lowest energy represents a threshold energy (the actual distance of the Class II defect levels above the valence band); for photons of higher energy than the threshold energy, the quenching arises from transitions from lower in the valence band.

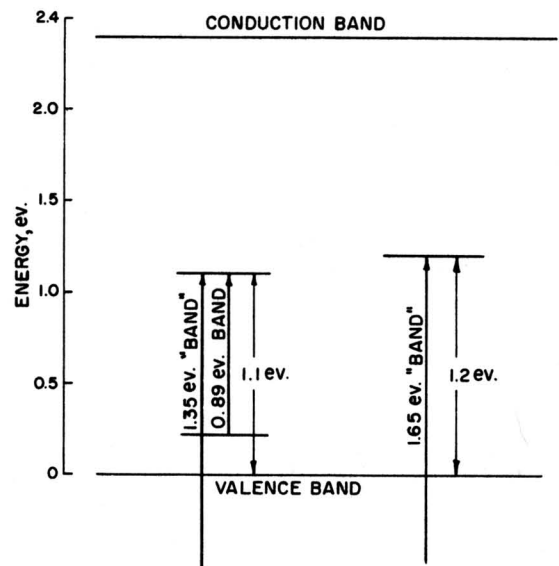


Fig. 7 - Schematic representation of the infrared quenching transitions in CdS.

II-11. Thermally Stimulated Current

If a crystal is cooled to a low tempera-

ture, excited, and then heated in the dark at a constant rate, the difference between the current measured during the heating and the normal dark current at the corresponding temperature is the thermally stimulated current. The thermally stimulated current (analogous to the glow curve for measurement of luminescence) is contributed by the thermal emptying of filled energy levels near the conduction band. In the interpretation of measurements of thermally stimulated current, it must be remembered that the magnitude of the current at a given temperature depends both on the concentration of levels emptying at that temperature and on the lifetime of a free electron at that temperature.

Fig. 8 shows typical curves of thermally stimulated current obtained for four crystals of CdS.⁸⁸ Such crystals show a remarkably reproducible trapping distribution from one crystal to another, as determined by these measurements; the curves of Fig. 8 indicate the presence of possibly as many as seven different current peaks which are common to all four crystals. The approximate depth of the trapping level can be determined by calculating the location of the electron Fermi-level from the temperature and the conductivity of the current maximum. Such values are listed on Fig. 8. The dotted curve, which is for a more sensitive crystal (the ordinates having been reduced by a factor of 10 before plotting), has its peaks shifted to higher temperatures relative to the curves for the less sensitive crystals; the shift in the peaks is exactly that which will give the same trap depths as calculated from the Fermi-level for the peak magnitudes and peak temperature locations for all four curves. A detailed study of the thermally stimulated current curves for the crystals of CdS and CdSe for which superlinearity and infrared quenching had been observed, indicate that trapping levels lying about 0.4 and 0.7 eV below the conduction band seem to be characteristic of CdS crystals, and levels lying about 0.4 eV below the conduction band seem to be characteristic of CdSe crystals.^{41, 88, 90}

Other investigations of thermally stimulated currents have been reported by Herman and Meyer⁹⁶, Muscheid⁷², and Jensen.⁹⁷ The concentration of trapping levels in CdS has been reported by Bube⁴¹ to vary between about $10^{18}/$

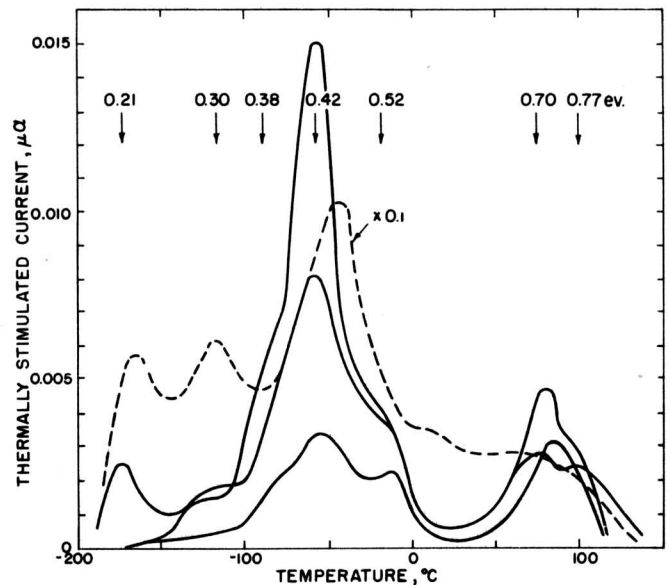


Fig. 8 - Thermally stimulated current curves for three "pure" insensitive CdS crystals (solid curves) and a sensitive CdS:Al crystal (dotted curve). Heating rate of $0.77^{\circ}/\text{sec}$.

cm^3 for "pure" insensitive CdS to $10^{17}/\text{cm}^3$ or higher for conducting CdS:Cl crystals. When only one thermally stimulated current peak is prominent, an estimate can also be made of the "attempt-to-escape" frequency from the trap levels and hence of the capture cross-section of these levels for free electrons; values of 10^6 sec^{-1} for the frequency and 10^{-20} cm^2 for the cross-section have been obtained for CdS.⁴¹

Other investigations on the nature of trapping, the distribution of traps, and the effect of trapping on the decay time of CdS photoconductor have been made by Thielemann⁸⁷, Broser and Warminsky⁹⁸, and Niekisch.⁹⁹

II-12. Space-Charge Limited Current

Although it might be expected from the nature of an insulator that carriers could move freely through the solid if they could be injected into the insulator, the magnitude of the current being limited only by the space charge of the carriers themselves, little experimental evidence for such currents was reported until the work of Rose and Smith.¹⁰⁰⁻¹⁰² They showed that large, steady space-charge limited currents (as high as $20 \text{ amp}/\text{cm}^2$) could be drawn through a thin insulating crystal of CdS fitted with ohmic electrodes. Low fields ($10^3 - 10^5$

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volts/cm) were used to eliminate the possibility of collision ionization or field emission from traps. The variation of the current as a high power of the voltage (the fourth power or higher) was explained in terms of the effect of traps on the build-up of the space-charge limited current. The dynamics of the space-charge-limited current build-up with varying field support this description.

Direct detection of the space charge in a crystal was made by dropping a crystal which had been subjected to an applied field, onto the pan of an electrometer. A negative charge was found regardless of the polarity of the initially applied field, and the magnitude of the charge agreed fairly well with the estimated value.

Fig. 9 shows the data obtained with a crystal of CdS, 2.5×10^{-3} cm thick and with an electrode area of 5×10^{-4} cm². Curve I_0 is for the current through the crystal in the dark after a time sufficient to establish thermal equilibrium. Curves F_1 , F_2 , and F_3 were taken with the crystal exposed to three different intensities of light, increasing in the order given. When the volume-generated carriers exceed the space-charge injected carriers, the behavior is ohmic. The initial space-charge limited current after application of the field, before trapping affected its magnitude, was detected using a pulse technique with the results shown in the upper curve of Fig. 9. The magnitudes of these currents are very close to the theoretical values of space-charge limited currents calculated for a trap-free solid.

Curve I'_0 of Fig. 9 is similar to curve I_0 , but it was taken within a few minutes after the crystal had been exposed to light. The much higher currents observed under these conditions can still be simply explained in terms of space-charge limited currents; an alternate explanation based on field emission from traps was proposed by Boer and Kuemmel.¹⁰⁹

The measurement of space-charge limited currents can be used as an additional tool for the determination of the concentration of trapping levels in insulators, especially useful when the concentration of such levels is small.

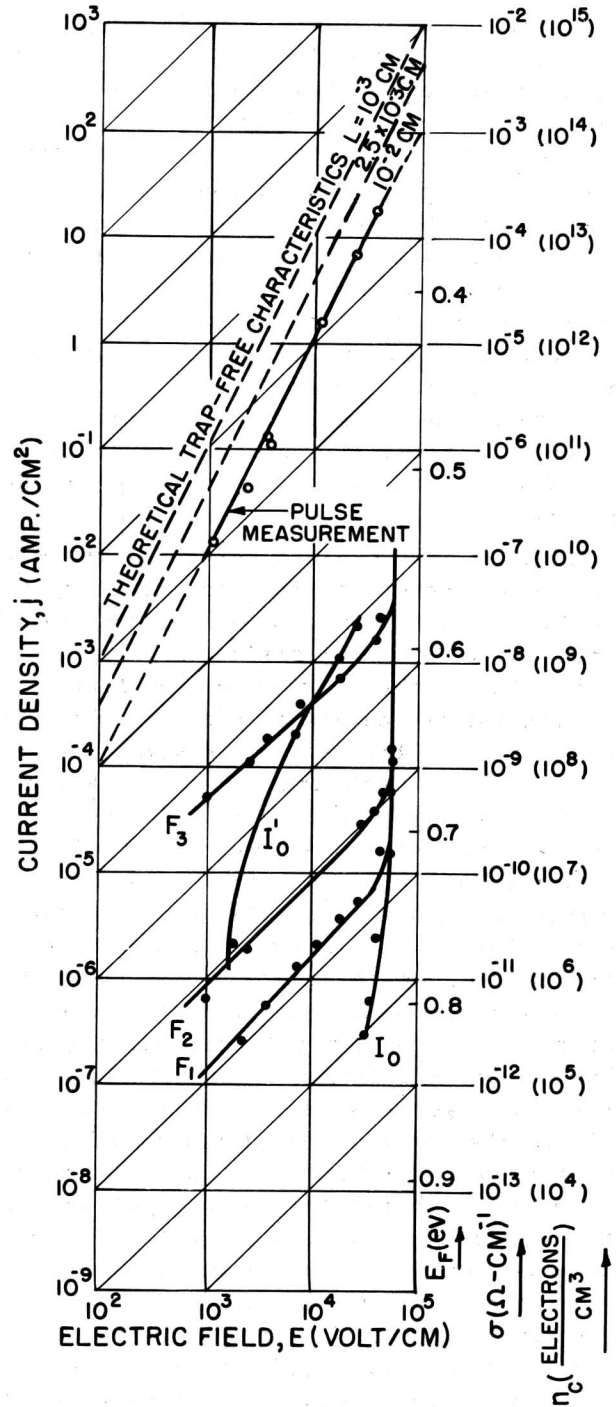


Fig. 9 - Space-charge-limited current in an insulator. I'_0 is initial dark current curve after exposure to light; I_0 is the thermal equilibrium dark current curve. F_1 , F_2 , and F_3 curves obtained with different light levels on the crystal, increasing in the order given. The current obtained from pulse measurements is compared with the theoretical space-charge limited current in a trap-free solid (calculated for $\mu = 100$ cm²/volt sec and dielectric constant of 10). The conductivity, σ , the density of carriers in the conduction band, n_c , and the calculated electron Fermi-level are also plotted on the right hand axis.

II-13. Photoconductivity and Luminescence

It has been only natural that investigators in the field should have sought for a correlation between photoconductivity and luminescence in the same material. Although there have been some statements on both extremes, i.e., either that photoconductivity is completely unrelated to luminescence, or that photoconductivity is exactly analogous to luminescence, the present consensus seems to be that photoconductivity and luminescence share many features in common, but that there are also some marked differences. The most striking difference is the dissimilarity in the decay times; luminescence emission generally decays much faster after the cessation of excitation than the photocurrent.^{104, 105} A qualitative picture can be given as follows: (1) as a result of excitation, many holes are captured at luminescence centers, and many others are captured at other centers throughout the crystal associated with defects and imperfections; (2) at the cessation of excitation, free electrons are captured most rapidly by the luminescence centers, the concentration in the conduction band being partially maintained by the emptying of shallow trapping levels; (3) after the major portion of the luminescence has decayed, the major portion of the photoconductivity still remains to undergo a slow recombination at those levels which have a smaller recombination cross-section than the luminescence centers.

Many investigators have set up theoretical models for comparing photoconductivity and luminescence, both in the steady state^{44, 46-48, 106, 107} and during the decay^{85, 96, 98}.

Although Wilkins and Garlick¹⁰⁸ have argued for an intimate relationship between luminescence centers and trapping centers, so that an electron freed from a trap need not contribute to the photocurrent in returning to the luminescence center, the similarity of excitation spectra for luminescence emission, trapping, and photoconductivity for ZnS, ZnS:Ag, and ZnS:Cu phosphors indicates that, at least in these materials, luminescence centers and trapping centers are separate, and that photoconductivity does result from the return to a luminescence center of an electron freed from a trap.²⁰

Smith⁸⁰ has reported on the electro-

luminescence of CdS crystals at low fields, associated with the recombination of injected electrons and holes, and Diemer¹⁰⁹ has reported on the light emission observed near DC breakdown of CdS:Cl crystals for which the current-voltage relationship is very similar to that of discharge in gases. Herforth and Krumbiegel¹¹⁰ describe the effect of ultrasonics on the conductivity and the luminescence of ZnS and CdS.

II-14. Photovoltaic Effect

Using crystals of CdS with one ohmic and one non-ohmic contact, Reynolds et al.^{111, 112} have developed a photovoltaic cell which gives an open circuit voltage of 0.4 volt in direct sunlight, and a short circuit current of 15 ma/cm². At 150 degrees C, the open circuit voltage is one-half of its room temperature value, and the short circuit current is one-fifth of its room temperature value. The spectral response for the photovoltaic effect of this cell has maxima at 5000Å and at 7000Å; the authors propose the existence of an intermediate band in the forbidden gap of CdS to explain the red photovoltaic response.

II-15. Photoemissive Effect

Apker and Taft¹¹³ have described the field emission obtained from sharp needles of CdS and CdSe. A large increase in the field emission current was observed when the crystals were irradiated with light of such a wavelength range as to excite photoconductivity.

II-16. Surface Photoconductivity

When the spectral response of photoconductivity is measured, it is quite frequently found that the sensitivity is very high in a narrow region of wavelengths near the absorption edge; for shorter wavelengths the sensitivity drops to a constant value smaller than the peak by an order of magnitude or more, and for longer wavelengths the sensitivity decreases rapidly to negligible values as the energy of the photons becomes much smaller than the band gap of the photoconductor.¹¹⁴ The reason for the decrease in photosensitivity for excitation by photons of greater energy than the band gap is sought in the difference between surface sensitivity, which is the important feature for these highly-absorbed photons, and volume

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sensitivity, which is the important feature for those photons which penetrate most of the crystal thickness.

An investigation of the effect of water vapor on the surface photoconductivity of CdS and ZnS crystals has shown that absorbed water vapor decreases the surface sensitivity by increasing the recombination rate at the surface.^{104, 115, 116}

The difference between surface and volume sensitivity of pure CdS crystals as determined by measurements of the spectral response of photoconductivity, becomes much more marked the greater the volume sensitivity of the crystal.¹¹⁷ The measurements by Klick⁸⁴ on CdS indicate that this difference disappears with decreasing temperature, being practically absent at 4 degrees K.

Tanaka and Aoki⁵⁰ deduce the presence of photosensitive surface barriers in CdS crystals from the dependence of surface potentials on wavelength. Wlerick¹¹⁸ has measured the variation of the contact potential of CdS with illumination.

Summary

The future should see the continuance of the multiplication of applications for photo-

conductors, branching out from a variety of simple control and detection uses to such elaborate utilization as in light amplification and picture reproduction, television camera pickup, electrophotography, and conversion of solar energy.

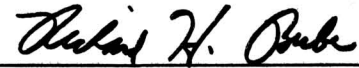
It would appear that an ideal photoconductor would have the following characteristics:

(1) A sufficiently large band gap to provide the required resistivity for the needs of the specific application.

(2) A sufficiently small band gap to insure response over the desired spectral range.

(3) A sufficiently perfect crystal structure with a minimum of trapping levels to permit the theoretical speed of response to be obtained at low light intensities.

(4) A sufficient control over the concentration and nature of defects to permit the exclusion of centers with a large recombination cross-section.



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