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Internal Photoeffect and Exciton Diffusion in Cadmium and Zinc Sulfides*

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The spectral response of photoconductivity of ZnS and CdS for both single-crystal and sintered-powder samples was measured for several distances between the area of illumination and the electrode region. The energy transport process for indirect illumination was studied by measuring the photocurrent pulses produced by high-intensity light flashes and by experiments with light transmission and electric fields. These studies demonstrate energy transport by electrically neutral entities other than photons, which we interpret as diffusion of excitons or mobile electron-hole pairs.

This indirect or transfer photocurrent occurs predominantly at frequencies below the absorption edge of the crystal, with the detailed response being sensitive to the impurity content of the samples. The diffusion parameters in this region generally lie in the following range: lifetime $\tau=10^{-4}$ to 10^{-6} sec, diffusion constant $D=10^3$ to 10^4 cm^2/sec, and diffusion length $L=0.1$ to 1 cm.

The transfer photocurrent for steady illumination shows a nearly linear dependence on the incident light intensity. The slow decay of the photocurrent indicates that trapping processes are important in the photocurrent mechanism. Measurement of photocurrent pulses for flash illumination shows a greater than linear dependence on intensity, indicating a second-order or bimolecular process. A proposed mechanism for the transfer photoeffect involves initial absorption of the light with creation of an exciton, which diffuses to a trap in the lattice. A second exciton reaching the trap then dissociates, using energy transferred from the trap.

INTRODUCTION

OPTICAL absorption measurements on nonmetallic crystals are of primary importance in elucidating their electronic energy-band structures. Photoconductivity studies yield additional information on the nature of the excited states. In the present work, the absorption spectra of CdS and ZnS and the photoconductivity produced by illumination at a distance from the electrodes were studied to determine the mechanisms of photon-electron interaction and energy transport in these materials.

The one-electron approximation in the quantum theory of solids leads to the familiar energy-band representation of the electronic states of a crystal. Normal, nonconducting crystals, having a filled valence band and an empty conduction band, are transparent at frequencies up to the absorption edge which corresponds to a transition from the highest occupied band to the lowest empty band. However, a weak, low-frequency tail below the characteristic absorption region may arise from lattice disturbances which allow violation of selection rules and also add their own impurity spectrum.

The description that an electron is transferred into a conduction band implies that the electron and hole are definitely separated, i.e., ionized, and can move independently of each other. However, the electron and hole carry opposite charges and will therefore attract each other in nonconductors even at considerable distances. Thus non-ionized, excited states can occur which may either be localized or diffuse through the lattice before returning to the ground state. The latter case has been designated an exciton state by Frenkel.[1]

Previous Experimental Evidence for the Existence of Excitons

The fundamental absorption bands for a number of crystals have recently been shown to possess a fine structure. Thus a complex spectrum has been observed[2] at low temperature for CdS. Gross and co-workers suggested that these transitions, or some of them, are characteristic of the pure crystal and may be interpreted as exciton production.

In their study of the relation between absorption spectra and the spectral distribution of the internal photoelectric effect, they show[3] that the photocurrent spectrum of CdS depends upon the orientation of the crystallographic axis with respect to the direction of propagation and polarization of the incident light. Comparison of photoconductivity spectra with absorption spectra shows that the frequencies of the narrow photocurrent maxima coincide very closely with those of the absorption bands. If the origin of these absorption bands is exciton production, it follows that the photocurrent in CdS crystals involves optical generation of excitons as a primary step.

An earlier investigation[4] of the kinetics of photoconductivity in CdS crystals led to the conclusion that excitons are important in internal photoeffects. They

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[3] Gross, Kaplyanski, and Novikov, Zhur. Tekh. Fiz. **26**, 913 (1956).

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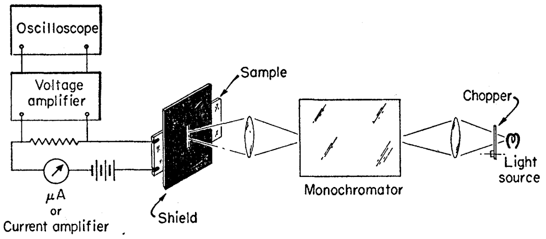

FIG. 1. Experimental arrangement for measuring the internal photocurrent by indirect illumination.

assumed that high exciton concentrations are produced by light absorption. Some excitons, on migrating through the crystal and being destroyed at sites of imperfections, give rise to trapped electrons subsequently liberated by means of energy transfer from other excitons. This mechanism is analogous to that proposed first by Apker and Taft[5] for the photoelectric effect in the alkali halides: production of F centers by excitons and migration of additional excitons to the F centers causing ionization by dissociation of these into vacancies and free electrons. In a recent study by Shuba,[6] the photoelectric emission from CdS can best be explained assuming the same mechanism.

The study by Gross and Yakobson[7] of the "azure" luminescence of CdS shows that by excitation with $\lambda = 3663$ A at $T = 77.3$°K one obtains an emission spectrum, attributable to excitons, with nine lines in complete coincidence with the absorption lines previously obtained by the same authors. They conclude that the blue luminescence of CdS may be due to a spectrum of excitons annihilated in the CdS lattice.

Grillot[8] also describes the fluorescence of CdS at 77°K in terms of fine lines whose frequencies correspond to the formula $\nu_n = 20\,700 - (6500/n^2)$ [cm^{-1}]. Because of the evidence that lattice imperfections are responsible for this fluorescence, he concludes that the process involves annihilation of excitons at defect sites in the CdS lattice. Lambe, Klick, and Dexter[9] and also Diemer, Van Gurp, and Meyer[10] have attributed similar fluorescence spectra to vibrational fine structure of the emission band.

To investigate energy-transfer processes in which diffusion can occur, Balkanski and Broser[11] utilized a special method of excitation. The crystal was illuminated only through a narrow slit at some distance from the electrodes, while the rest of the crystal remained covered. They measured the photoconductivity spectrum resulting from energy diffusion through the crystal. It was demonstrated by experiments with a variable electric driving field that this diffusion process involves neutral entities. The mechanism of photocurrent production can be explained by the generation of excitons which diffuse toward the electrodes and dissociate at imperfections giving trapped electrons, followed by their ejection into the conduction band upon interaction with other excitons.

Diemer and Hoogenstraaten[12] have performed similar experiments with masked crystals and also studied the photoelectromagnetic effect in CdS. The diffusion lengths of photoexcitation by the two methods are incompatible, leading the authors to conclude that both ambipolar and exciton diffusion are important mechanisms in the photoconductivity.

At liquid nitrogen temperature, the photocurrent spectra for indirect illumination of certain CdS crystals show a series of maxima at 5700, 5450, 5160, 4880, 4730, and 4640 A, which fit roughly into a hydrogen-like formula

$$E_n = h\nu_n = A - \frac{B}{n^2}[\text{ev}], \tag{1}$$

where E_n is the energy difference between the fundamental state and the nth excited state, n an integer ($n = 2, 3, \cdots$), and ν_n the absorption or emission frequency.

This behavior led Broser and Warminsky[13] to list the energy levels of CdS and ZnS obtained by emission, absorption, and excitation to see if there is any regularity in their distribution. Many of the impurity levels can be put in a series corresponding to Eq. (1). For both substances (CdS and ZnS) these authors found two series, each with different values for B: for CdS, $A = 2.82$ ev; $B = 6.4$ and 5.0 ev; for ZnS, $A = 4.1$ ev; $B = 6.8$ and 5.4 ev. For both substances the transition $n = 2$ corresponds to one of the bands generally attributed to the Cu-impurity level. The authors conclude that the experimental data indicate the existence of discrete impurity-center levels rather than exciton levels.

The presence or absence of a hydrogen-like spectrum spectrum neither proves nor disproves the existence of excitons since impurity atoms may also give rise to a similar spectrum, and excitons themselves may have hydrogenlike energy levels only in certain crystals with cubic symmetry.[14] The experimental determination of characteristic parameters of the energy migration

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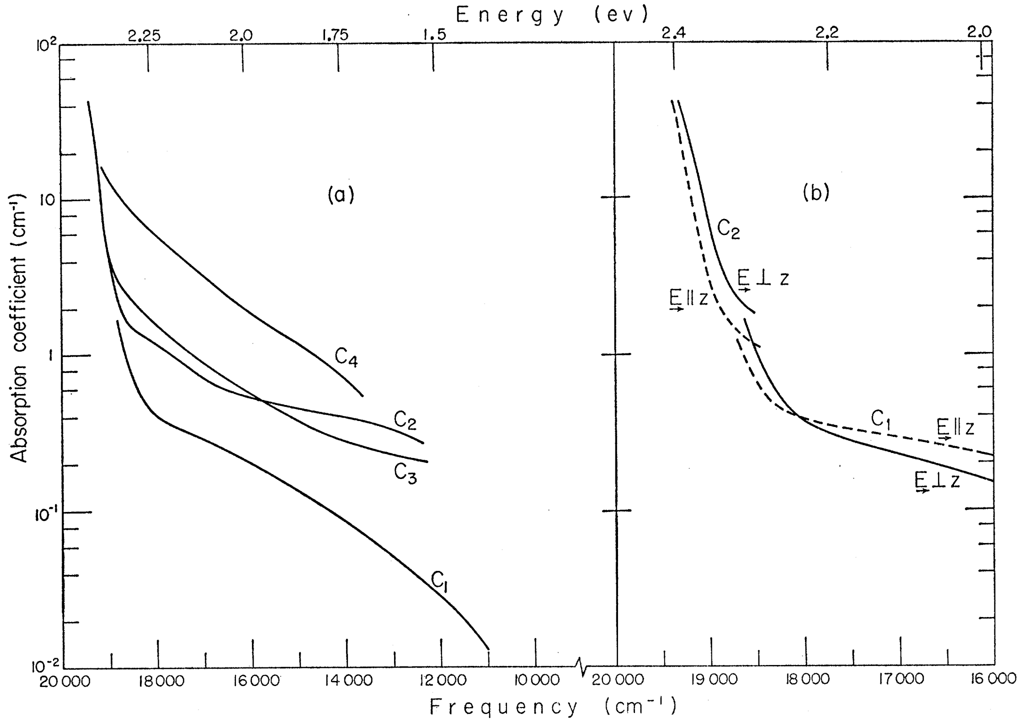

FIG. 2. Absorption spectra of CdS single crystals (C_1 to C_4): (a) unpolarized light; (b) polarized light, ⊥ and ‖ to z axis.

(diffusion length and lifetime) is of fundamental importance for the establishment of the mechanism of the energy transport and has been accomplished in the work reported in the present paper.

EXPERIMENTAL TECHNIQUE

The initial process of light absorption, the photoelectric response, and the energy diffusion in CdS were studied in the present work. Information as to the initial excitation process is derived from measurements of the absorption spectra between 11 000 and 50 000 cm^{-1} (2000 to 9000 A). The measurements were made with the Cary Model 12 spectrophotometer, a quartz-prism double monochromator, with samples orientated to permit polarization measurements perpendicular or parallel to the optic axes of the crystal. Transmission of thin films and reflectivity measurements were also made.

Photocurrent measurements of the particular kind of excitation spectra first described by Balkanski and Broser[11] were performed (Fig. 1). A Beckman IR-3 spectrophotometer, with a tungsten lamp and CaF_2 or SiO_2 prisms, was used and the photocurrents were recorded for constant incident radiant energy by variation of the slit width with wavelength. The monochromator output was focused on a thermocouple and the signal amplified and fed to a servocircuit which opened or closed the slit to maintain a constant signal level. The positions of the slits were recorded on a tape and upon playback the slit was automatically returned to its respective opening for constant energy at each wavelength, while the photospectra were recorded.

The photoresponse to modulated radiation was measured by chopping the incident light at a frequency of 10 cps and biasing the sample with 165-v dc. The 10-cycle component of the photocurrent was amplified using the Beckman IR-3 amplifier. Photospectra recorded in this manner are dependent on the scanning rate and illumination prehistory, but are reproducible under fixed conditions. Even for infinitely slow scanning rates they differ from steady illumination photospectra, since relaxation effects which are slow compared to the chopping time are not recorded. With the same monochromator the excitation spectra for unmodulated radiation were also traced and the equilibrium photocurrent under dc bias was measured with a microammeter or a current amplifier.

The diffusion constant and lifetime of the excitation energy were calculated from measurements of the rise time t_m and the maximum height h of the photocurrent pulse at the electrodes following a light flash through a slit at a distance from the site of the electrodes. The photocurrent at the electrodes, as a function of elapsed time, was measured by a sensitive Tektronix No. 513D oscilloscope. A single-stage pentode amplifier of rapid-response characteristic was used to provide additional amplification when the photocurrent pulses were weak. The light flash was produced by discharging 0.1 μf at 16 000 v through a 1-atmos xenon lamp of

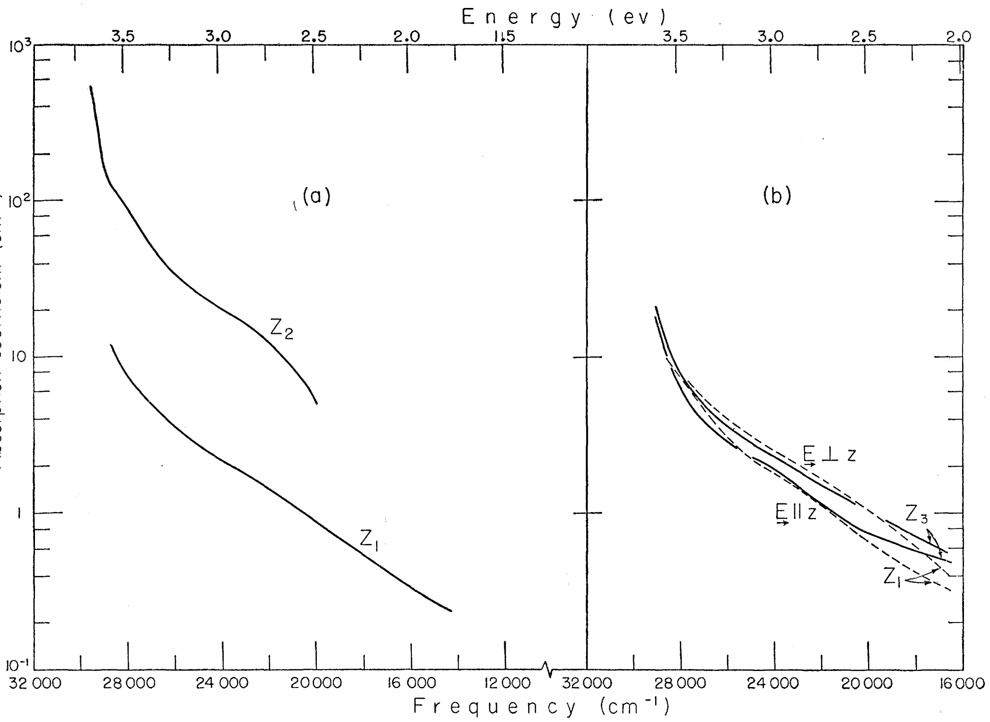

FIG. 3. Absorption spectra of ZnS single crystals (Z_1 and Z_2): (a) unpolarized light; (b) polarized light, ⊥ and ∥ to z axis.

4-mm diam, with an electrode gap of 1.2 cm in series with an air gap. The time constants of both the flash lamp and the photocurrent circuit were less than 1 μsec. For monochromatic-light pulse experiments the electronic flash lamp was inserted directly in the IR-3 source compartment. The slit width was set to give

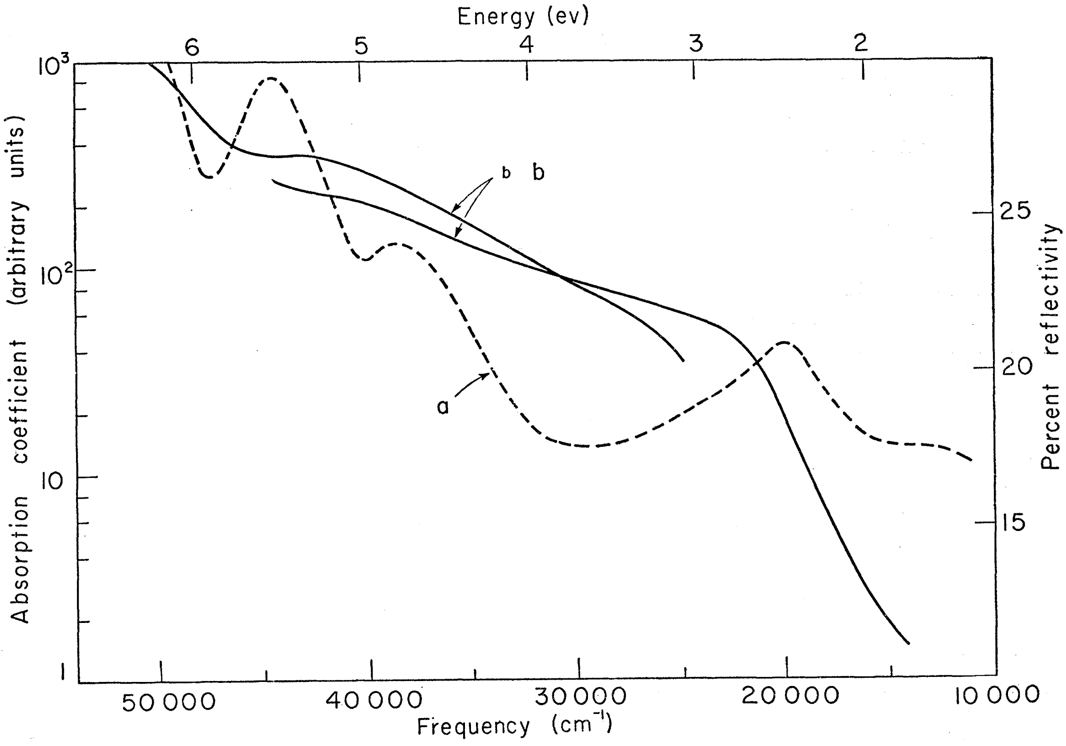

FIG. 4. Reflection (a) and absorption (b) spectra of CdS (C_3).

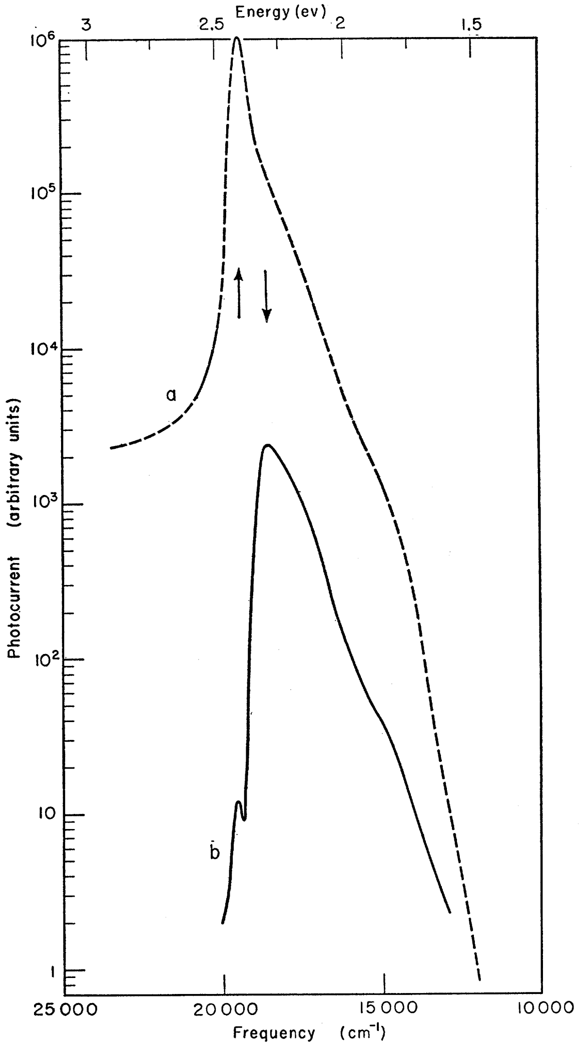

FIG. 5. Excitation spectra of CdS (C_2) for chopped illumination (a) over the electrodes; (b) 0.3 cm from the electrodes.

constant incident energy at each of several wavelengths by oscilloscopic examination of the amplified pulses from a thermocouple. Measurements for different slit openings at a fixed wavelength were also made.

For measurements at low temperatures a metallic Dewar cell with insulated electrical leads and a quartz window was used.

Most of the experiments were made with CdS single crystals obtained from several laboratories; measurements were also performed on ZnS single crystals from two sources and on sintered CdS powders with known impurity centers.

MEASUREMENTS

1. Absorption and Reflection Spectra

The transmission T of radiant energy I through a sample of single surface reflectivity R and thickness d is given by $T=I/I_0=(1-R)^2\,10^{-kd}$ for random phase differences, where $k=(1/\mathrm{d})[-\log_{10}T+2\log_{10}(1-R)]$ is the absorption coefficient. The transmission curves of CdS were corrected for reflection losses using the measured reflectivity; for ZnS a constant reflectivity computed from the refractive index (D line) was used.

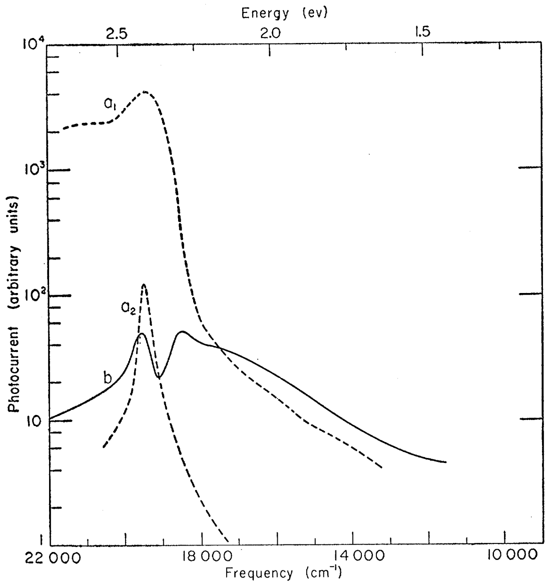

FIG. 6. Excitation spectra of pure CdS (C_5) for chopped illumination (a_1) over the electrodes at constant incident energy; (a_2) over the electrodes at constant slit opening (low intensity); (b) at a distance from the electrodes.

Figure 2 shows the absorption spectra of four CdS crystals and, in addition, the polarization spectra of two of the samples, while Fig. 3 shows corresponding data for ZnS. The absorption coefficient for all samples increases monotonically with increasing frequency in the range measured with a sharp break in slope corresponding to the absorption edge. The position of the absorption edge in CdS is shifted from 100 to 150 cm^{-1} to higher frequency for $\mathbf{E}\|z$ than for $\mathbf{E}\perp z$ ($\mathbf{E}$ designates the direction of the electric vector of the radiation and z the optic axis of the crystal). The position of the edge is essentially independent of impurity concentration, but below 19 000 cm^{-1} for CdS and 28 000 cm^{-1} for ZnS the absorption coefficient in the tail of the band increases with increasing impurity content. For example, the value of k for the Cu-doped crystal (C_4) at 18 000 cm^{-1} is 15 times greater than for C_1, the purest sample measured. A small shoulder occurs for sample C_2 near 18 000 cm^{-1}. No discrete band structure other than this is observed in the low-frequency side of the absorption edge at room temperature.

The absorption coefficient below the sharp break in slope near 18 000 cm^{-1}, while modified by impurities, increases much more slowly than the impurity concentration. This band is probably caused by alteration of the dipole-moment transition probability of the pure crystal by perturbation from impurity atoms. Exciton absorption in this region must correspond to

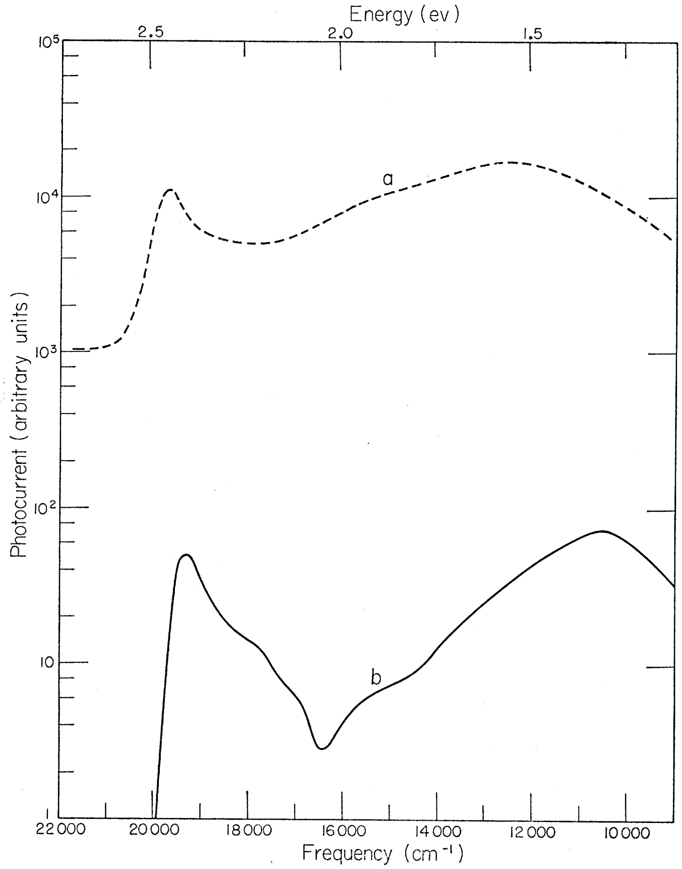

FIG. 7. Excitation spectra of copper-doped CdS (C_4) for chopped illumination (a) over the electrodes; (b) at a distance from the electrodes.

forbidden transitions since k is several orders of magnitude below that for allowed absorption bands.[15]

Structure in the high absorption region of CdS is indicated from the spectra of evaporated films (Fig. 4). The upper shoulder of the absorption coefficient occurs at about 22 000 cm^{-1}, with additional peaks at about 43 000 and $>$50 000 cm^{-1}, in good agreement with the reflection spectrum of C_1, which has maxima at 20 000, 38 500, 44 500, and $>$50 000 cm^{-1}.

Previous studies[7,16] have established the temperature dependence of the absorption edge below room temperature. The edge shifts about 1150 cm^{-1} toward higher frequency when cooled from room temperature to 77°K.

The attenuation of energy through the sintered CdS samples was also measured using an experimental arrangement in which more than 10% of the total hemispherical radiation emerging from the highly scattering sample was detected. The transmission of a sample (C_b, 50 μ thick) is below 10^{-4} at all frequencies between 12 000 and 25 000 cm^{-1}; hence the total energy transmission of such a sample is certainly less than that 10^{-3} in this range. The opacity of such samples is sufficiently high that radiation can be neglected as an energy transfer process over slit-electrode distances of the order of a centimeter.

2. Photocurrent Spectra

The spectral dependence of photocurrent differs according to the nature of the individual samples. All CdS samples, when illuminated directly over the electrodes, show a primary peak of photocurrent near 5100 A (2.43 ev) which is rapidly attenuated as one moves the region of illumination away from the electrodes. This primary photocurrent is intrinsic and believed due to direct liberation of free charge-carriers with a diffusion length of the order of microns. For indirect illumination at a distance from the electrodes, the principal photoresponse occurs at lower frequencies than the primary peak and undergoes only gradual attenuation with increased slit-electrode distance. We shall call this diffusible photoeffect a transfer photocurrent whose efficiency and spectral response differ according to the nature of the samples. We may qualitatively classify our samples as (1) low-sensitivity CdS in which the efficiency of the transfer photocurrent is low, the frequency of maximum photocurrent is only slightly lower than for the primary

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[15] The absorption coefficient even for allowed transitions may be quite low for very loosely bound states close to the absorption edge, since the absorption coefficient should decrease with binding energy [see, for example, G. Dresselhaus, Phys. Rev. **106**, 76 (1956)].

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peak, and the absorption coefficient below 18 000 cm^{-1} is small; and (2) high-sensitivity CdS in which the transfer-photocurrent efficiency is high, the photocurrent peak occurs at much lower frequencies (<2.1 ev), and the absorption coefficient in the low-frequency tail of the band is high. Our purest crystals C_1 and C_5, and silver-doped samples C_s and C_2, belong to the low sensitivity class, while the copper-doped samples C_3, C_4, and C_a are representative of the high-sensitivity group.

Figures 5 to 10 show the typical photoresponse for CdS samples. It should be noted that transfer photocurrent occurs even for direct illumination, while some remainder of the primary peak occurs for indirect illumination as the result of scattered light reaching the electrode region. A residual response can also occur if a certain fraction of the charge carriers recombine, converting their recombination energy to form excitons of lower energy.

To establish the nature of the transfer photoeffect and to distinguish clearly between diffusion of excitons and internal reflection and scattering of light as the dominant energy transport process, we have performed the following experiments on a highly sensitive CdS crystal C_3 ($2\times0.5\times0.07$ cm). Two parallel sets of electrodes were mounted at the two extremities of the crystals; each pair could be connected alternately to the current-measuring circuit. The crystal was illuminated at the center through a narrow slit and the photoresponse from each side recorded separately. The two curves obtained [Fig. 8(a)] are quite similar and characterized by a peak in the transfer photocurrent at $\lambda=6140$ A ($E=2.02$ ev). The much less intense primary peak is observed at $\lambda=5102$ A ($E=2.43$ ev).

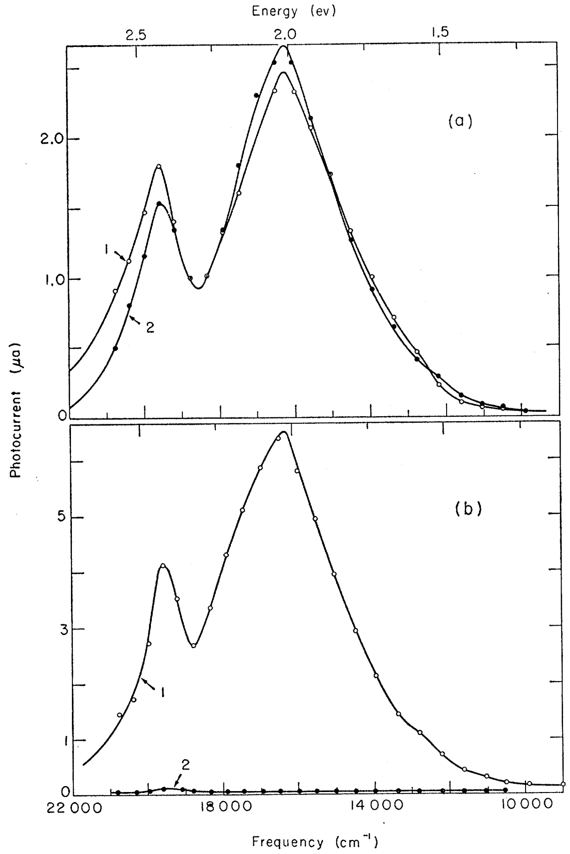

FIG. 8. Excitation spectra of CdS (C_3) for continuous illumination at 0.8 cm from each pair (1 and 2) of electrodes at the extremities of the crystal (a) before and (b) after cleaving the crystal.

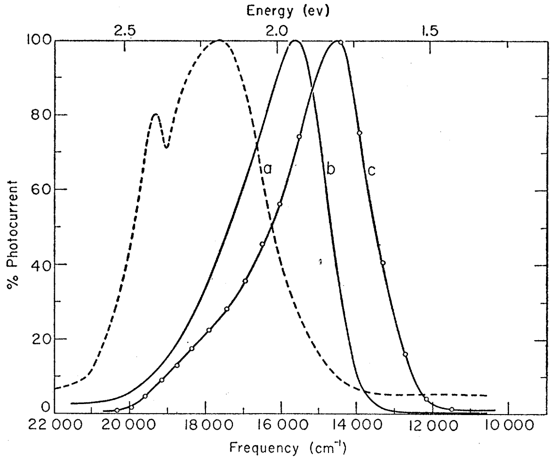

FIG. 9. Excitation spectra of copper-doped, sintered CdS (C_a) for illumination (a) over the electrodes (chopped); (b) at a distance from the electrodes (chopped); (c) at a distance from the electrodes (continuous).

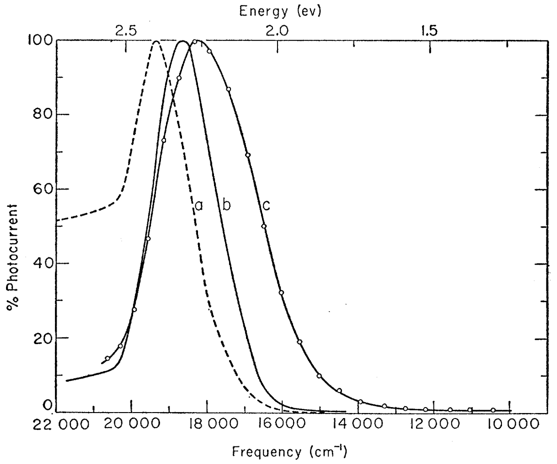

FIG. 10. Excitation spectra of silver-doped, sintered CdS (C_s) for illumination (a) over the electrodes (chopped); (b) at a distance from the electrodes (chopped); (c) at a distance from the electrodes (continuous).

The crystal was afterwards cleaved nearer to the right side and the boundary immersed in diiodomethane having a refractive index of $n_D=1.76$ (CdS, $n_D=2.52$). This immersion increases the cone of light not subject to total internal reflection from 0.51 to 1.79 steradians and decreases the normal reflectivity from 18.6 to 3.1%

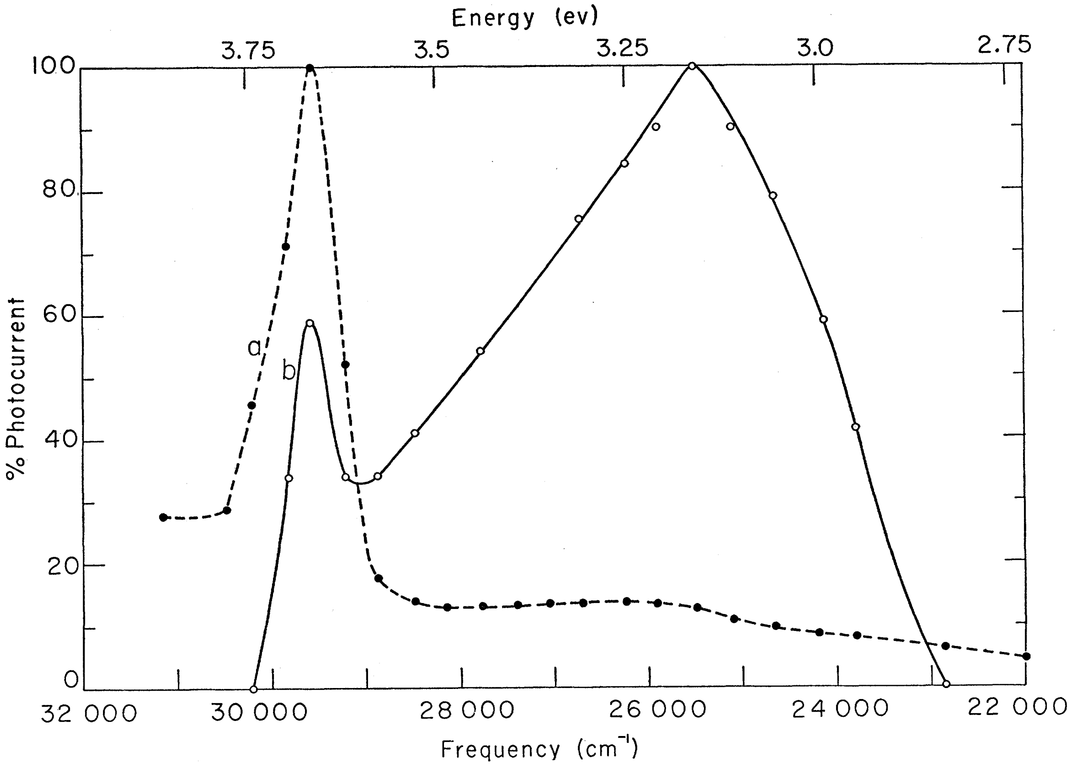

FIG. 11. Excitation spectra of ZnS (Z_4) for continuous illumination (a) over the electrodes; (b) at a distance from the electrodes.

compared with an air-CdS boundary; thus the percent transmission of hemispherically uniform light through two plane-parallel interface is increased from 5.1 to 26.7%. The photocurrent spectra of both sides of the crystal were taken again, maintaining the slit at the center. The photoresponse on the left side is the same as that previously established, but on the right side it is drastically changed compared with the first diagram. No trace of the transfer-photocurrent peak is left, while a slight indication of the primary peak can still be discerned (Fig. 8). One may conclude on the basis of this experiment than when a gross discontinuity is established in the crystal, the energy transport giving rise to the transfer photocurrent is interrupted across the boundary. This eliminates the possibility of interpreting the transfer photocurrent by any process based on light transmission. The presence of transfer photoresponse in the virtually opaque, sintered CdS samples (Figs. 9 and 10) lends added confirmation to this view.

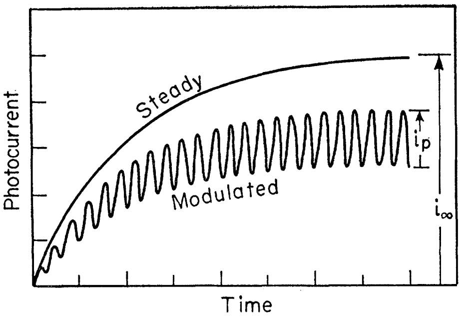

FIG. 12. Rise of photocurrent following illumination of a dark crystal with (a) modulated or (b) unmodulated radiation.

The photocurrent spectra obtained with ZnS single crystals (Fig. 11) are analogous to those observed for CdS. The primary peak of photoresponse for direct illumination occurs at $\lambda = 3380$ A (3.68 ev) with a very low peak occurring at $\lambda = 3745$ A (3.3 ev). Indirect illumination produces a maximum of the transfer photocurrent at $\lambda = 3920$ A (3.18 ev), and only a slight remainder of the primary peak.

The spectral behavior of the transfer photoresponse was studied for both modulated and unmodulated radiation. Since the spectra taken by the two procedures are not identical, we shall analyze the methods in greater detail.

If one applied a dc bias to a dark crystal and at time $t=0$ illuminates it with chopped or steady light of a fixed wavelength, the corresponding photocurrent at time t will be represented as shown in Fig. 12. The modulated photoresponse is measured by the pulse height i_p which depends on the time constants for both rise and decay of the photocurrent, while the steady photocurrent is measured by the limiting value i_∞. The maxima for the two methods will not, in general, coincide since the photoresponse is not linear, and a finite scanning speed is used for the modulated measurements. However, the chopped method gives the approximate location of the equilibrium-photocurrent peaks and is much more convenient for accumulating data.

The difference in response for modulated or steady radiation for sample C_3 can be seen from Figs. 8 and 13. The main transfer-photocurrent maximum is practically unaffected, shifting by only 0.01 to 0.02 ev, while the intensity of an additional shoulder at about 1.6 ev is somewhat changed. For the sintered samples (Figs. 9 and 10) the transfer-photocurrent maxima shift from 1.81 to 1.93 and from 2.27 to 2.31 ev, respectively.

The positions of the transfer-photocurrent maxima seem quite variable even for samples doped with the same impurity (copper). Thus for modulated radiation, C_4 has a peak response at 1.3 to 1.5 ev while C_a has a peak at 1.93 ev. Since the magnitude of transfer photocurrent depends on the product of efficiencies for the successive steps in the mechanism (initial absorption, diffusion, active trapping or decay, and eventual conversion to free charge carriers), it is not surprising that the detailed shape of the photoresponse may differ from one sample to another; only if all impurities, deffects, strains, etc., were identical would one expect identical photoresponse.

The spectral response of the transfer photocurrent of the sintered samples shows the effect of impurity doping most clearly. These samples were prepared by stirring an aqueous slurry of one part soluble copper or silver salt with 1000 parts CdS with added $CdCl_2$, followed by drying and heating in an oven to allow ionic diffusion. The material was then finely ground in a nonaqueous suspension, painted on a glass substrate, and baked to sinter the particles.

At room temperature, the copper-doped samples (C_a, Fig. 9) show a maximum in the transfer photoresponse at $\lambda = 6870$ A (1.81 ev) for steady illumination, while for silver-doped samples (C_s, Fig. 10), the corresponding peak occurs at $\lambda = 5465$ A (2.27 ev).

Most of the previous studies concerning the absorption spectrum and photoresponse[2,3] ascribed to excitons were made at low temperature. To allow a comparison between our results and those of others, the photocurrent for indirect illumination of sample C_3 was measured at liquid nitrogen temperature (Fig. 14), and revealed a series of peaks whose separations increase toward lower frequencies. The energy levels (Table I) corresponding to these maxima in the photoresponse can be fitted roughly to a hydrogen-like formula (Eq. 1) with different constants than reported by Broser and Warminsky,[13] but the variability of spectral response from sample to sample prevents an unequivocal interpretation.

TABLE I. Maxima in the transfer-photocurrent spectra at 78°K for indirect illumination.

	Wave number of the excitation cm^{-1}	Energy levels ev	Intervals 10^{-2} ev
Photoresponse for direct illumination	20 775	2.58	
Maxima of the photoresponse for indirect illumination at 78°K	20 020	2.50	8
	19 000	2.36	14
	16 600	2.08	28
	15 490	1.78	30
	10 500	1.30	48

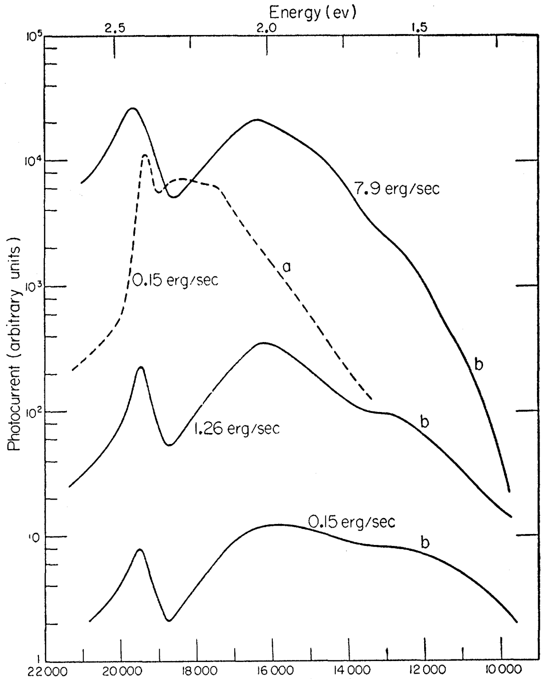

FIG. 13. Excitation spectra of CdS (C_3) for chopped illumination with different radiant power (a) over the electrodes (0.15 erg/sec); (b) at 0.8 cm from the electrodes (7.9, 1.25, and 0.15 erg/sec).

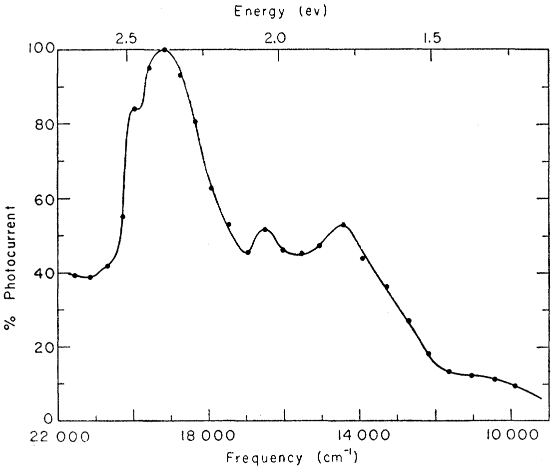

FIG. 14. Excitation spectrum of CdS (C_3) at $T = 78°$K for continuous illumination at a distance from the electrodes.

The efficiency of production of transfer photocurrent increases and of primary photocurrent decreases at low temperatures. The mobility of excitons seems to be greater and therefore the diffusion process becomes more efficient at low temperature.

The photocurrent impulses for flashes of given input-radiant power for frequencies below the absorption edge also increase as the temperature is lowered. The peak height of the transfer photocurrent at $\lambda = 6056$ A is greater at 78°K than at 300°K (Table II), even though the photocurrent maximum has shifted some distance from this wavelength at low temperature (Fig. 14). Low-temperature measurements with chopped radiation and reasonable scanning times proved unreliable because of the slower decay processes encountered at 78°K.

A series of curves (Fig. 13) shows the photoresponse for different incident intensities of chopped indirect illumination, all other conditions being identical. The position of the transfer-photocurrent peak (2.02 ev) is not apprecialy affected by the intensity of the incident light when the radiant power varies between 0.15 and 7.9 ergs/sec. The intensity of the photocurrent, in contrast, is closely correlated with the intensity of the radiation: the photoresponse for illumination with 7.9 ergs/sec at a distance of 0.3 cm from the electrodes is even higher than the one for direct illumination with an incident intensity of 0.15 ergs/sec.

The dependence of the photocurrent i on the absorbed radiant power p for continuous illumination at a distance from the electrodes (Fig. 15) may be approximated by the equation $i = kp^{0.8}$, indicating a nearly linear relationship. The curve giving the photocurrent as a function of the incident light intensity at 78°K is above that at 300°K. The quantum efficiencies at the lowest intensities measured were 0.031 at room temperature and 0.044 at liquid nitrogen temperature.

The intensity dependence of the height h of the photocurrent peak produced by flash illumination at a distance from the electrodes is shown in Fig. 16. The photocurrent can be represented by the equation $i = k_n p^n$, where $n = 0.35$ or 1.1 in the low- or high-intensity regions, respectively. Here also the photoresponse on flash illumination at liquid nitrogen temperature is higher than the one at room temperature. The greater-than-linear dependence of the photocurrent on flash intensity at high levels indicates a contribution to the photocurrent which is quadratic in exciton density, characteristic of a bimolecular process. At low intensities the current is nearly independent of power level which may indicate an impurity-limited process. This is to be contrasted with the intensity dependence of photocurrent for steady illumination, where the response is nearly linear (Fig. 15).

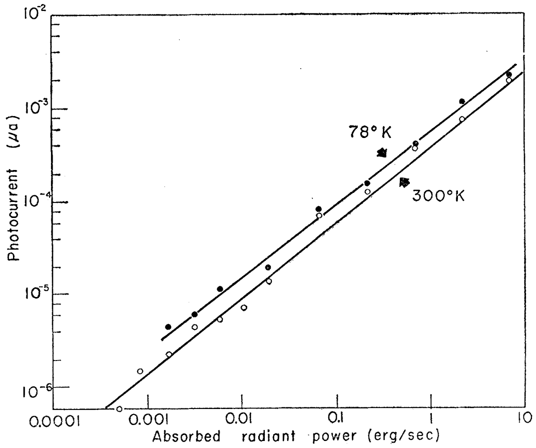

FIG. 15. Dependence of the transfer photocurrent on the absorbed radiant power of CdS (C_3) at $\lambda = 6056$ A.

The kinetics of the energy transport process were investigated to elucidate the mechanisms involved in the diffusion of energy in the transfer photoeffect.

TABLE II. Dependence of the maxima of indirect photocurrent impulse on the incident flash intensity.

ϕ[a] ergs/sec	h (arbitrary units)[b] 78°K	300°K
13.8	8.4	4.3
76.8	41	8.3
189	59–70	...
391	195	101

[a] The total luminous flux through the slit situated at a distance from the electrodes.

[b] The maximum of the photocurrent impulse generated by the flash illumination.

Let us consider a crystal of uniform cross section, infinite in the x direction, illuminated uniformly by a light pulse in a thin section of the yz plane. At the instant of illumination ($t=0$), the excitation-energy density $\rho = \rho(x,y,z,t)$ in the crystal is given by

$$\rho(x,y,z,0) = \chi(y,z)\delta(x), \tag{2}$$

where $\delta(x)$ is the Dirac delta operator, defined as $\int_{-\infty}^{+\infty}\delta(x)dx = 1$, where $\delta(x) = 0$ for $x \neq 0$.

In the region of linear response, the function $\rho(x,y,z,t)$ satisfies the partial differential equation

$$\frac{\partial\rho}{\partial t} + \frac{\rho}{\tau} = D\left(\frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2}\right), \tag{3}$$

where τ is the lifetime and D is the diffusion constant. The solution in one dimension is

$$\rho_1(x,t) = \frac{1}{(4\pi Dt)^{\frac{1}{2}}} \exp\left(-\frac{t}{\tau} - \frac{x^2}{4Dt}\right). \tag{4}$$

For a cylindrical crystal illuminated uniformly in the yz plane at $x=0$, $t=0$, the general solution is

$$\rho_3(x,y,z,t) = g(y,z,t)\frac{1}{(4\pi Dt)^{\frac{1}{2}}} \exp\left(-\frac{t}{\tau} - \frac{x^2}{4Dt}\right), \tag{5}$$

where $g(y,z,t)$ is determined by $\partial g/\partial t=D(\partial^2 g/\partial y^2+\partial^2 g/\partial z^2)$, and $g(y,z,0)=\chi(y,z)$; and $D(dg/d\eta)=sg$, where η is the normal to the cylindrical surface and s is a surface-annihilation factor. The determination of $g(y,z,t)$ is not necessary for the computation of diffusion parameters in the x direction. Equation (4) gives the distribution of excitation energy in the crystal at any time after illumination. It is possible to compute this distribution function, introducing experimental values for τ and D for a fixed slit-electrode distance as a function of time, or for a fixed time interval as function of slit-electrode distance.

According to Eq. (4) the maximum energy density for a given slit distance x occurs after time

$$t_M=\frac{\tau}{4}\left[\left(1+\frac{4x^2}{D\tau}\right)^{\frac{1}{2}}-1\right]. \tag{6}$$

The following approximations are justifiable in two limiting cases:

$$t_M=\frac{x^2}{2D},\quad \text{for}\quad \frac{4x^2}{D\tau}\ll 1, \tag{6a}$$

$$t_M=\frac{x}{2}\left(\frac{\tau}{D}\right)^{\frac{1}{2}},\quad \text{for}\quad \frac{4x^2}{D\tau}\gg 1. \tag{6b}$$

In the latter case, Eq. (4) reduces to

$$\rho_{\max}(x,t_M)=e^{-x/L}/(2\pi x L)^{\frac{1}{2}}, \tag{7}$$

where L is the diffusion length $[L=(D\tau)^{\frac{1}{2}}]$. The transit time t_M (the time interval between the flash illumination and occurrence of maximum photocurrent) as well as the ratio of the photocurrent maxima h_1/h_2 for two values $x_1>x_2$ of the slit-electrode distance x, can be experimentally determined. If we assume that the rate of free charge-carrier production by the annihilation of the excitation is proportional to ρ/τ, the ratio ρ_1/ρ_2 in first approximation will be equal to the ratio of photocurrent peaks h_1/h_2. The mean life τ will then be given by

$$\tau=\frac{2t_{M1}(1-x_2/x_1)}{\ln[(h_2/h_1)(x_2/x_1)^{\frac{1}{2}}]}, \tag{8}$$

the diffusion constant by

$$D=\frac{x_1^2(1-x_2/x_1)}{2t_{M1}\ln[(h_2/h_1)(x_2/x_1)^{\frac{1}{2}}]}, \tag{9}$$

and diffusion length by

$$L=\frac{x_1(1-x_2/x_1)}{\ln[(h_2/h_1)(x_2/x_1)^{\frac{1}{2}}]}. \tag{10}$$

The agreement with experiment is satisfactory except at very high intensities, where bimolecular terms become important.

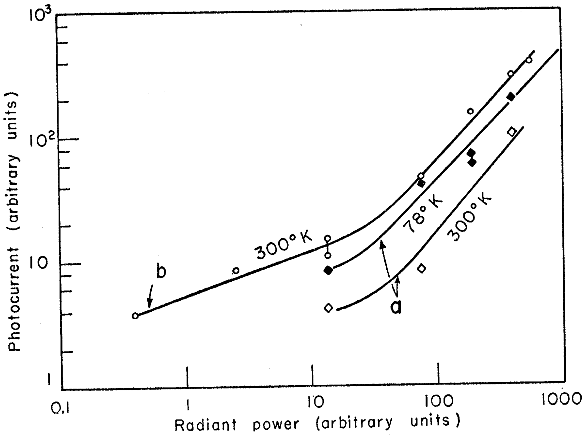

FIG. 16. Dependence of the transfer-photocurrent pulse height on the radiant power of the light flash for CdS (C_3) at $\lambda=6056$ A: (a) 0.3 cm slit-electrode distance at 300° and 78°K; (b) 0.25 cm slit-electrode distance at 300°K.

In this treatment only the problem of a pure random diffusion has been considered. We have implicitly assumed that the diffused particles were not charged. For the experimental proof of such an assumption, we should establish that an external electric field is without action on the diffusion process.

Let us consider an electric field E applied in the direction of the x axis. The differential equation of the diffusion [Eq. (2)] can now be rewritten

$$\frac{\partial\rho}{\partial t}+\frac{\rho}{\tau}=D\left(\frac{\partial^2\rho}{\partial x^2}+\frac{\partial^2\rho}{\partial y^2}+\frac{\partial^2\rho}{\partial z^2}\right)+\mu E\frac{\partial\rho}{\partial x}, \tag{11}$$

where the mobility μ of the dominant free charge-carrier is given by the Einstein[17] relationship, $\mu=eD/kT$. Its solution in the one-dimensional case is

$$\rho=\rho(x,t)_{E=0}\exp\left(-\frac{\mu E x}{2D}-\frac{(\mu E)^2 t}{4D}\right). \tag{12}$$

This may be expressed in the following form

$$\rho[x,t]_{E\neq 0}=[\rho(x',t)]_{E=0}, \tag{13}$$

where $x'=x+\mu Et$.

The diffusion process for charged particles is thus dependent on the electric field, but in the present case no effect was observed for fields as high as 10^3 v/cm, although even a field of 10 v/cm should have given a measurable displacement of the photocurrent maximum. This insures that we are measuring energy transport by neutral entities and need not consider this field effect.

The lifetime of the diffusion excitons was calculated by inserting the measured values of t_{M1}, h_1, and h_2 in Eq. (8). For sample C_3 (1.4×0.5×0.07 cm) the

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[17] A. Einstein, Ann. Physik **17**, 549 (1905); Müller-Poullet, *Lehrbuch der Physik* (Friedrich Vieweg und Sohn, Braunschweig, 1933), Chap. 4, p. 316.

TABLE III. Dependence of the characteristic diffusion parameters of excitons in CdS (C_3) on the incident energy of excitation.

Photon energy ev	Mean life (τ) sec	Diffusion constant (D) cm^2/sec	Diffusion length (L) cm
2.58 to 2.38	3.2×10^{-3}	0.405×10^3	1.1
2.28	8×10^{-6}	5.0×10^3	0.2
2.17	1.4×10^{-5}	6.2×10^3	0.30
2.06	2.2×10^{-5}	6.2×10^3	0.37
1.80	9.3×10^{-6}	6.4×10^3	0.25
1.52	1.7×10^{-5}	7.5×10^3	0.25
1.16	6.9×10^{-5}	7.5×10^3	0.72

computed mean life τ of an excitation produced by monochromatic light at $\lambda=5730$ A ($E=2.17$ ev) is $\tau=1.4\times10^{-5}$ sec. For the same crystal, applying Eqs. (9) and (10), we obtain the diffusion constant $D=6200$ cm^2/sec and the diffusion length $L=0.30$ cm. The estimated probable error in the determination of the diffusion parameters was $\pm25\%$.

With the same crystal we made a series of measurements using monochromatic light of various wavelengths. Table III shows that for all excitation energies below the absorption edge in CdS, values of τ of the same order of magnitude ($\tau\simeq10^{-5}$ sec) were obtained; the diffusion constant D has a mean value of about 6.5×10^3. For excitation energies above the absorption edge, $\tau\simeq3\times10^{-3}$ sec, $D\simeq400$ cm^2/sec, and $L\simeq1$ cm. There are reasons for believing that the values of τ and D for these energy levels are not characteristic of a diffusion process of excitons, since the initial illumination generates free-charge carriers predominantly; nor do they correspond to pure electron or hole diffusion. Recently reported[12] measurements on the photoelectromagnetic effect give $L=0.1\ \mu$. The efficiency of the exciton process for energies above the absorption edge is very low compared with that for excitation with lower energy. The efficiency of the energy-transport process for indirect illumination is lower for $\lambda=5000$ A ($E=2.48$ ev) than for $\lambda=6900$ A ($E=1.8$ ev), even though the efficiency of production of free charge-carries for direct illumination is more than 150 times greater for the higher frequency. Since diffusion lengths are comparable, the efficiency of exciton generation is at least 100 times lower for frequencies of the order of the absorption edge than for lower frequencies. This indicates that nearly all of the free charge-carriers are trapped near the site of their generation and the mechanism of this energy diffusion is probably a migration of excitons produced gradually by secondary processes with a slow period. The diffusion parameters of excitons are actually measured only for excitation by energies below the absorption edge. These measurements were made in a dark room with complete protection from stray illumination to eliminate any background stimulation.

Measurements were also made with the room light turned on. The results presented in Table IV show small differences in the values of the diffusion parameters but the order of magnitude is not affected. If the differences are not due to statistical deviations, although they are within the limits of the experimental precision, the shortened lifetime of excitons with background illumination would be expected for a bimolecular process. Thus, if the annihilation rate of excitons is proportional to the product of the concentration of excitons and excited traps, one should shorten the excitons' lifetime by the external stimulation of traps.

Measurement of the transit time as a function of radiant intensity at a fixed wavelength shows that t_M also decreases with an increase of the total luminous flux over the crystal (Table V). The higher the concentration of excitons initially created, the greater the probability of bimolecular interaction ending the diffusion process. This explains the dependence of the diffusion parameters on exciton density.

A Cu-doped sample, C_4, showed $\tau\simeq10^{-6}$ sec, somewhat lower than that of samples with lower impurity concentrations. A sintered CdS sample C_b, copper-doped, gave $\tau=1.7\times10^{-6}$ sec, $D=1\times10^4$ cm^2/sec, $L=0.126$ cm. A ZnS single crystal Z_2 showed: $\tau=7\times10^{-6}$ sec, $D=4\times10^4$ cm^2/sec, $L=0.52$ cm. A silver-doped sintered sample C_s prepared by the same method gave $\tau=7.6\times10^{-6}$ sec, $D=8\times10^3$ cm^2/sec, $L=0.85$ cm.

The values of D are only slightly affected by decreasing the concentration of impurities by a factor greater than 100 or even by changing the chemical identity of the doping agent. Such behavior eliminates the possible interpretation of energy transport in the transfer photoeffect by a nonradiative mechanism involving only the impurity atoms, since the transit time for such a process should increase exponentially with increasing interatomic distance between impurity atoms and vary with the chemical nature of the impurity.

The computed diffusion constants at room temperature are much larger than one would obtain if free-charge carriers provided the energy transport. If electrons or holes are responsible for this transport process, the Einstein equation,[14] $\mu=eD/kT$, gives immediately the values of D corresponding to measured mobilities. For electrons the values of μ obtained from

TABLE IV. Dependence of the diffusion parameters of excitons in CdS (C_3) on the incident energy of excitation with a background stimulation.

Photon energy ev	Mean life (τ) sec	Diffusion constant (D) cm^2/sec	Diffusion length (L) cm
2.48	8.6×10^{-4}	0.049×10^3	0.20
2.38	7.2×10^{-4}	0.087×10^3	0.16
2.28	8.2×10^{-6}	1.4×10^3	0.11
2.17	7.9×10^{-6}	4.1×10^3	0.18
2.06	9.3×10^{-6}	4.3×10^3	0.20
1.80	1.4×10^{-5}	5.6×10^3	0.28
1.52	2.1×10^{-5}	9.3×10^3	0.45

Hall-effect measurements fall in a range about 200 cm^2/v sec, which would give a value about 0.5 for D; for holes the mobility is supposed to be still lower than that of electrons. This shows that the value for D computed from photocurrent measurements (Table IV) cannot be the electron or hole diffusion coefficient.

Before concluding definitely as to the nature of the diffusion process, we shall examine another possibility, i.e., the transport of energy from a secondary luminescent process. Although our experiments obliged us to exclude the possibility of appreciable energy transport by light diffusion or luminescence, there exists some parallelism between luminescence and transfer photocurrent that deserves more careful examination.

Broser[18] has performed a series of experiments from which he concludes that the energy transport at considerable distances is propagated predominantly by a light process (internal reflection or scattering of the light, or luminescence following the time of direct illumination) and transmitted through the crystal. The corresponding transfer photocurrent would then be caused by absorption of the scattered radiation. This mechanism seems to make a negligible contribution to the transfer photocurrent in the impurity concentration range of our samples in view of the following considerations: (1) cracking the crystal eliminates the transfer photocurrent, (2) light-flash, photocurrent pulse experiments indicate a dependence of transit time on the slit-electrode distance; (3) the transfer photocurrent spectra show fine structure at low temperatures; (4) the spectral response of transfer photocurrent is different from luminescence excitation efficiency and is independent of slit-electrode distance; and (5) the quantum efficiency is too high for a process involving reabsorption of light.

TABLE V. Dependence of transit time t_M and maximum photocurrent h on incident radiant intensity ($\lambda = 6056$ A).

ϕ^{a} erg/sec	Room temperature Slit-electrode distance, 0.25 cm $10^5 t_M$ (sec)	h ($\pm 10\%$)
0.41	7	3.8
2.51	2	8.5
13.8	2.5	11–15
76.8	1	46
189	...	150
391	1	310
551	0.8	380

[a] The total luminous flux through the slit over the crystal.

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[18] I. Broser (private communication).