PHYSICAL REVIEW VOLUME 110, NUMBER 5 JUNE 1, 1958

# Photoconductivity of Zinc Selenide Crystals and a Correlation of Donor and Acceptor Levels in II–VI Photoconductors

RICHARD H. BUBE AND EDWARD L. LIND
*RCA Laboratories, Radio Corporation of America, Princeton, New Jersey*

(Received February 13, 1958)

Photosensitive crystals of zinc selenide have been prepared by incorporating suitable proportions of Group VII donors (e.g., bromine) and either Group I acceptors (copper or silver) or Group V acceptors (antimony or arsenic) in crystals prepared from the vapor phase. Photoconductivity phenomena characteristic of other II–VI photoconductors, such as (a) variation of photocurrent with a power of light intensity greater than unity, (b) temperature quenching of photoconductivity, and (c) infrared quenching of photoconductivity, are also found for zinc selenide. Sensitizing centers in ZnSe:Br:Cu and ZnSe:Br:Ag have levels lying at the same distance above the top of the valence band (0.6 ev) as sensitizing centers in CdSe, even though the band gap of ZnSe is 50% larger than that of CdSe. Crystals with Group V acceptors are characterized in addition by a long-wavelength spectral response, out to 1.4 microns, associated with levels lying about 1.3 ev above the top of the valence band. By a consideration of known data on the conductivity, photoconductivity, and luminescence of II–VI compounds, a consistent correlation of donor and acceptor levels in these materials is possible.

## INTRODUCTION

DETAILED investigations of the mechanism of photoconductivity in II–VI materials have been concentrated mainly on CdS and CdSe.[1] Photosensitive single crystals of CdS and CdSe have been prepared both by incorporation of suitable impurities (Group VII donors plus Group I acceptors),[2] and by vacuum annealing to introduce suitable deviations from stoichiometry.[3] A successful description of the phenomena observed with these materials has been made on the basis of the hypothesis[4] that the photosensitivity is associated with the capture of holes by sensitizing centers which subsequently have a small cross section for capturing free electrons. As long as holes are stably captured by these centers, high photosensitivity is obtained; when, however, the holes are released to the valence band, either by thermal or optical energy, quenching of the photosensitivity results, as the holes are captured by other centers with a subsequent large cross section for free electrons.

Some investigations have been made on other II–VI photoconductors. Many general studies have been made on photoconductivity in ZnS powders, but few, if any, on the mechanism of photoconductivity in single crystals. Photoconductivity in ZnTe has been briefly reported.[5] Investigations on CdTe have been limited mainly to its semiconducting properties.[6,7]

This paper describes the preparation and sensitization of ZnSe single crystals. The temperature dependence of the spectral response of ZnSe crystals has been previously reported,[8] but no detailed study of the photoconductivity characteristics was undertaken at that time. The results of the present study show that photoconductivity in ZnSe is markedly similar to that found in CdS and CdSe when sensitization is by Group VII donors and Group I acceptors, but that certain new phenomena occur when Group V acceptors are used.

A consideration of the results obtained with ZnSe, together with known data on other II–VI materials, leads to a consistent correlation of donor and acceptor levels in these materials. The key to this correlation is the observation that the donor ionization energy is determined primarily by the cation of the compound, whereas the acceptor ionization energy is determined primarily by the anion of the compound. In this way the conductivity and photoconductivity properties of these materials may be correlated with their luminescence properties.

## EXPERIMENTAL

Crystals of ZnSe were prepared from the vapor phase reaction between zinc and selenium. A modification of the Frerichs technique, similar to that used previously for CdS and CdSe,[2] was used. A flow of hydrogen, at the rate of 50 ml/min, carried zinc vapor, over zinc at 710°C, to react with a similar stream of selenium vapor, carried by hydrogen over selenium at 525°C, into a reaction zone at 1100°C. The useful crystal growth usually occurred in the first 10 minutes of operation, and the final yield was about 10 to 15%.

X-ray analysis of many crystals[9] showed the presence of both cubic and hexagonal crystal forms. This result is similar to that found in ZnS.[10] Most of the crystals grow in the form of needles. One plate-like crystal which grew in a region of high vapor concentration was found to be completely cubic.

---

[1] R. H. Bube, Proc. Inst. Radio Engrs. **43**, 1836 (1955).

[2] R. H. Bube and S. M. Thomsen, J. Chem. Phys. **23**, 15 (1955).

[3] R. H. Bube and L. A. Barton, J. Chem. Phys. (to be published).

[4] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957).

[5] R. H. Bube and E. L. Lind, Phys. Rev. **105**, 1711 (1957).

[6] D. A. Jenny and R. H. Bube, Phys. Rev. **96**, 1190 (1954).

[7] F. A. Kröger and D. De Nobel, J. Electronics **1**, 190 (1955).

[8] R. H. Bube, Phys. Rev. **98**, 431 (1955).

[9] X-ray analysis by J. White.

[10] L. W. Strock and V. A. Brophy, Am. Mineralogist **40**, 94 (1955).

Halide impurity was introduced into the crystals by passing a portion of the carrier gas for the zinc over or through a suitable halide source during the growth of the crystals. Bromine was used principally; a portion of the carrier gas, between 20 and 100%, was passed over bromine at 0°C. Best crystal growth observed for any preparation conditions was found when 80% of the carrier gas passed over bromine. For very high bromine proportions, excess $ZnBr_2$ was observed in the preparation. The color of the crystals varied markedly with the proportion of bromine incorporated, from light yellow to orange.

Crystals of ZnSe:Br prepared in this way were subsequently treated to incorporate copper or silver. Optimum results were obtained when 0.1 g of ZnSe:Br crystals were placed in 10 cc of a $10^{-5}M$ solution of copper nitrate. After washing and drying, the crystals were heated at 900°C for 20 minutes to diffuse copper into the crystals.

To incorporate antimony impurity, antimony was placed in the same furnace zone as the zinc, so that at the temperature of that zone, there was about 1 mm of antimony vapor pressure. Similarly, to incorporate arsenic, arsenic was placed in the same furnace zone as the selenium; the exact vapor pressure involved is not certain because of the likelihood of the formation of an arsenic selenide. The presence of antimony or arsenic in the preparation strongly inhibited crystal growth, particularly in the absence of bromine; such ZnSe:Sb and ZnSe:As crystals showed very high resistivity and almost negligible photosensitivity.

## PHOTOCONDUCTIVITY WITH GROUP I ACCEPTORS

### Spectral Response

Spectral response curves for several crystals of ZnSe are shown in Fig. 1. "Pure" ZnSe crystals show maximum photosensitivity at about 4620 A (2.68 ev) which corresponds to the absorption edge of "pure" ZnSe. This value is somewhat lower than that reported in a previous publication,[8] but agrees well with the value obtained from measurement of edge luminescence emission.[1] In crystals with halide impurity, the maximum is shifted about 100 A to longer wavelengths. In most crystals of ZnSe:Br:Cu, the maximum is shifted even further to longer wavelengths, by as much as 300 A; in these crystals a second impurity-associated shoulder in the spectral response curve occurs at about 5100 A, with a long-wavelength tail extending out to about 6000 A.

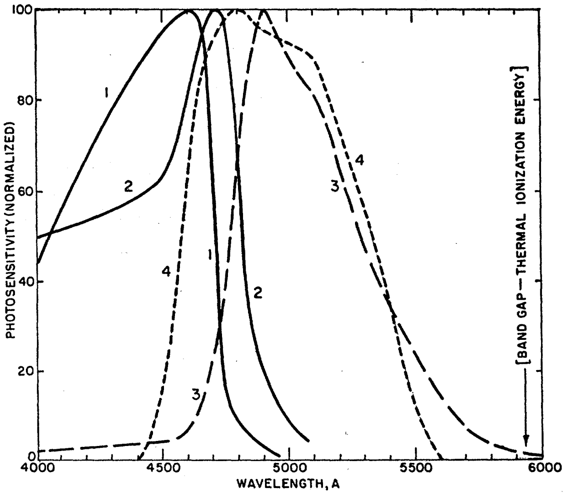

Fig. 1. Spectral response curves for photoconductivity in ZnSe crystals. (1) "Pure" ZnSe, (2) ZnSe with halide impurity, (3) ZnSe:Br:Cu, and (4) ZnSe:Br:Cu at −183°C.

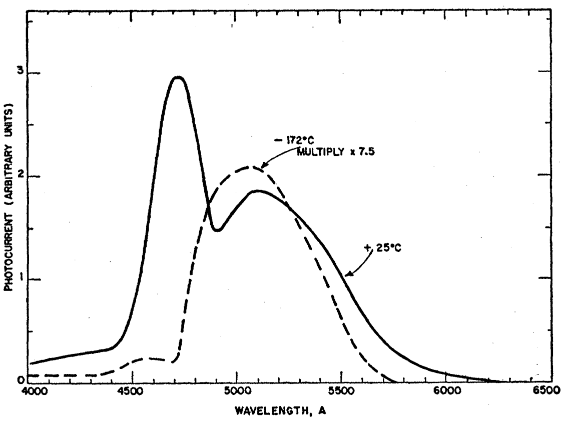

Fig. 2. Spectral response curves for photoconductivity in ZnSe: Br:Cu with high bromine and copper concentration.

The spectral response for one of the most sensitive ZnSe:Br:Cu crystals prepared is shown in Fig. 2. This crystal was prepared with all the hydrogen carrier gas passed over the bromine and was later treated with $10^{-3}M$ copper nitrate. At liquid nitrogen temperature, the photoresponse is determined by the impurity response band.

Spectral response curves for ZnSe:Br:Ag are shown in Fig. 3. A semilogarithmic plot has been used to show the sharp cut off at 5500 to 6000 A, characteristic of all ZnSe:Br:Cu and ZnSe:Br:Ag crystals.

### Photosensitivity

The specific sensitivity of unsensitized "pure" ZnSe crystals is about $10^{-6}$ to $10^{-5}$ mho cm$^2$ per watt. This appears to be a common value for sensitivity in "pure" crystals, being found also in CdS and CdSe. The maximum sensitivity obtained in ZnSe:Br:Cu and ZnSe:Br:Ag insulating crystals (conductivity less than $10^{-10}$ mho/cm at room temperature in the dark) is about $4\times10^{-3}$ mho cm$^2$ per watt. The sensitivity of photosensitive CdS and CdSe crystals is about $10^{-1}$ mho cm$^2$/watt. Higher photosensitivities can be obtained in ZnSe:Br:Cu crystals if a higher dark conductivity is permitted. The crystal corresponding to the spectral response of Fig. 2, for example, had a room temperature

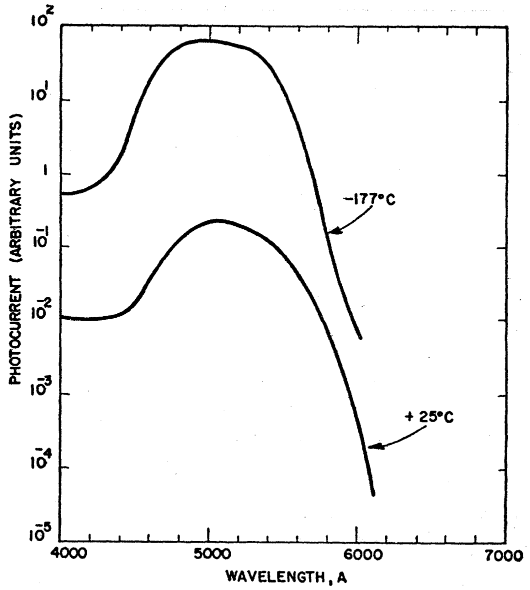

FIG. 3. Spectral response curves for photoconductivity in ZnSe:Br:Ag.

dark conductivity of $6\times10^{-6}$ mho/cm and a specific sensitivity of $4\times10^{-2}$ mho cm$^2$ per watt.

## Speed of Response

The decay time of photoconductivity was measured for both the insulating and the more conducting ZnSe:Br:Cu crystals after illumination by 1740 ft-c of incandescent light. The insulating crystals had a measured decay time of 2 milliseconds; the more conducting crystals had a decay time of 14 milliseconds. Both values, together with the measured photoconductivity gain, lead to a calculated effective mobility of 4 cm$^2$/volt sec. (Data on insulating sensitive ZnSe:Br:As crystals gave an effective mobility of 18 cm$^2$/volt sec.)

The low-light speed was also measured for the insulating ZnSe:Br:Cu crystals. At 0.2 ft-c, the rise time was about 1 sec, and the decay time was less than 0.1 sec.

## Temperature Dependence

### (a) *Insulating ZnSe:Br:Cu*

The photocurrent for an insulating ZnSe:Br:Cu crystal was measured as a function of light intensity at several temperatures between that of liquid nitrogen and 100°C, using a broad band of exciting wavelengths from 4800 to 5200 A from a monochromator. The variation of photocurrent with temperature for different exciting intensities is shown in Fig. 4. The data are completely analogous to similar data obtained on CdSe crystals.[4] At low temperatures the photosensitivity is high, corresponding to the stable capture of holes by sensitizing centers. Above some critical temperature, which decreases with decreasing light intensity, temperature quenching sets in as holes in sensitizing centers begin to be thermally released. When all the holes have essentially been released from the sensitizing centers, the thermal quenching ceases. At higher temperatures the sensitivity may increase again; centers with levels lying near the conduction band, which act as recombination centers at lower temperatures, change over to acting as trapping centers, thereby decreasing the total density of recombination centers. The loci of the approximate points for the onset and end of temperature quenching are indicated in Fig. 4.

As indicated in a previous publication,[4] the following relationships hold:

$$\ln n_{\max}=\ln(N_vS_p/S_n)-E_a/kT_{\max}, \qquad (1)$$

$$\ln n_{\min}=\ln(N_rN_v/N_a)-E_a/kT_{\min}, \qquad (2)$$

where $n_{\max}$ is the density of free electrons at the onset of temperature quenching at temperature $T_{\max}$, $n_{\min}$ is the density of free electrons at the end of temperature quenching at temperature $T_{\min}$, $N_v$ is the effective density of states in the valence band, $S_p$ is the capture cross section of a sensitizing center for a hole when occupied by an electron, $S_n$ is the capture cross section of a sensitizing center for an electron when occupied by a hole, $E_a$ is the height of the level corresponding to the sensitizing centers above the top of the valence band, $N_a$ is the density of sensitizing centers, and $N_r$ is the total density of large cross-section recombination centers. The photocurrent at the onset of temperature quenching is shown on a semilogarithmic plot as a

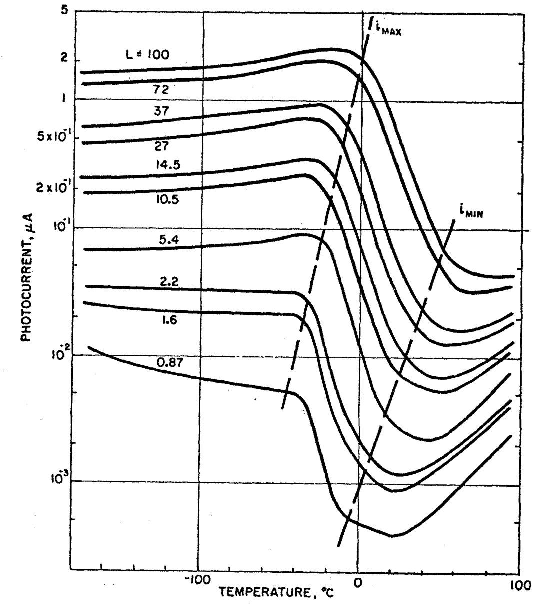

FIG. 4. Variation of photocurrent with temperature for different intensities of excitation for ZnSe:Br:Cu crystal. Dashed lines show loci of approximate points of beginning and end of temperature quenching.

function of $1/T_{\max}$ in Fig. 5; also the photocurrent at the end of temperature quenching is shown on a semilogarithmic plot as a function of $1/T_{\min}$. The lines shown in the figure are the result of a least-squares analysis. The lines are approximately parallel with a slope corresponding to $E_a=0.60$ ev, essentially the same as for CdSe. From the intercept of the curve for $i_{\max}$ at $1/T=0$, a value of $S_p/S_n \approx 10^4$ is obtained, to be compared with a ratio of $8 \times 10^5$ for CdSe. From the intercept of the curve for $i_{\min}$, $N_r/N_a=3$ is obtained.

If the photocurrent is considered as a function of light intensity at temperatures in the quenching range, it is found that the photocurrent varies as about the square of the light intensity.

### (*b*) *ZnSe:Br:Cu of Higher Conductivity*

Crystals such as the one corresponding to the spectral response of Fig. 2 also showed temperature quenching which could be treated by the same analysis as that just discussed. A value of 0.6 ev was obtained for the ionization energy of the sensitizing acceptors. Instead of the region of temperature quenching being associated with a transition from a variation of photocurrent as the first power of light intensity to a variation with a higher power, however, temperature quenching is associated with a transition in the variation of photocurrent with light intensity from a power 0.5 to a power unity. This is consistent[3] with the fact that there is probably a much greater density of shallow levels, lying above the Fermi-level, in the higher conductivity crystals.

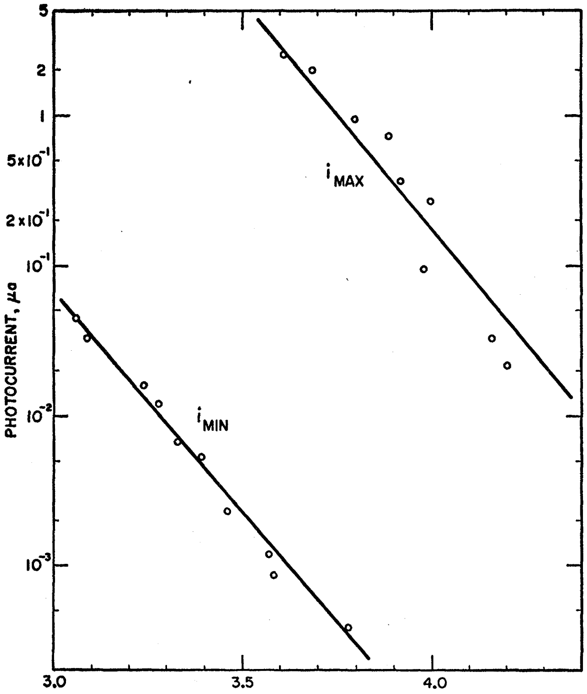

FIG. 5. Photocurrent at beginning of temperature quenching ($i_{\max}$) and end of temperature quenching ($i_{\min}$) as a function of the corresponding reciprocal temperature.

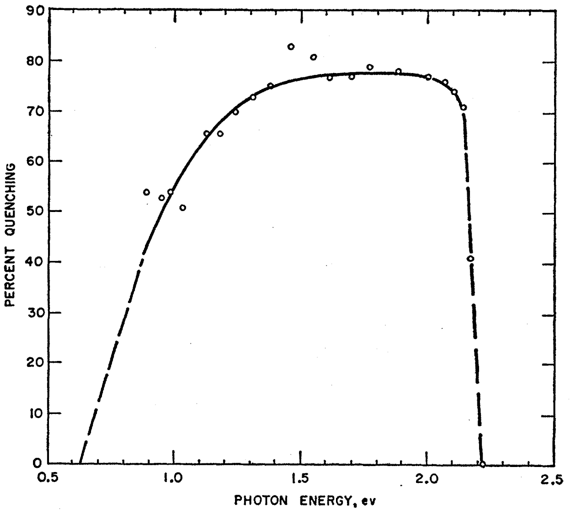

FIG. 6. Infrared quenching spectrum for ZnSe:Br:Cu crystal at −183°C. Primary excitation by blue light from Corning 5113 filter; secondary radiation from monochromator.

### (*c*) *ZnSe:Br:Ag*

Temperature quenching in the ZnSe:Br:Ag crystals could also be treated by the same analysis. A value of 0.64 ev was found for the ionization energy of the sensitizing acceptors, with a ratio of cross sections of about $10^5$. In the temperature quenching range, the photocurrent varied as about the 2.4 power of the light intensity.

## Infrared Quenching

Under conditions of temperature and light intensity such that holes are stably captured in the sensitizing centers, quenching of photoconductivity can be caused by optical excitation of electrons from the valence band to the centers. At low temperatures, such optical quenching is very strong in the ZnSe:Br:Cu and ZnSe:Br:Ag crystals. A quenching spectrum, measured for an insulating ZnSe:Br:Cu crystal, is given in Fig. 6, measured at −183°C for primary excitation by blue light passed by a Corning 5113 filter. For secondary excitation by photons with energy greater than 2.2 ev, the apparent quenching disappears because light of this energy begins to cause efficient excitation of photoconductivity. The quenching spectrum is flat from 2.0 ev to about 1.4 ev, and then decreases to a cut off near about 0.6 ev. The data shown in Fig. 6 have been corrected for the measured observation that the percent quenching varies as the 0.6 power of the secondary radiation intensity.

The general interpretation of the quenching spectrum given here is the same as that previously given for that of CdS.[11] In that case, however, it was not so obvious

---

[11] R. H. Bube, Phys. Rev. **99**, 1105 (1955).

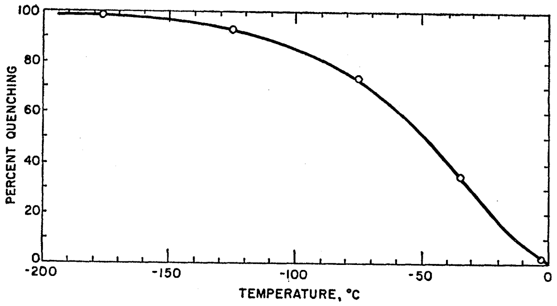

FIG. 7. Temperature dependence of infrared quenching in ZnSe:Br:Cu using a secondary radiation of 9500 A.

that the interpretation was valid, because the spectrum had much more the appearance of a symmetric quenching band. The data obtained for ZnSe confirm the conclusion that the main quenching occurs as a transition between the valence band and the sensitizing centers, the apparent decrease in quenching for high photon energies being caused by the high excitation caused by these same photon energies.

When photoexcited holes are no longer thermally stable in sensitizing centers, it is clear that the existence of infrared quenching must disappear. The temperature dependence of infrared quenching for a constant photocurrent excited by the primary radiation and for a constant secondary intensity of 9500 A is shown in Fig. 7. This dependence on temperature is again completely identical with that previously reported for CdSe.[11]

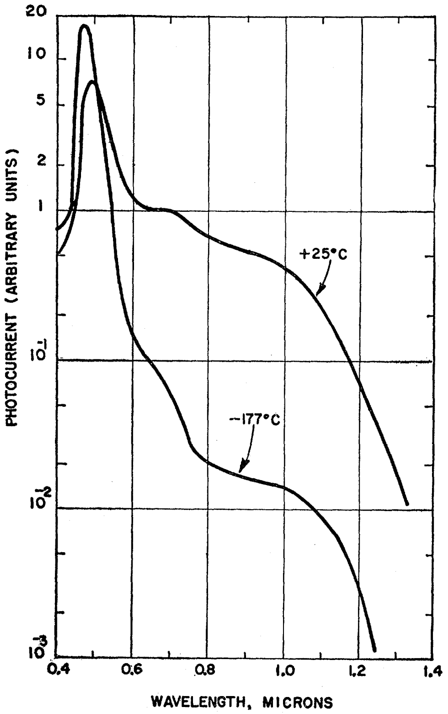

FIG. 8. Spectral response curves for photoconductivity in ZnSe:Br:Sb.

## Saturation of Photocurrent with Voltage

In the course of the investigation of ZnSe crystals with apparently ohmic indium contacts, it was frequently found that the photocurrent saturated with voltage, at fields of about $10^3$ volt/cm or less applied perpendicular to the crystal striations. This was particularly common for sensitive ZnSe crystals. The phenomena are sufficiently complex, however, that considerable further research is necessary before a useful discussion can be given. It is highly probable, however, that the saturation of photocurrent, presence of stacking faults, and occurrence of a high-voltage photovoltaic effect[12] in both ZnS and ZnSe are mutually interrelated.

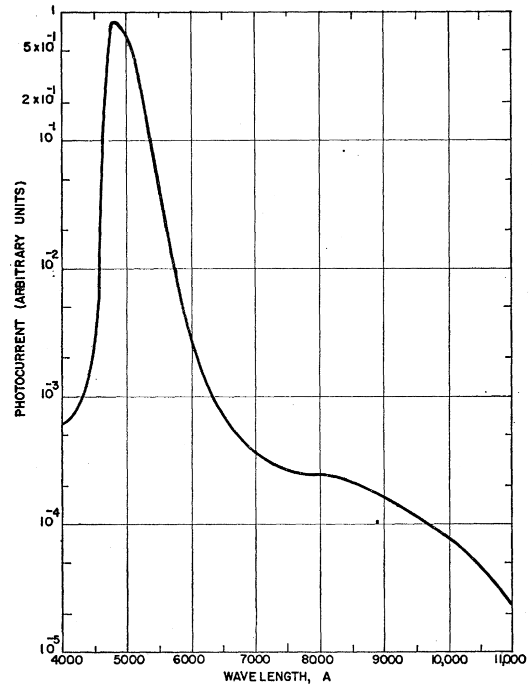

FIG. 9. Spectral response curve for photoconductivity in ZnSe:Br:As.

## PHOTOCONDUCTIVITY WITH GROUP V ACCEPTORS

### Spectral Response

Spectral response curves for photosensitive ZnSe:Br:Sb and ZnSe:Br:As are given in Figs. 8 and 9, respectively. The curves of Fig. 8, which are representative for all ZnSe:Br:Sb tested, show a main peak near the absorption edge of ZnSe, a shoulder breaking at about 7000 A, and a long-wavelength tail with threshold wavelength near 1.1 microns. The two long-wavelength shoulders indicate transitions of about 1.8 ev and 1.1 ev, respectively. The long-wavelength response is so much less at −177°C than at 25°C principally because of the strong simultaneous quenching caused by light of these wavelengths. The long-wave-

---

[12] B. Goldstein, Phys. Rev. **109**, 601 (1958).

length tail occurred much less frequently in ZnSe:Br:As than in ZnSe:Br:Sb.

### Photosensitivity

Insulating crystals of ZnSe:Br:Sb, like insulating crystals of ZnSe:Br:Cu and ZnSe:Br:Ag, have a maximum photosensitivity of about $4\times10^{-3}$ mho cm$^2$/watt. Insulating crystals of ZnSe:Br:As with a sensitivity of $4\times10^{-2}$ mho cm$^2$/watt have been obtained. Higher conductivity crystals have likewise a higher sensitivity. A ZnSe:Br:As crystal, for example, with a dark conductivity of about $10^{-2}$ mho/cm, had a specific sensitivity of $3\times10^{-1}$ mho cm$^2$ per watt.

ZnSe:Sb and ZnSe:As crystals prepared without bromine show a sensitivity of about $10^{-7}$ mho cm$^2$/watt, about the lowest yet found in any II–VI compounds.

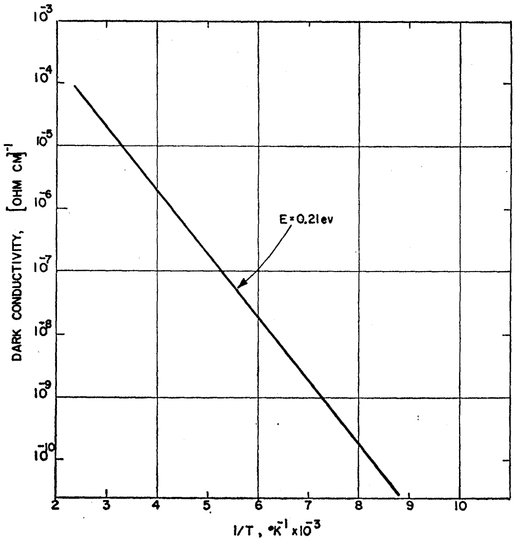

FIG. 10. Dark conductivity as a function of temperature for ZnSe:Sb:Br, giving bromine ionization energy of 0.21 ev.

### Dark Conductivity

The best measurement of the ionization energy for bromine donors in ZnSe was obtained for a crystal of ZnSe:Br:Sb with a conductivity of $7\times10^{-6}$ mho/cm at room temperature. The dark conductivity varied exponentially with $1/T$ for more than six orders of magnitude, giving an ionization energy of 0.21 ev. The curve is shown in Fig. 10.

### Infrared Quenching

If the energy separations between the top of the valence band and the levels indicated by the spectral response are calculated, values of about 0.8 and 1.5 ev are obtained. If such levels are associated with sensitizing acceptor centers, the thermal or optical release of captured holes from them should be manifest in thermal or optical quenching effects. Figure 11 shows infrared quenching spectra obtained for a ZnSe:Br:Sb crystal at both −177° and 25°C. Infrared quenching at the low temperature is associated with transitions from the valence band to a level about 0.7 to 0.8 ev above the top of the valence band, and to higher levels. Infrared quenching at room temperature is associated with transitions to levels lying about 1.2 to 1.3 ev above the top of the valence band. The absence of the low-energy infrared quenching at room temperature appears to be caused by the thermal release of holes from these centers. Thus the infrared quenching spectra give values for the height of the acceptor levels above the top of the valence band which agree well with the values estimated from the response spectra.

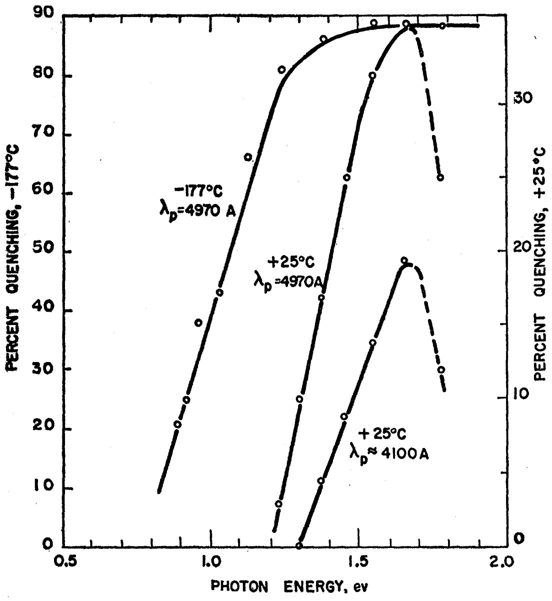

FIG. 11. Infrared quenching spectra for ZnSe:Br:Sb.

The lower of the two acceptor levels has about the same ionization energy as the acceptor levels found in crystals with Group I acceptors. The presence of a higher level in which holes can be stably held at room temperature and above is very similar to the results reported for annealing-sensitized CdSe crystals[3]; acceptor levels in that case were found 0.6 and 1.0 ev above the top of the valence band.

Evidence of thermal quenching should be found in measurements of photocurrent as a function of temperature. Figure 12 shows such data for a ZnSe:Br:Sb crystal measured at different light intensities. There is a small quenching just below 0°C, which is the correct temperature range for thermal release of holes from levels lying about 0.6 ev above the top of the valence band (compare with Fig. 4). In addition there is a high-temperature quenching of much greater magnitude, which sets in near 100°C, about the right range for levels lying slightly more than 1.0 ev from the top of the valence band. The low-temperature quenching is associated with a transition in the variation of photo-

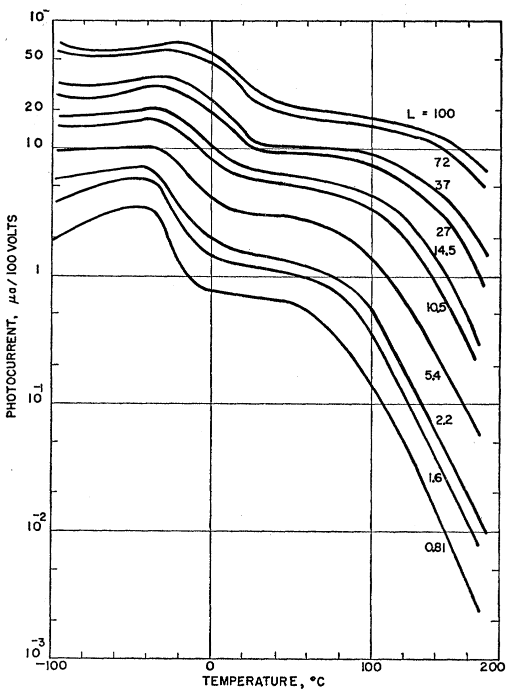

FIG. 12. Variation of photocurrent with temperature for different intensities of excitation for ZnSe:Br:Sb crystal.

current with light intensity from a 0.6 power to a 1.0 power; the high-temperature quenching is associated with a variation of photocurrent with a power of light intensity greater than unity, up to 1.8 over the range measured.

Although the above aspects of the temperature dependence data fit into the whole picture, there are two additional features which do not. (a) If the analysis of Eqs. (1) and (2) is applied to the data of Fig. 12, the thermal ionization energies determined in this way do not agree at all with the infrared-quenching determined energies; a value of 0.35 ev is obtained for the low-temperature quenching, and a value of 0.45 ev is obtained for the high-temperature quenching. (b) This discrepancy may be associated with the second different feature, i.e., the form of the high-temperature quenching. Instead of the quenching being confined to a fairly narrow range of temperature, as has been found for all previous data on CdS, CdSe, and ZnSe with Group I acceptors, the range of temperature quenching is much broader, and the photocurrent decreases exponentially with temperature. The power of the dependence of photocurrent on light intensity increases with temperature in the range of temperature quenching. This behavior suggests a distribution of acceptor levels, instead of a discrete level. Identical behavior has been found in one other case, namely low-temperature data on $In_2S_3$ crystals,[13] indicating that this type of behavior has real physical significance.

In ZnSe:Br:As crystals which do not exhibit the long-wavelength response tail, infrared quenching is associated only with transitions from the valence band to levels lying about 0.7 to 0.8 ev above the top of the valence band. Analysis of temperature quenching of photoconductivity in such crystals, according to Eqs. (1) and (2), gives an acceptor ionization energy of about 0.6 ev, in reasonable agreement with the spectral response and infrared quenching values.

## Other Effects

In addition to the fairly frequent occurrence of a photocurrent saturating with voltage, mentioned in the previous discussion of Group I acceptors, two other effects were found with the ZnSe:Br:Sb crystals which are worthy of description.

(*a*) *Enhancement of photoconductivity.*—Photocurrent caused by a wavelength shorter than the absorption edge was appreciably enhanced by simultaneous excitation by wavelengths longer than the absorption edge, but shorter than those giving quenching, i.e., the sum of the photocurrents measured independently was less than the photocurrent measured for both radiations present simultaneously. Values of the measured photocurrent for both radiations present were as much as 30% greater than the sum of the individual photocurrents. The photocurrent for either radiation separately did not vary with a power of light intensity greater than unity. The effect was much smaller if the primary excitation was by light of wavelength longer than the absorption edge. The enhancement caused by the secondary radiation had a slow decay over several seconds.

(*b*) *Oscillating photocurrents.*—Oscillating photocurrents have been observed under steady light and field conditions in CdS by Liebson[14] and by Loebner.[15] The same phenomena were found over a small range of temperature near liquid nitrogen temperature for a ZnSe:Br:Sb crystal. Figure 13 summarizes the main characteristics of the effect. (a) The photocurrent saturated with voltage, saturating at a lower voltage the lower the light intensity. Oscillations occurred only for a voltage in the saturation region. (b) The oscillations were associated with an abrupt *cutting off* of the normal photocurrent. The maximum photocurrent in the oscillating range was about the same as the steady-state current expected in the absence of oscillations. The minimum photocurrent varied linearly with light intensity, oscillations ceasing at both high and low light intensities. (c) The ratio of maximum to minimum photocurrent in the oscillations decreased as the 0.67 power of light intensity. The amplitude of the oscillations is constant at high lights and then decreases rapidly at low lights. (d) The period of the oscillations decreases linearly with light intensity, from a value of 34 sec to a value of 1.5 sec over the light intensity

---

[13] Unpublished data on crystals prepared by W. H. McCarroll.

[14] S. H. Liebson, J. Electrochem. Soc. **102**, 529 (1955).

[15] E. E. Loebner (private communication).

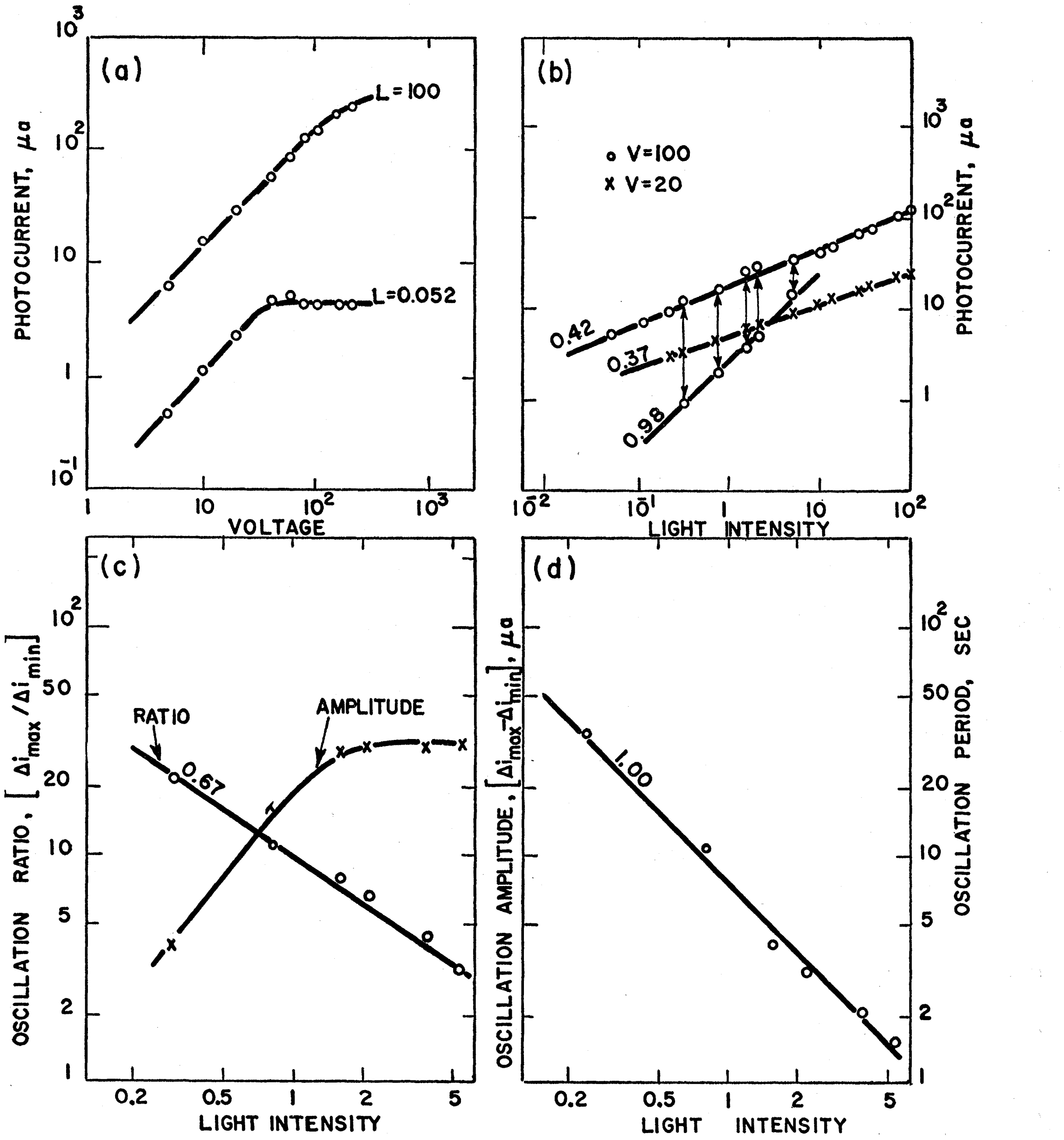

Fig. 13. Data pertinent to oscillating photocurrent in ZnSe:Br:Sb crystal at −183°C. (a) Photocurrent as a function of applied voltage for two different light levels. (b) Photocurrent as a function of light intensity for two different voltages, indicating the presence of oscillations by the arrows. (c) Ratio and amplitude of the oscillations as a function of light intensity. (d) Period of the oscillations as a function of light intensity.

range measured. The actual complicated but fairly reproducible wave form of the oscillations for a light intensity of 2.2 ft-candles is given in Fig. 14. (e) Oscillations were obtained both for light with wavelength shorter than the absorption edge and for light with wavelength longer than the absorption edge.

## CORRELATION OF DONOR AND ACCEPTOR LEVELS IN II–VI PHOTOCONDUCTORS

One of the striking results of the above investigation is that the sensitizing levels lie the same distance above the top of the valence band in ZnSe as in CdSe, even though the band gap itself is 55% larger in ZnSe. This fact suggests that the sensitizing levels, which are acceptor levels, are determined primarily by the nature of the anion. This is not surprising when it is realized that the electronic transitions involved should be considered in most cases to be to and from perturbed anions in the neighborhood of the acceptor impurity or imperfection. This is probably clearest in the case of a cation-vacancy acceptor; the holes which this center can release exist in the form of missing electrons from

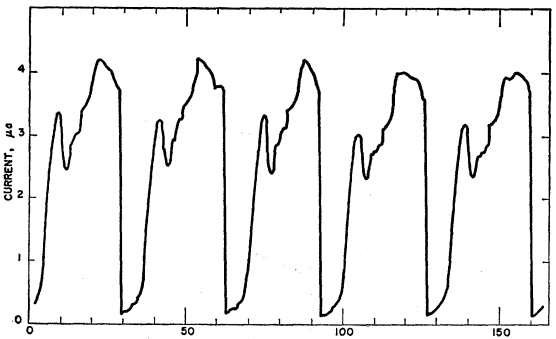

FIG. 14. Tracing of the oscillating photocurrent in ZnSe:Br:Sb, when excitation is by 2.2 ft-c and period is about 34 seconds.

anions around the vacancy. By analogy we might expect that the location of donor levels would be determined predominantly by the cation. Following this line of reasoning, it is possible to see an internal consistency to scattered data on conductivity and photoconductivity in II–VI compounds.

Typical donor and acceptor ionization energies are listed in Table I. Only tellurides have been definitely prepared in *p*-type form to date; of the tellurides, ZnTe has not to date been prepared as *n* type because of the difficulty of removing small traces of *p*-type copper impurity. Photoconductivity shows temperature quenching below room temperature in ZnTe, near room temperature for ZnSe and CdSe, and above room temperature for CdS. Figure 15 presents an energy scheme with representative donor and acceptor levels. A shallow donor level (~0.03 ev) characteristic of cadmium compounds and a deeper donor level (~0.25 ev) characteristic of zinc compounds are shown. Also indicated are three acceptor levels: a deep level (~1.0 ev) characteristic of sulfur compounds, a shallower level (~0.6 ev) characteristic of selenium compounds, and a still shallower level (~0.3 ev) characteristic of tellurium compounds.

TABLE I. Donor and acceptor ionization energies in II–VI compounds.

| Compound | Impurity | Donor ionization energy, ev | Acceptor ionization energy, ev |
|---|---|---|---|
| ZnS | Cl | 0.25,[a] 0.37[b] | |
| | Cu | | 0.95[c, d] |
| | Ag | | 0.55[c, d] |
| CdS | Cl | 0.04[e, f] | |
| | Cu | | 0.6,[g, h] 1.0[i] |
| ZnSe | Br | 0.21 | |
| | Cu | | 0.6 |
| | Ag | | 0.6 |
| | Sb | | 0.7, 1.3[j] |
| CdSe | Cl | 0.03 | |
| | (Anion vacancy) | 0.14[k] | |
| | Cu | | 0.6[l] |
| | (Cation vacancy) | | 0.6, 1.0[j, k] |
| ZnTe | Cu | | 0.11,[h] 0.34[m] |
| CdTe | I | 0.003[n] | |
| | Li | | 0.27[n] |
| | Sb | | 0.36[n] |
| | P | | 0.38[n] |

[a] F. A. Kröger, Physica **22**, 637 (1956).
[b] R. C. Herman and C. F. Meyer, J. Appl. Phys. **17**, 743 (1946).
[c] G. F. J. Garlick and A. F. Gibson, J. Opt. Soc. Am. **39**, 935 (1949).
[d] R. H. Bube, Phys. Rev. **90**, 70 (1953).
[e] Kröger, Vink, and Volger, Philips Research Repts. **10**, 39 (1955).
[f] R. H. Bube, J. Chem. Phys. **23**, 18 (1955).
[g] See reference 11.
[h] Found only for very high copper concentrations.
[i] S. M. Thomsen and R. H. Bube, Rev. Sci. Instr. **26**, 664 (1955).
[j] Possible second ionization levels.
[k] See reference 3.
[l] See reference 4.
[m] See reference 5.
[n] See reference 6.

There are two further points which must be mentioned. First is the fact that it is possible that the photoconductivity data on ZnSe:Br:Cu, ZnSe:Br:Ag, ZnSe:Br:Sb, ZnSe:Br:As, CdSe:I:Cu, annealing-sensitized CdSe, etc., which show the same level at 0.6 ev above the top of the valence band, may be associated with one and the same type of vacancy defect center, rather than with the different acceptor impurities which have been incorporated to control the dark conductivity. Second is the fact that in the previous discussion, we have had in mind the first ionization energies. In divalent compounds there is obviously at least the possibility of double ionization processes. Some evidence for such double donor and acceptor ionizations has been found for CdSe,[3] and for ZnSe:Br:Sb and ZnSe:Br:As as discussed in this paper. We have also neglected certain secondary complexities, such as the low-energy quenching band in CdS, corresponding to a transition from a low-lying level to the acceptor level described in the above discussion.[11]

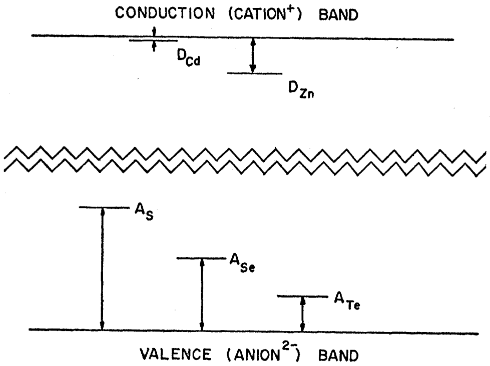

FIG. 15. Representative energy levels for donors and acceptors in II–VI materials. $D_{Cd}$—donors in Cd compounds, $D_{Zn}$—donors in Zn compounds, $A_S$—acceptors in S compounds, $A_{Se}$—acceptors in Se compounds, $A_{Te}$—acceptors in Te compounds.

It is probably correct to interpret the magnitude of the ionization energy as being at least a qualitative indication of the effective mass of the corresponding free carriers, as has been suggested by Kröger and De Nobel.[7] We may conclude then that the effective mass of both electrons and holes decreases with increasing atomic number of the corresponding cation or anion.

We may also tentatively conclude that the effective mass of holes is greater than the effective mass of electrons in all II–VI compounds, with the possible exception of ZnTe.

The reasoning which has been presented here based on conductivity and photoconductivity processes is directly analogous to that presented by Klasens[15] from the point of view of luminescence. One need only realize that the same type of centers are called by different names according to the field involved.[16] Klasens discussed how luminescence emission and trap depths varied in the solid solutions ZnCdS and ZnSSe. In going from ZnS to CdS through ZnCdS, the luminescence emission undergoes a continuous shift (only one S type of emission center present), whereas the trap depths show the presence of both Zn type and Cd type centers. On the other hand, in going from ZnS to ZnSe through ZnSSe, the trap depths show a continuous shift (only one Zn type of trapping center present), whereas evidence of emission from both S type and Se-type emission centers is found.

## SUMMARY

Photosensitive crystals of ZnSe have been prepared from the vapor phase with incorporation of Group VII donors and either Group I or Group V acceptors. The general photoconductivity characteristics of ZnSe are identical with those previously reported for CdS and CdSe. Temperature quenching of photoconductivity, a variation of photocurrent with a power of light intensity greater than unity in the temperature range of temperature quenching, and infrared quenching of photoconductivity at temperatures below the onset of temperature quenching, are all present.

The levels associated with the sensitizing centers for photoconductivity in ZnSe:Br:Cu and ZnSe:Br:Ag were found to lie 0.6 ev above the top of the valence band, the same location as previously found for the sensitizing levels in CdSe crystals. Two sets of levels are found in photosensitive ZnSe:Br:Sb and ZnSe:Br:As crystals, one at about this same location, and a second lying 1.3 ev above the top of the valence band. The double set of levels found in ZnSe with Group V acceptors is very similar to that previously ascribed to double vacancy ionization in annealing-sensitized CdSe crystals. The high-lying acceptor levels provide photoresponse out to about 1.4 microns.

A consistent picture of donor and acceptor levels in II–VI photoconductors can be developed by considering donor ionization energies to be primarily determined by the cation of the compound, and acceptor ionization energies to be primarily determined by the anion of the compound. This viewpoint correlates observations in semiconductivity, photoconductivity, and luminescence.

---

[15] H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953).

[16] Cation-determined levels near the conduction band are alternatively called coactivator, electron trap, desensitizing, donor, or recombination levels; anion-determined levels near the valence band are alternatively called luminescence, poison, sensitizing, hole trap, acceptor, or recombination levels.