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Properties of Cadmium Sulfide Crystals with High Impurity Concentrations*

RICHARD H. BUBE,† EDWARD L. LIND,‡ AND ARTHUR B. DREEBEN
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

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Photoelectronic properties have been measured for cadmium sulfide single crystals with 10^{18} to 10^{20} cm^{-3} iodine, and copper, silver, or gold impurities. Highly photosensitive crystals with broad spectral response have been prepared from the vapor phase by chemical transport. The hypothesis that electrical and luminescence properties are to be associated with the specific acceptor impurity, whereas the photosensitivity is to be associated with other defects, such as cation vacancies, is supported by the following observations. (1) The thermal hole-ionization energy of sensitizing centers decreases with increasing impurity concentration, but the optical electron-ionization energy from copper centers does not change. (2) The optical electron-ionization energy from silver and gold centers is appreciably greater than that from copper centers, but the thermal hole-ionization energy of sensitizing centers is about the same for all three acceptors.

INTRODUCTION

A DECREASE in the hole-ionization energy of sensitizing centers with increasing impurity concentration has been observed in photoconducting powders of CdS:Ga:Cu.[1] A series of such powders were prepared with a Cu concentration slightly greater than the Ga concentration, and varying from 4×10^{17} to 2×10^{20} cm^{-3}. Decreases in the hole-ionization energy of sensitizing centers were measured for concentrations greater than 4×10^{18} cm^{-3}, either by the appearance of a region of supralinear photoconductivity at room temperature or by the shift of the temperature for thermal quenching of photoconductivity to lower temperatures. The data obtained in this way can be fit by an expression of form

$$E_T = 0.92 - 9\times10^{-8} N_I^{1/3} \text{ eV}, \tag{1}$$

which plots as indicated in Fig. 1. Here, E_T is the thermal hole-ionization energy, and N_I is the total impurity concentration. An expression with the functional relationships of Eq. (1) can be derived in a variety of simple ways, as for example, by considering the electrostatic interaction between a positively charged ion and a negatively charged acceptor to which a hole is bound. The potential energy of a hole located at a distance r from a negatively charged ion is decreased by the presence of a positively charged ion located at a distance of r' from the negatively charged ion. Under the assumptions that $r' \propto N_I^{-1/3}$ and that $r \ll r'$, the ionization energy is given by

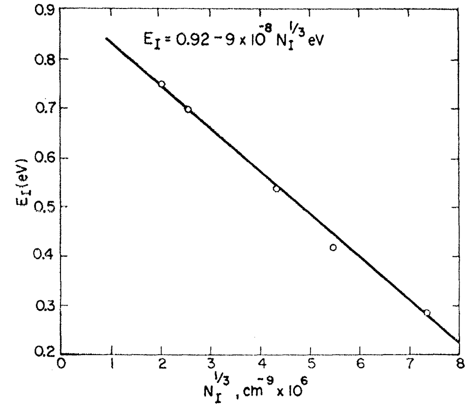

FIG. 1. Thermal hole-ionization energy of sensitizing centers in CdS:Ga:Cu photoconducting powders as a function of the 1/3 power of the total impurity concentration. Data are taken from reference 1.

$$E_T = E_0 - (e^2/K) N_I^{1/3}, \tag{2}$$

where $E_0 = e^2/Kr$ and K is the dielectric constant.

The problem of interactions between ionized impurities and mobile carriers has been treated by Harvey[2] using the Debye-Hückel theory of strong electrolytes. An expression is obtained with one adjustable parameter a indicated by the theory to be the distance of closest approach between the two interacting species:

$$E_T = E_0 - (e^2/K)[A N_I^{1/2}/1 + aA N_I^{1/2}], \tag{3}$$

where $A = [(4\pi e^2)/(KkT)]^{1/2}$. The dependence of E_T on N_I predicted by Eq. (3) is essentially indistinguishable from that of Eqs. (1) or (2). Since, however, it assumes basically that the interacting species are mobile, it can be applicable to the problem of interacting charged ions only at the high temperature of formation. Using the temperature of powder firing for T in the expression for A, it is not possible to obtain a fit to the data with positive a. The difficulty may lie in the fact that the possible ionic positions in the electrolyte theory are virtually unlimited, whereas they are limited to crystal sites in the solid, a limitation which becomes important particularly for high impurity concentrations.

This type of reasoning might be profitably extended to provide a better description of the results, *if* the basic assumption is reliable, i.e., if the sensitizing centers measured through photoconductivity are indeed the same as the acceptor impurity centers, the concentra-

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† Present address: Stanford University, Stanford, California.

‡ Present address: Harshaw Chemical Company, Solid State Division, Cleveland, Ohio.

[1] R. H. Bube and A. B. Dreeben, Phys. Rev. **115**, 1578 (1959).

[2] W. W. Harvey, Phys. Rev. **123**, 1666 (1961).

tion of which is being varied. If, on the other hand, the sensitizing centers were to be associated with a third type of imperfection, the density of which is only indirectly connected with the concentrations of donor and acceptor impurities being incorporated, a somewhat different and more complex problem would exist. It was to answer this question, as well as to determine more precisely the nature of the effects observed in powders, that single crystals of cadmium sulfide were grown with high impurity concentrations. The results indicate that the variation of hole-ionization energy of sensitizing centers with impurity concentration is quite similar in single crystals to that found in powders, and that it is most probable that these sensitizing centers are associated with cation vacancies and not directly with the incorporated acceptor impurities. Several other problems, such as the change in the spectral response of photoconductivity with impurity concentration, and the effects of incorporating copper or silver without a compensating donor, are also elucidated by the single crystal investigation.

EXPERIMENTAL

The crystals described in this paper were grown from the vapor phase by the method of chemical transport,[3–5] combined with a horizontal Bridgman arrangement in which the crystal growth is controlled by slow motion through a sharp temperature gradient. Large rectangular parallelepipeds of typical dimensions 7×5×2 mm^3 were cut from larger boules. Iodine was used as the transport agent and as the donor incorporated in the crystals. To incorporate the acceptors, Cu_2S, Ag_2S, or Au_2S was co-transported with the CdS. Reasonably good control over the concentration of acceptor in the grown crystal could be exercised by the proportion of acceptor added to the original CdS. The actual concentrations used in the preparation of measured crystals are given in the data summary of Table I. The kinetics associated with the pertinent transport equilibria, e.g.,

$$CdS+I_2 \rightleftharpoons CdI_2+S, \tag{4a}$$

$$Cu_2S+I_2 \rightleftharpoons Cu_2I_2+S, \tag{4b}$$

appear to be sufficiently similar so that the incorporated copper and iodine impurities are homogeneously distributed throughout the crystal. Insulating crystals are obtained over the whole range from 10^{18} to 10^{20} cm^{-3} Cu, indicating that the crystals grow in such a way as to produce almost complete compensation of iodine donors.

For electrical measurements, ohmic contacts of melted indium were applied to the crystals and temperature variations were made in a cryostat in which the crystals were surrounded by an inert atmosphere of dry helium. Monochromatic radiation was obtained with a Bausch & Lomb grating monochromator, using neutral wire-mesh filters to vary the light intensity.

TABLE I. Summary of ionization energies.

Crystal type	% Metalous sulfide used	Impurity	mg/ml I_2 used	E_I, eV[a]	E_T, eV[b]
Dendrite	0.01	Cu	0.5	2.2	High conductivity
Lsc[c]	0.01	Cu	5	1.63	1.17
Lsc	0.01	Cu	5	1.69	···
Lsc	0.05	Cu	1	1.77	High conductivity
Lsc	0.05	Cu	1	1.80	1.07
Needles	0.05	Cu	0.4	···	0.93
Needles	0.05	Cu	0.4	···	0.97
Dendrite	0.1	Cu	0.5	1.6	0.88
Needles	0.1	Cu	0.5	···	0.90
Lsc	0.1	Cu	5	1.73	0.72
Lsc	0.1	Cu	5	1.73	0.74
Lsc	0.1	Cu	5	···	0.72
Lsc	0.1	Cu	5	···	0.77
Lsc	0.3	Cu	5	1.73	0.59
Lsc	0.3	Cu	5	1.73	0.58
Dendrite	1.0	Cu	0.5	1.7	0.66
Lsc	1.0	Cu	5	···	0.50
Lsc	1.0	Cu	5	1.65	0.64
Lsc	1.0	Cu	5	1.62	0.60
Lsc	1.0	Cu	0	1.21	···
Lsc	0.1	Ag	5	1.96	0.78
Lsc	0.1	Ag	5	2.02	···
Lsc	0.1	Ag	5	2.01	···
Lsc	1.0	Ag	0	<1.0	···
Lsc	0.1	Au	5	2.01	>0.92
Lsc	0.1	Au	5	1.96	···
Lsc	0.1	Au	5	1.96	···

[a] Optical electron-ionization energy from absorption data.
[b] Thermal hole-ionization energy from photoconductivity data.
[c] Large single crystal.

RESULTS

General

As indicated in the summary of Table I, a series of CdS:I:Cu crystals with proportions of Cu_2S of 0.01, 0.05, 0.1, 0.3, and 1.0%, CdS:I:Ag crystals with proportions of Ag_2S of 0.1%, and CdS:I:Au crystals with proportions of Au_2S of 0.1% were investigated. In addition, crystals of CdS:Cu with 1.0% Cu_2S and crystals of CdS:Ag with 1.0% Ag_2S were grown by sublimation in the absence of iodine donors.

All of the CdS:I:Cu, CdS:I:Ag, and CdS:I:Au crystals, with the possible exception of a few crystals with the lowest acceptor concentrations, were insulating highly photosensitive crystals. Typical dependence of dark conductivity on temperature for two of the CdS:I:Cu crystals is shown in Fig. 2. An activation energy of 0.41 eV is indicated, corresponding to deep donors; this is an ionization energy frequently encountered in compensated initially high-conductivity CdS crystals. The specific sensitivity of the compensated crystals, below the temperature of thermal quenching, was of the order of 1 to 10 cm^2/Ω-W. Hall

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[3] R. Nitsche, J. Phys. Chem. Solids **17**, 163 (1960).

[4] R. Nitsche, H. U. Bölsterli, and M. Lichtensteiger, J. Phys. Chem. Solids **21**, 199 (1961).

[5] J. A. Beun, R. Nitsche, and H. U. Bölsterli, Physica **28**, 184 (1962).

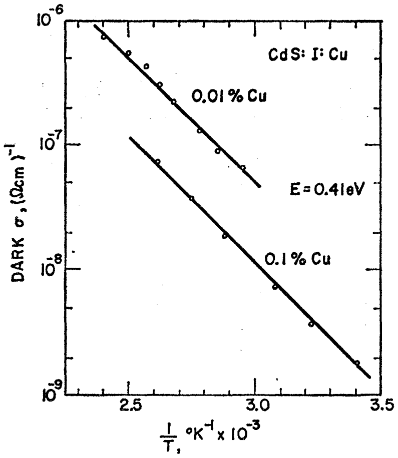

FIG. 2. Dark conductivity vs temperature for CdS:I:Cu crystals.

effect measurements on a typical CdS:I:Cu(0.1) crystal confirmed the *n*-type nature of the photoconductivity and gave an electron mobility of 96 cm^2/V-sec.

Crystals grown by sublimation in the absence of iodine donors and of acceptor impurities regularly come out high-conductivity *n* type because of nonstoichiometry. It is expected, therefore, that even when CdS:Cu or CdS:Ag crystals are grown in this way without intentionally added donor impurities, some degree of compensation will occur and high-resistivity crystals may result. Such high-resistivity crystals with photosensitivity were obtained in the case of the CdS:Ag preparation and for a certain region of the CdS:Cu boule with clearly less Cu (by measurement of transmission) than the remainder of the boule. This remainder of the CdS:Cu boule showed a dark conductivity of 10^{-3} mho/cm with no detectable photosensitivity. No detectable Hall voltage could be found for this crystal, indicating a mobility less than about 5 cm^2/V-sec, but the circumstances as described suggest that it might well be *p* type.

Photoconductivity vs Light Intensity

The dependence of photoconductivity on light intensity at room temperature is shown in Fig. 3 for both 0.01% and 0.1% Cu. The crystal with 0.01% Cu shows a nearly linear dependence of photoconductivity on light intensity over the whole range of measurements, and indeed begins to show the onset of supralinearity only at the lowest light levels when the temperature is raised as high as 418°K. Supralinearity becomes quite important over most of the measurable range for the crystals with 0.1% Cu.

The large dimensions of the crystal permit, in addition, the distinction between back-surface and front-surface illumination shown in Fig. 3. Electrodes are applied to one of the large flat faces of the crystal; when this face is opposite to that exposed to illumination, the excitation condition is called back-surface, whereas when this face is illuminated directly, the excitation condition is called front surface. It is found that curves closely similar to that given by back-surface excitation by white light are given by excitation by $\lambda > 7000$ Å in the front-surface condition; also that curves closely similar to that given by front-surface excitation by white light are given by front-surface excitation by light with wavelength λ such that $5100\text{ Å} < \lambda < 7000\text{ Å}$. This behavior is explainable as soon as it is realized that there is strong impurity absorption, particularly in the crystals with higher Cu concentration, between 5100 and 7000 Å. Thus, when white light is used in front-surface excitation, the major contribution to the photocurrent comes from wavelengths between 5100 and 7000 Å which are absorbed in only a small fraction of the total volume. When white light is used in back-surface excitation, only the 7000 Å or greater wavelengths can penetrate throughout the volume to produce photoconductivity. Since the onset of supralinearity with decreasing light intensity occurs at the same position of the steady-state electron Fermi level in all cases, hence at the same conductivity, it must occur at a lower photocurrent when this photocurrent is confined to a small volume of the crystal. The data indicate that photocurrents generated by light with wavelength between 5100 and 7000 Å are confined to about 5% of the volume in this particular crystal.

Spectral Response

Another way of looking at the same differences caused by the variation of absorption with wavelength is to examine the spectral response of photoconductivity. The difference between front- and back-surface excitation is relatively small for a 0.01% Cu crystal,

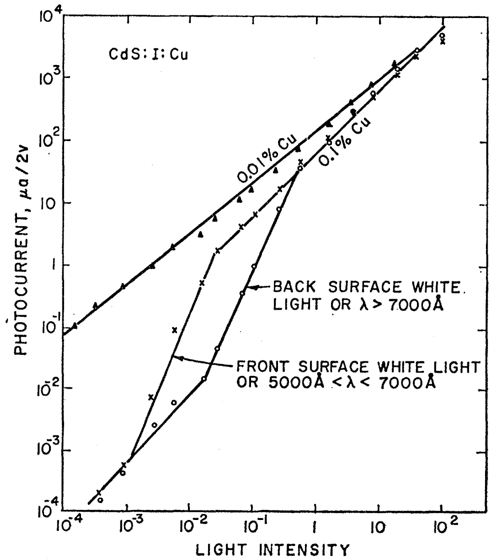

FIG. 3. Photocurrent vs light intensity for CdS:I:Cu crystals.

because of its lower impurity absorption, as indicated by the spectral response curves of Fig. 4. The strong effect previously described for the 0.1% Cu crystal is shown by the spectral response curves of Fig. 5.

Absorption

Transmission measurements were made for many of the crystals involved in this investigation. Approximate values of absorption constant for two crystals of 0.01% Cu and two crystals of 0.1% Cu are given in Fig. 6. The results agree with the observation that the photoconductivity spectral response of the 0.01% Cu crystals extends to longer wavelengths than that of the 0.1% Cu crystals. The energy corresponding to the principal impurity absorption may be obtained from curves like those of Fig. 6 by plotting α^2 vs photon energy, under the assumption that a direct optical transition from compensated Cu centers to conduction band is involved; energies obtained in this way are essentially the same as energies obtained from extrapolation of I_0/I transmission data back to unity. Values of these energies are listed in Table I as E_I.

The measured value of the absorption constant for the 0.1% Cu crystals in the region of impurity absorption is about 120 to 150 cm^{-1}. If we take the photoconductivity data with its information that photocurrents generated by impurity absorption are confined to about 5% of a 1.2-mm thick crystal, and if we take the absorption constant to be approximately equal to the reciprocal of this reduced thickness, a value of $\alpha = 170$ cm^{-1} is obtained. Analysis of this particular crystal[6] indicated that the Cu concentration was 2×10^{19} cm^{-3}, which combined with an absorption cross-section of 10^{-17} cm^2 would predict $\alpha = 200$ cm^{-1}. The three ways of obtaining the absorption constant are in reasonably good agreement.

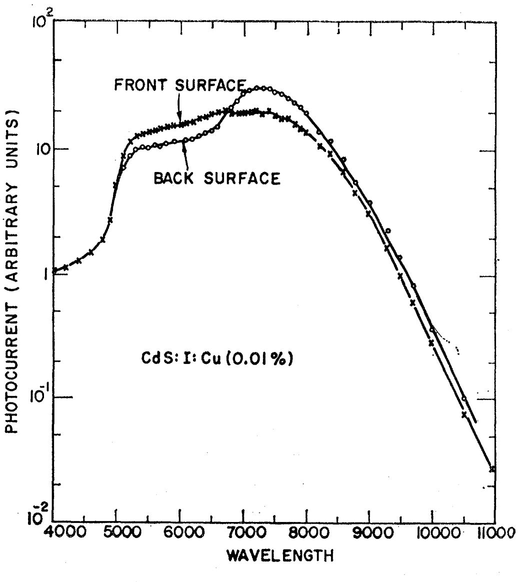

FIG. 4. Spectral response curves of photoconductivity for CdS:I:Cu crystal prepared with 0.01% Cu$_2$S.

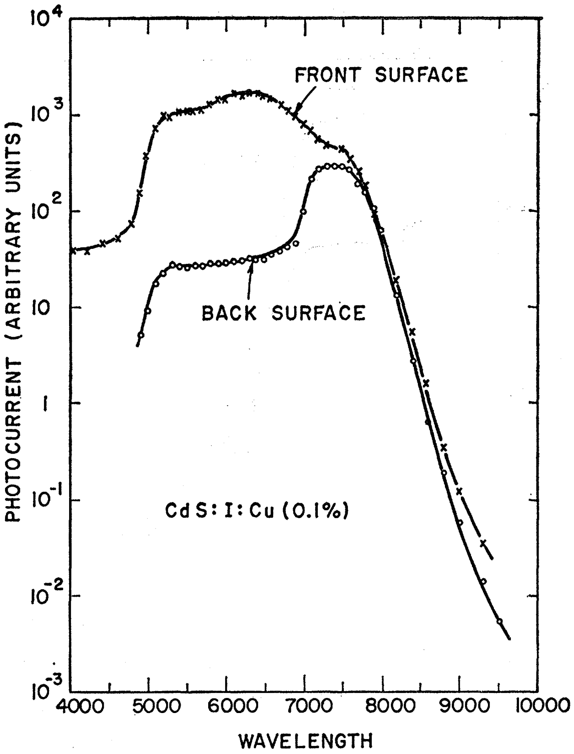

FIG. 5. Spectral response curves of photoconductivity for CdS:I:Cu crystal prepared with 0.1% Cu$_2$S.

If the high-energy absorption is to be associated with the Cu impurity, the problem remains as to the cause of the long-wavelength absorption tail. An absorption constant of unity is not reached by the 0.01% Cu crystals until the photon energy drops below 1.2 eV, whereas the absorption constant for the 0.1% Cu crystals reaches unity when the photon energy drops below 1.6 eV. If the location of the energy level from which the absorption transition is made is related to these terminal energies, it would indicate that the transition is made from a level about 1.2 eV above the valence band in 0.01% crystals and from a level 0.8 eV above the valence band in 0.1% crystals. This is in good numerical agreement with the location of the energy levels for the sensitizing centers in these crystals, as listed in Table I under E_T. An absorption constant of unity would correspond to a density of about 10^{17} cm^{-3}, a reasonable density for these centers. In addition, it may also be noted that the wavelengths in the spectral response spectra at which the response has decreased to 1% of its peak value agree for both the 0.01% Cu and 0.1% Cu crystals with the wavelengths at which $\alpha = 1$ cm^{-1} is observed.

The transmission of the CdS:Cu crystal is quite different from that of the compensated crystals. I_0/I transmission data for the same crystal polished to three thicknesses are given in Fig. 7. In addition to some

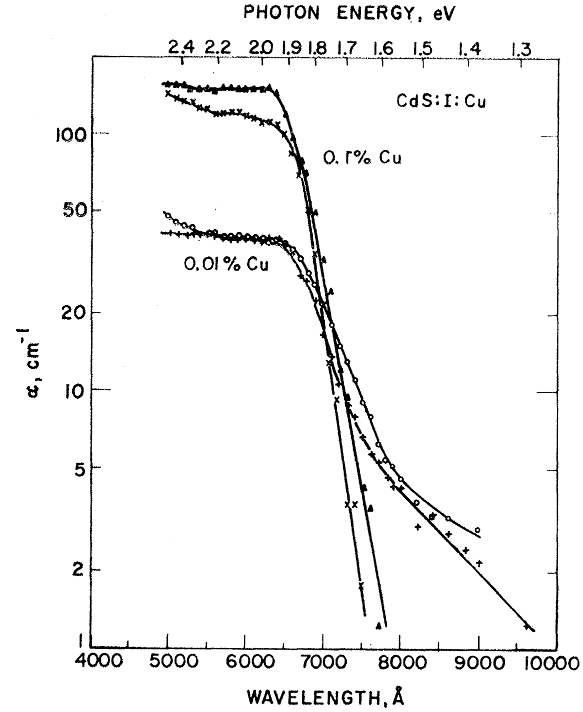

FIG. 6. Absorption spectra for two CdS:I:Cu crystals prepared with 0.01% Cu_2S and for two crystals prepared with 0.1% Cu_2S.

evidence for compensated-Cu absorption between 5100 and 7000 Å, there is strong absorption out to 10 000 Å. A new type of center or complex exists when CdS crystals are grown with only Cu present. The transmission of the CdS:Ag crystals showed a broad structureless absorption beyond 5100 Å and extending at least to 12 000 Å, the limit of the range investigated.

Determination of Thermal Hole-Ionization Energies

Listed in the final column of Table I are the values of E_T, the thermal hole-ionization energy of sensitizing centers. These values are determined from the location of the hole demarcation level at the onset of supralinearity with decreasing light intensity at fixed temperature, or at the onset of thermal quenching of photoconductivity with increasing temperature at fixed light intensity. Actually, the steady-state electron Fermi level is determined from the measurements of conductivity and temperature, and the location of the hole demarcation level relevant to the sensitizing centers is determined

$$E_{dp}=E_{fn}+kT\ln(S_p/S_n), \qquad (5)$$

where E_{dp} is the height of the hole demarcation level above the valence band, $E_{dp}=E_T$ at the onset of supralinearity or thermal quenching, E_{fn} is the depth of the electron Fermi level below the conduction band, S_p is the capture cross section of the sensitizing centers for holes, and S_n is the subsequent capture cross section of the sensitizing centers for electrons. The use of these relationships is the same as that described in the previous publication dealing with CdS:Ga:Cu powders[1] and need not be repeated here.

A survey of the values of E_T given in Table I indicates that there is some influence of the I_2 concentration on the measured values. In general, however, there is a continuous decrease in E_T with increasing Cu concentration, and hence presumably with increasing iodine concentration also, since close to complete compensation is maintained. It is well known that the proportion of halide incorporated in Group II sulfides as compensated donors is a function of the concentration of Group I acceptors being incorporated at the same time.[7]

Equation (5) indicates that, for phenomena occurring at a fixed value of E_{fn}, an apparent decrease in E_{dp} would be caused if the cross-section ratio were to decrease because of interaction. The cross-section ratio, however, is intimately associated with the measured photosensitivity and the photosensitivity of all crystals measured is comparable before supralinearity or thermal quenching sets in. A value of $S_p/S_n=10^6$, based on previous work,[8] is used throughout.

There is little difference between the values of E_T for 0.3 and 1.0% Cu, and this may indicate an upper limit to the concentration of Cu and I which can be in-

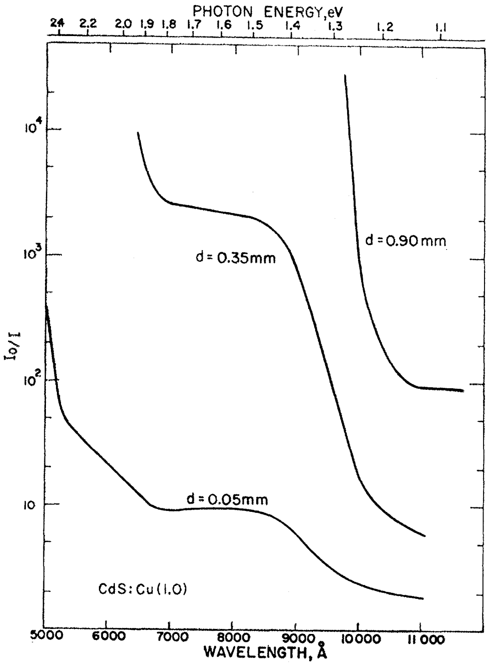

FIG. 7. Ratio of incident to transmitted intensity vs wavelength for a CdS:Cu crystal prepared with 1.0% Cu_2S and no donor impurities.

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[6] Spectrochemical copper analysis by S. Adler and B. L. Goydish.
[7] R. H. Bube, J. Chem. Phys. 19, 985 (1951).
[8] R. H. Bube, J. Phys. Chem. Solids 1, 234 (1957).

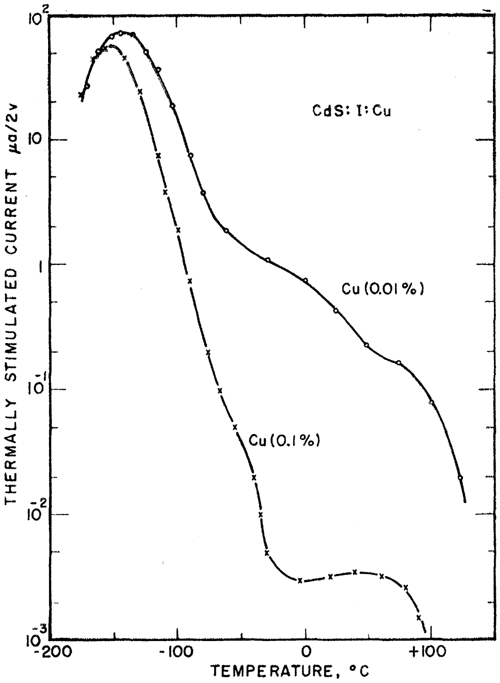

FIG. 8. Thermally stimulated current curves for a CdS:I:Cu crystal prepared with 0.01% Cu_2S and for a crystal prepared with 0.1% Cu_2S.

corporated under these conditions of crystal growth. The onset of the phenomena involved, however, becomes much less abrupt for the 1.0% Cu crystals, indicating perhaps a distribution of E_T values.

Trapping Distribution

A monotonic trap distribution has been previously reported for CdS:I:Cu crystals of this type.[9] Similar behavior was found for the large single crystals of the present investigation, and typical curves for 0.01% Cu and 0.1% Cu crystals are shown in Fig. 8. The curve for the 0.01% Cu crystal has essentially a constant electron lifetime throughout its entire range, but the curve for the 0.1% Cu crystal is affected by the decrease in electron lifetime associated with thermal quenching which sets in at about −40°C. Definite structure is observed superposed on the monotonic distribution found for these crystals. The distribution found for the 0.01% Cu crystal indicates 5×10^{17} cm^{-3} traps with depth of 0.15 eV, 6×10^{14} cm^{-3} traps with depth of 0.40 eV, and 2×10^{14} cm^{-3} traps with depth of 0.58 eV. The distribution found for the 0.1% Cu crystal indicates 2×10^{17} cm^{-3} traps with depth of 0.14 eV, and 5×10^{15} cm^{-3} traps with depth of 0.63 eV, no attempt being made in this case to separate out the intermediate trap.

In spite of the fact that the total density of traps in CdS:I:Cu(0.1) crystals is several times 10^{17} cm^{-3}, the form of the distribution is such that the density of traps effective for room temperature operation is three to four orders of magnitude less than this. Improved speed of response for low-level excitation intensities (of the order of mft-c), as compared to standard CdS:Cl:Cu (0.001) crystals, is achieveable, therefore, particularly in those crystals which exhibit supralinearity at low light intensities. When the excitation is turned off, not only are electrons freed from traps, but also holes are freed from sensitizing centers, thus decreasing the free-carrier lifetime for the freed electrons and effectively shortening the decay time.[8] CdS:I:Cu crystals with 0.05% and 0.1% Cu were shown to exhibit improvements in photoconductivity performance for low-intensity excitation at room temperature by factors up to 75 compared to standard CdS:Cl:Cu crystals.

DISCUSSION

In order to discuss the main trends of the data obtained in this investigation, the average energy values of E_I and E_T from Table I have been summarized in Table II. Values of (E_G-E_I) are also included, where E_G is the band gap, taken as 2.40 eV for CdS. The value of (E_G-E_I) gives the height of the impurity acceptor level above the valence band before excitation; this is to be compared with E_T, the height of the sensitizing center level above the valence band after excitation.

The values of E_T obtained from single crystals may be compared with values obtained from CdS:Ga:Cu powders.[1] To do this quantitatively a somewhat more realistic value for the absorption must be assumed than was previously done for the powders, for which an effective penetration distance of only 1μ was assumed. Using the absorption information obtained in this investigation, the powder data give $E_T=1.18$ eV for a Cu concentration of 10^{17} cm^{-3}. This is in good agreement with the unperturbed value of E_T found for low impurity concentrations in single crystals. Data obtained from optical quenching of photoconductivity in CdS[10] also consistently indicate that the sensitizing centers lie 1.1 eV above the top of the valence band.

As mentioned previously, a detailed analysis of the 0.1% Cu crystals revealed a Cu concentration of 2×10^{19} cm^{-3}. For this concentration in the CdS:Ga:Cu powders, a value of $E_T=0.71$ eV is obtained when the calculation is made assuming an effective penetration

TABLE II. Average values of ionization energies.

Impurity	Impurity concentration, %	E_I, eV[a]	(E_G-E_I), eV	E_T, eV[b]
Cu (compensated)	0.01	1.66	0.74	1.17
	0.05	1.78	0.62	0.99
	0.1	1.73	0.67	0.74
	0.3	1.72	0.68	0.58
	1.0	1.64	0.76	0.55
Cu (uncompensated)	1.0	1.21	(1.19)	...
Ag (compensated)	0.1	2.00	0.40	0.78
Ag (uncompensated)	1.0	<1.0	...	...
Au (compensated)	0.1	1.98	0.42	>0.92

[a] Optical electron-ionization energy from absorption data.
[b] Thermal hole-ionization energy from photoconductivity data.

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[9] R. H. Bube, J. Appl. Phys. 32, 1621 (1961).

of the light in the powders corresponding to $\alpha=100$ cm^{-1}. This is in good agreement with the value of $E_T=0.74$ eV found for the CdS:I:Cu single crystals.

The present investigation adds several more pieces to a body of information on the nature of acceptor impurities and sensitizing centers in II-VI compounds, which has been growing for some time. The indicated conclusion of this evidence is that electrical and luminescence properties are associated with the acceptor impurity directly, but that sensitizing centers for photoconductivity are a separate species of imperfections, most likely cation vacancies. This evidence can be summarized as follows.

(1) High-conductivity II-VI compounds, e.g., CdS:I crystals, in which only donor halogen impurities have been incorporated, are usually highly photosensitive.[11] Because of the high dark conductivity the relative change in conductivity with excitation may be quite small, but the absolute change in conductivity is as large as that in the most sensitive crystals prepared by any technique. The sensitivity of these crystals requires the presence of centers which will capture photo-excited holes, but will then have a small cross-section for the capture of photo-excited electrons. The substitution of I for S in CdS, for example, can occur in one of two ways: (a) either by formation of a donor center with resulting high conductivity, or (b) by formation of a Cd vacancy for every two substitutions of I for S. The second of these two processes naturally introduces into the crystal exactly that type of negatively charged center which can act as a sensitizing center for photoconductivity. The introduction of Cu acceptors into such high-conductivity crystals reduces the dark conductivity, but there is no evidence that the incorporation of Cu has any effect on the photosensitivity except to decrease it.

(2) Highly photosensitive insulating crystals of CdS can be grown by introducing just a trace of halogen such as iodine in the preparation.[11]

(3) Measurements of spectral response[12] and of values of E_T for *low* concentrations of Cu and Ag as acceptors in CdS:Cl crystals reveal no differences between the two different acceptors. This is in clear distinction to the marked difference between these two impurities on the luminescence properties of CdS and ZnS, the luminescence emission transition being shifted by about 0.5 eV to higher energies for Ag impurity in both CdS and ZnS.

(4) Measurements of E_T in crystals of CdSe without added impurity, and with Cu and Ag compensated acceptors, indicate a single value of 0.6 eV regardless of the nature of the acceptor imperfection.[13]

(5) Measurements of the shape of the absorption spectra associated with Cu in CdS:I:Cu crystals in the present study indicate that it is the long-wavelength tail which is associated with absorption by sensitizing centers, whereas the absorption due to the Cu centers terminates by as much as 0.5 eV to higher energies.

(6) Optical quenching of photoconductivity in CdS crystals reveals the same level structure regardless of the type of acceptor impurity present, or in the absence of any added acceptor impurity. As a clear example of this fact, consider the crystal of CdS grown in this research with 1.0% Ag_2S and no added donors. The crystal was high resistivity in the dark and was fairly photosensitive with spectral response maximum at the absorption edge of CdS. The optical quenching spectrum showed the typical CdS form: a broad band terminating in an edge at 1.1 eV plus a narrow band with maximum at about 0.9 eV. This is the same quenching spectrum which has been measured for every photosensitive CdS crystal ever tested. The only exceptions are those crystals in which quenching could not be observed because of the extension of excitation to long wavelengths overlapping and overwhelming the quenching effect.

(7) As the concentration of impurity in the CdS:I:Cu crystals of the present study is varied, the value of E_I remains unchanged, whereas the value of E_T decreases by 0.6 eV. If the Cu centers were also the sensitizing centers, then (E_G-E_I) would represent the height of the Cu level above the valence band in the unexcited state, and E_T would represent the height of the Cu level above the valence band in the excited state. The difference, $E_T-(E_G-E_I)$, should represent the energy change in the level corresponding to readjustment of the surrounding ions as a result of the excitation. For low impurity concentrations the values of E_T and (E_G-E_I) do not violate this concept. The fact that (E_G-E_I) does not change with increasing impurity concentration, while E_T does, could at least formally be explained by proposing that the effect of impurity interaction was to decrease the readjustment energy. But at high impurity concentrations, this picture would lead to the conclusion that the unexcited level lies *higher* than the excited level.

(8) Although the location of the unexcited impurity level lies about 0.3 eV further from the conduction band for Ag and Au impurities than for Cu impurity, as evidenced by obvious differences in absorption and spectral response of photoconductivity in the *high* impurity range, the values of E_T appear to be essentially the same for all three impurities.

It may be concluded, therefore, that in the systems to which the above discussion is pertinent, the role of the acceptor impurity is an electrical one, i.e., it decreases the dark conductivity of an *n*-type crystal, and probably also a luminescence one, i.e., it serves as the ground state for a luminescence transition; the seat of

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[10] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 349.

[11] R. H. Bube and L. A. Barton, RCA Rev. **20**, 564 (1959).

[12] See reference 10, p. 166.

[13] E. H. Stupp, Bull. Am. Phys. Soc. **7**, 173 (1962).

photosensitivity, however, appears to lie in other centers, probably cation vacancies. As long as the acceptor impurities are present in a compensated state, they apparently have only a slight deleterious effect on the photosensitivity; if the acceptor concentration exceeds the donor concentration, however, the photosensitivity decreases rapidly, indicating that the uncompensated acceptors are effective recombination centers.

A contributing factor to the uncertainty which surrounds this area is undoubtedly the fact that the excited level for the Cu impurity center itself, as estimated from the luminescence emission energy of 1.23 eV,[14] is very close in location to the excited level for the cation vacancy in crystals with low impurity concentration.

The crystal of CdS:Cu prepared with uncompensated Cu showed a different absorption with $E_I = 1.21$ eV. This cannot be the absorption from an uncompensated Cu center itself, for the level of such a center must lie further from the conduction band than the level of the compensated center. Indeed, Avinor[14] has found evidence of a level 2.13 eV below the conduction band associated with uncompensated Cu. Avinor[14] has also identified a level lying 1.38 eV below the conduction band which he finds for high concentrations of In and Cu in CdS:In:Cu crystals; he has tentatively associated this level with a complex consisting of an In and an interstitial Cu. It is unlikely that this level is the one observed in the present investigation, both because of the difference in energies, and because of the absence of donor impurities in our crystals. On the other hand, an absorption edge of 1.2 eV agrees reasonably well with that for Cu_2S,[15] considered as a second phase distributed throughout the crystal. Such a conclusion would also be consistent with the relatively high, probably *p*-type, conductivity, and with the absence of a measurable Hall voltage which might well be shorted out by conducting regions of Cu_2S. The transmission data on the CdS:Ag crystal is also consistent with the inclusion of Ag_2S with band gap of about 0.9 eV.

CONCLUSIONS

Highly photosensitive crystals of CdS with iodine donors and copper, silver, or gold acceptors in concentrations of 10^{18} to 10^{20} cm^{-3} can be grown with a broad spectral response. The hole-ionization energy of sensitizing centers in these crystals is controllable through the impurity concentrations used, and hence a variety of photoconductivity characteristics can be changed at will.

A consideration of the optical and photoelectronic data of the present investigation, together with the results of the past, indicate that the sensitizing centers are not associated with the acceptor impurities in any direct way but are a separate species, probably cation vacancies. The reduction in the hole-ionization energy of these centers with increasing impurity concentration can be considered as the result of the electrostatic interaction of positively charged donor centers on the negatively charged vacancies. Although increasing the impurity concentration increases the concentration of both positive donor and negative acceptor impurities, the net effect will be a reduction in the hole-ionization energy of the negatively charged vacancies, as positively charged donor impurities are preferentially located nearer than negatively charged acceptor impurities. The electrical and luminescence properties of these same crystals, on the other hand, are associated with the particular acceptor impurity.

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[14] M. Avinor, thesis, University of Amsterdam, 1959 (unpublished).

[15] L. Eisenmann, Ann. Phys. (New York) **10**, 129 (1952).