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COMPARISON OF SURFACE-EXCITED AND VOLUME-EXCITED PHOTOCONDUCTION IN CADMIUM SULFIDE CRYSTALS

RADIO CORPORATION OF AMERICA
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Surface-excited photoconduction is compared with volume-excited photoconduction in cadmium sulfide crystals with a wide range of sensitivities. Measurements are presented as a function of exciting wavelength for (1) spectral response, (2) photocurrent as a function of light intensity, (3) photocurrent decay time, (4) infrared quenching, and (5) thermally stimulated current. The results supply additional evidence that the free electron lifetime for surface excitation is smaller than the lifetime for volume excitation because of a higher rate of recombination at the surface, associated with the adsorption of moist air on the crystal surface.

Correlations are found between the distribution of traps, as indicated by thermally-stimulated-current measurements, and both (1) the low-temperature spectrum for photoconduction-photostimulation published by Lambe for CdS:Ag, and (2) the variation of photocurrent with light intensity.

Introduction

Recent investigations on the properties of photoconductor powders and sintered layers[1] have made evident the importance of photoconduction excited by strongly-absorbed radiation, i.e., photoconduction which occurs principally near the surface. In the literature, the discussion of surface-excited and volume-excited photoconduction in cadmium sulfide has been given in terms of the shape of the spectral sensitivity curve. For most crystals of cadmium sulfide, there is a sharp maximum of photosensitivity at a wavelength corresponding approximately to the absorption edge.[2-5] The decrease in sensitivity for wavelengths shorter than that of the absorption edge is associated with excitation confined to regions of the crystal near the surface.

The photosensitivity for surface excitation could be less than that for volume excitation if either the mobility or the lifetime of the free electron were smaller near the surface than in the volume of the crystal. Experimental results to date, from measurements of the spectral sensitivity and photocurrent decay time,[6-9] point to a smaller lifetime for a free electron for surface excitation than for volume excitation as the probable cause of the low sensitivity for surface excitation. DeVore[10] has shown that the observed shapes of spectral sensitivity curves can be described in terms of the effect of high surface recombination.

The lifetime for surface excitation may be smaller than that for volume excitation either because[11,12] (1) strongly-absorbed excitation creates a high density of free carriers near the surface, resulting in the predominance of bimolecular recombination and a decreased lifetime for the free electrons, or (2) there are either a greater density of recombination centers near the surface than in the volume, or their capture cross-section for free electrons is larger, i.e., the surface is inherently less sensitive than the volume. If the first mechanism is effective in producing a maximum in the spectral sensitivity curve, the photocurrent will vary as a lower power (near 0.5) of the light intensity for strongly-absorbed than for slightly-absorbed radiation.

It is the purpose of this bulletin to compare surface-excited photoconduction with volume-excited photoconduction, in cadmium sulfide crystals with a wide range of photosensitivities. In addition to measurements of spectral response and decay time, such as have been described in previous publications, measurements were made as a function of exciting wavelength on (1) the variation of photocurrent with light intensity, (2) infrared quenching, and (3) thermally stimulated current. Most of the results can be explained by assuming that the surface is inherently less sensitive than the volume, the surface-sensitivity being very dependent on the atmosphere surrounding the crystal.

Experimental

Measurements were made in the photoconductivity apparatus previously described.[13] Single crystals of cadmium sulfide without intentionally added impurities were prepared; electrical contacts were made using melted indium electrodes[14,15] on the same side of the crystal as the exciting radiation.

Excitation was primarily with a 500-mm Bausch and Lomb monochromator, used to give 50A resolution. In measurements of infrared quenching, the monochromator was used as the source of secondary radiation, and the source of primary (bias) radiation was a GE 1493 incandescent lamp with an interference wedge made by Geraetebau-Anstalt Balzers of the Principality of Liechtenstein. When used with a 1 mm slit, the transmission through this wedge has a half-width at least as small as 100A. Variations in excitation intensity were made by the interposition of calibrated neutral wire-mesh filters. The currents were recorded on a Leeds and Northrup X-Y recorder. Decay times were measured with a Type 535 Tektronix oscilloscope. Unless otherwise noted, measurements were made in an atmosphere of room air.

Discussion of Results

Spectral Response

Fig. 1 shows the spectral response for five crystals of cadmium sulfide. The ratio between the photocurrent at the absorption edge and the photocurrent for strongly-absorbed excitation (hereafter called simply the *sensitivity-ratio)* increases with the value of the photocurrent at the absorption edge, i.e., with the volume sensitivity. The maximum occurs at that wavelength for which the incident radiation penetrates most of the crystal, but for which most of the radiation is absorbed.

The variation of photosensitivity among the crystals of "pure" CdS measured must be attributed to a purely random incorporation of crystal defects (or conceivably of traces of beneficial impurity) during growth. It is clear from Fig. 1 that the long-wavelength response increases very markedly with volume sensitivity, indicating the presence of levels above the filled band.

Fig. 2 summarizes the variation of the sensitivity-ratio as a function of the volume sensitivity for eighteen crystals of CdS selected at random. Only two of the points fail to fall on the curve, which indicates an increase in sensitivity-ratio with increasing volume sensitivity from a value of unity at low volume sensitivities.

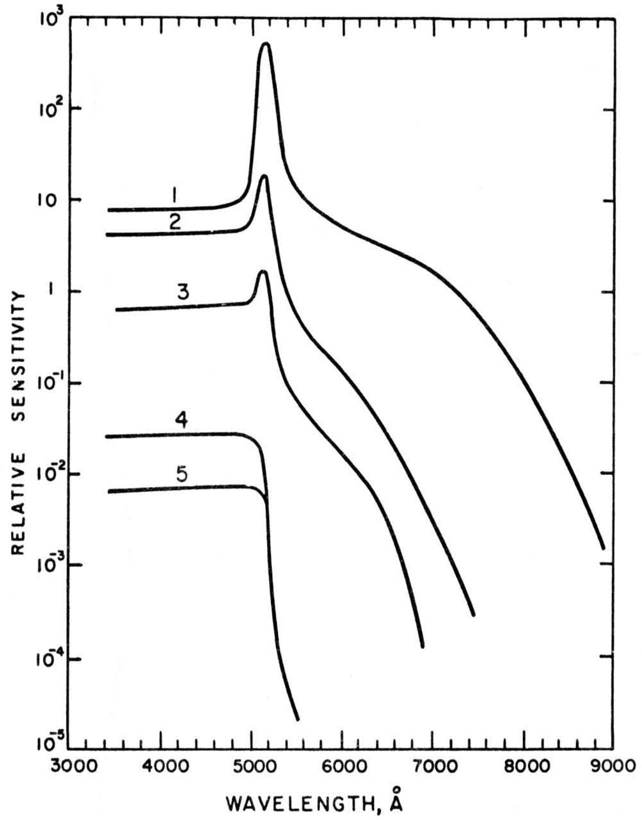

Fig. 1 – Spectral response curves for five crystals of cadmium sulfide prepared from the vapor phase without added impurity, measured with equal photon flux at each wavelength.

Photocurrent vs. Light Intensity

In most crystals the exponent n in the power-law relation between photocurrent and light intensity ($I \propto L^n$) undergoes an abrupt change as the wavelength of excitation passes through the absorption edge. Results for ten crystals are summarized in Table I.

The values of n given in Table I refer to the variation of photocurrent with light intensity either (1) over the whole light intensity range investigated, when there was no transition to a smaller value of n at high light intensities, or (2) only over the lower part of the light intensity range, when there was a transition to a smaller value of n at high light intensities. The light intensity was varied over a range of 2000:1, maximum intensity being that of full monochromator output. In Table I, the "apparent sensitivity-ratio" is the ratio measured for maximum excitation used; the "extrapolated sensitivity-ratio" is the ratio calculated for that same light intensity, assuming no transition in n at high light intensities. In crystals that do not show a transition in n to lower values for high light intensities, therefore, the apparent and the extrapolated sensitivity-ratio are the same.

The data of Table I indicate that Δn, the magnitude

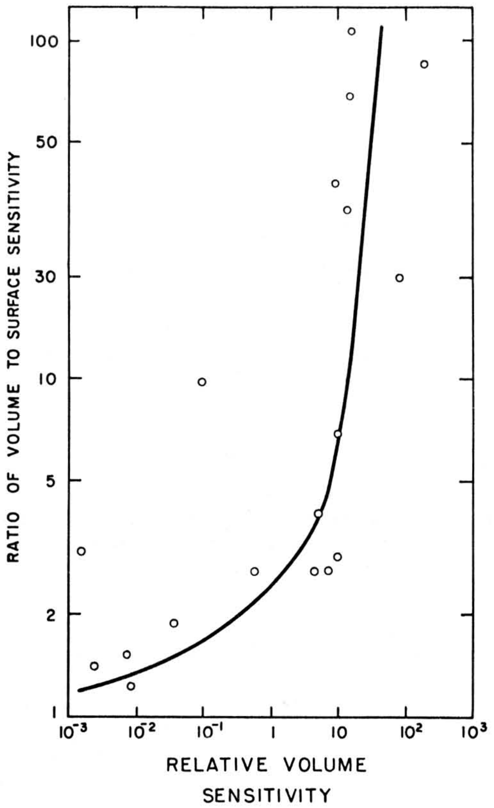

Fig. 2 – The ratio of the maximum photocurrent to the photocurrent for excitation inside the absorption edge as a function of the maximum photocurrent for eighteen crystals of cadmium sulfide prepared without added impurity, randomly selected.

of the change in n at the absorption edge, shows no simple correlation with the sensitivity-ratio. Even for the three crystals listed where the sensitivity-ratio is approximately unity, only one crystal shows a Δn of zero. For strongly-absorbed light the value of n is never smaller than 0.8, which is considerably different from the value of 0.5 which would be expected from bimolecular recombination. The exact value of n is dependent on the distribution of levels in the forbidden gap near the conduction band;[12] that the density or the distribution of these levels might be somewhat different between surface and volume regions of the crystal is not unreasonable.

Specific examples of the variation of n with wavelength for three representative crystals are given in Fig. 3. Fig. 3-a shows the variation in n with wavelength for a crystal which did not show a transition in n to a lower value for high light intensities. Fig. 3-b shows the variation of n at low intensities, n at high light intensities, and the photocurrent at the transition between low-light-n and high-light-n, for a crystal showing a transition in n to a lower value for high light intensities. The high-light-n, when a transition has taken place, generally shows a minimum at the absorption edge. The photocurrent at the transition in n increases sharply at the absorption edge; the interpretation of this is discussed in the section on thermally stimulated currents. Fig. 3-c shows the one example found for a crystal with unity sensitivity-ratio and no change in n across the absorption edge.

TABLE I

Variation of n Across the Absorption Edge

Crystal No.	Crystal Dimensions, mm^3 *	Apparent Sens.-Ratio	Extrap. Sens.-Ratio	Avg. n		Δn
				$\lambda<\lambda_e$	$\lambda>\lambda_e$	
2	1.3x1.3x0.031	51	51	0.90	1.07	0.17
8	1.0x0.7x0.0087	44	44	0.91	1.00	0.09
16	0.5x2.0x0.056	3	25	0.95	1.03	0.08
5	1.0x0.9x0.020	15	18	0.83	1.00	0.17
10	1.0x1.3x0.046	1.7	13	0.83	0.99	0.16
11	1.1x1.3x0.036	1.6	11	0.93	1.00	0.07
18	–	7	7	0.82	1.00	0.18
17	1.0x1.0x0.026	1.9	1.9	0.96	1.01	0.05
12	–	1.6	1.6	0.98	1.11	0.13
15	1.4x1.6x0.0087	1.2	1.2	1.14	1.14	0.00

* Dimensions given as length (between electrodes) x width x thickness.

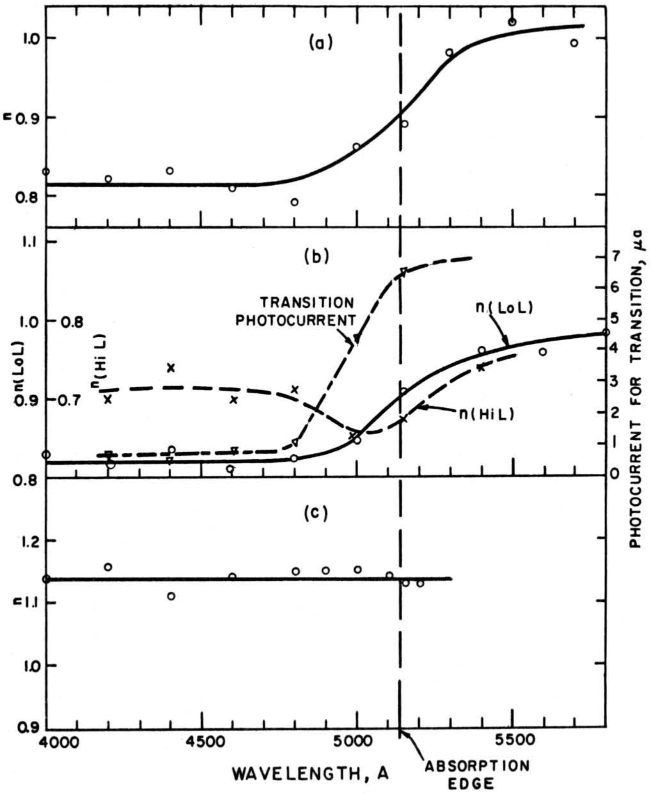

Fig. 3 – Variation of n with excitation wavelength, for (a) crystal 18, (b) crystal 5, and (c) crystal 15. Data in (b) also show difference between n at low light intensities and n at high light intensities, and the variation of the photocurrent at which the transition occurs between low-light-n and high-light-n.

In order to measure the variation of n with temperature, a crystal of CdS was heated to 125 degrees C in dry helium and measurements of n were made at various temperatures during the cooling to room temperature. Fig. 4 shows the results; both volume excitation and surface excitation are characterized by a decreasing n with decreasing temperature, but Δn appears to be approximately temperature independent. The values of n obtained at room temperature after this cooling, however, were quite different from those obtained initially in room air. The following experiment, data for which are shown in Fig. 5, was performed to prove that the nature of the surface of the crystal had been changed by the heating in dry helium. The crystal was heated fairly quickly to 110 degrees C (Fig. 5-a, Curve 1), was allowed to stand at 110 degrees C for about an hour (Fig. 5-a, Curve 2), and was then slowly cooled to room temperature (Fig. 5-a, Curve 3). The photocurrent for surface excitation increased only slightly during the heating from room temperature to 100 degrees C, but then increased by a factor of about three while standing at 110 degrees C. Upon cooling to room temperature the photocurrent was about two-and-a half times its initial value. Fig. 5-b shows the decay of this additional surface photosensitivity upon exposure to room air. First, room air was admitted at a high rate through a liquid nitrogen trap; then the trap was removed from the liquid nitrogen bath; then the trap was warmed by the application of heat externally. Exposure of the crystal to moist air causes the surface photocurrent to decay slowly to the value it had initially before heating in helium. These results are in agreement with those previously reported.[6-8]

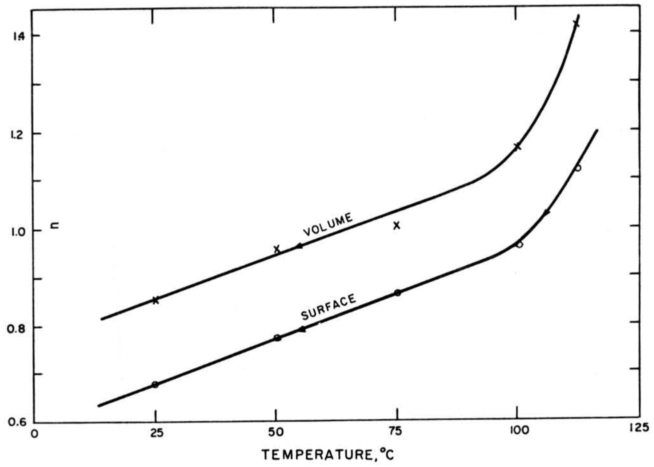

Fig. 4 – Variation of n with temperature for both volume and surface excitation for crystal 18. Crystal was heated to 125 degrees C in dry helium and measurements were made during cooling.

Table II compares the sensitivity-ratio, the surface-excited photocurrent, and the values of n for three different conditions of the surface of the same crystal. As the sensitivity-ratio increases, the value of n for surface excitation apparently approaches unity; this is additional evidence against bimolecular recombination at the surface because of density of excitation, being an important factor in determining the sensitivity-ratio.

Infrared Quenching

Measurements of infrared quenching were made on several crystals of cadmium sulfide as a function of the primary radiation wavelength. For crystals with a large sensitivity-ratio, the percent quenching (for the same bias photocurrent at constant voltage, excited by the primary radiation) was considerably larger for primary radiation with wavelengths longer than that of the absorption edge than for primary radiation with wavelengths shorter than that of the absorption edge. An example of such a result is given in Fig. 6-a. The shape of the infrared quenching spectrum is the same for both volume and surface excitation, and the same as has been previously reported.[16]

Most of the crystals with approximately unity sensitivity-ratio have low sensitivity and do not show meas-

TABLE II

Variation of Photoconduction with the Condition of the Surface
(Crystal 18)

Surface Condition	Sensitivity Ratio	Surface-Excited Photocurrent, Microamp.	*n*	
			Surf.	Vol.
Heated to 110°C in dry helium and cooled to room temperature without exposure to room air	2	1.5	0.68	0.85
Standing in room air	5	0.5	0.82	0.96
Soaked in acetone and standing in room air	43	0.07	0.95	1.03

urable infrared quenching. One such crystal, however, did show infrared quenching which did not vary appreciably with the wavelength of the primary radiation, as indicated in Fig. 6-b.

The detailed variation of percent quenching with wavelength of the primary radiation is given in Fig. 7, for different secondary wavelengths and bias currents, for a crystal with a large sensitivity-ratio. The percent quenching increases rapidly at the absorption edge, and then in most cases decreases again for primary radiation wavelengths considerably longer than that of the absorption edge. The percent quenching for surface excitation was decreased after the acetone-soaking of the crystal

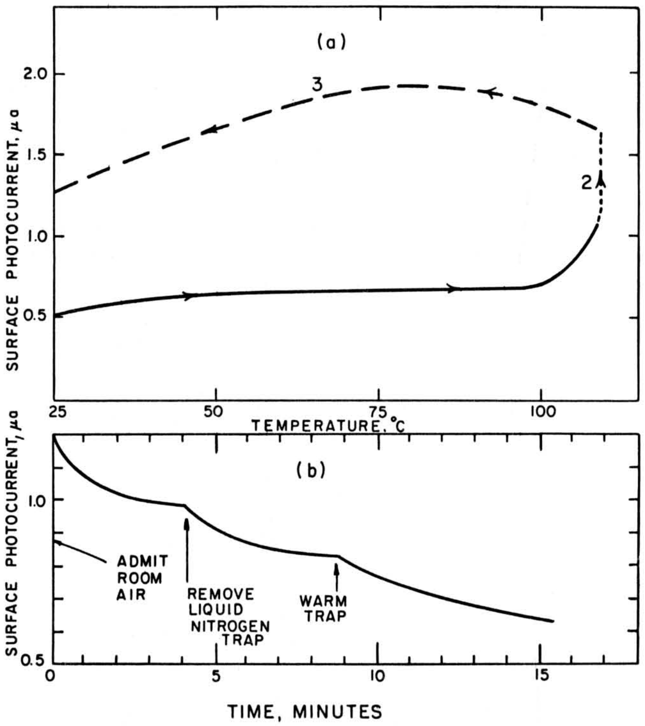

Fig. 5 – (a) Variation of surface-excited photocurrent for crystal 18 with temperature in an atmosphere of dry helium. Part 1 of the curve is for a rapid heating, Part 2 a period of standing at 110 degrees C, and Part 3 a slow cooling. (b) Decay of surface-excited photocurrent with time, but with continuous excitation, after heating in dry helium, upon admission of moist air to the system.

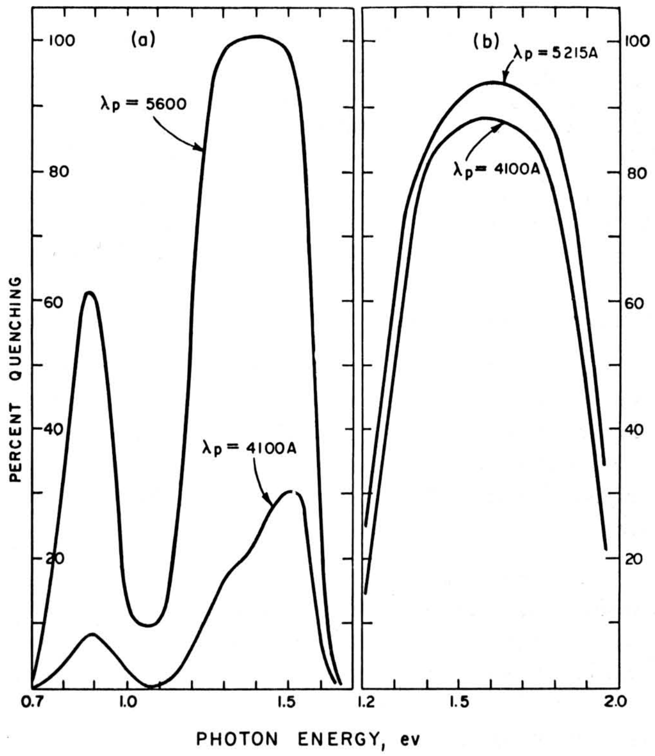

Fig. 6 – Infrared quenching spectra for (a) crystal 8 for primary radiation wavelengths of 4100A and 5600A, (b) for crystal 17 for primary radiation wavelengths of 4100A and 5215A.

which reduced the photocurrent for surface excitation, as indicated in Table II.

The interpretation of the measurements of infrared quenching can be made most conveniently in conjunction with the discussion of the measurements of decay time which follows.

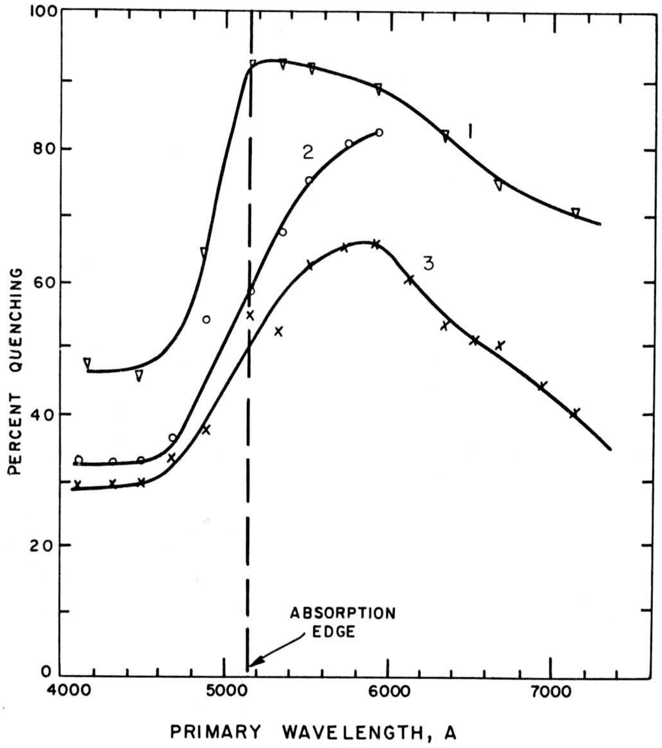

Fig. 7 – Percent quenching for crystal 2 as a function of primary wavelength for (1) a secondary wavelength of 9200A and a bias photocurrent of 0.05 microamp for 100 volts applied, (2) a secondary wavelength of 9200A and a bias photocurrent of 0.17 microamp for 100 volts applied, and (3) a secondary wavelength of 14,000A and a bias photocurrent of 0.05 microamp for 100 volts applied. Bias photocurrent was varied by varying the primary radiation intensity.

Photocurrent Decay Time

Measurements of the decay time of the photocurrent in room air show that the decay time for surface excitation is always considerably less than that for volume excitation, regardless of whether the measurements are made for equal-photon-flux-incident or equal-photocurrent-excited.

It is desired to compare the sensitivity-ratio with the ratio of the lifetime of a free electron for volume excitation to that for surface excitation. A quantitative correlation between the lifetime and the measured decay time is complicated in most crystals, however, by the effects of trapping, which act to make the measured decay time longer than the true lifetime.[12] In order to overcome the complications introduced by trapping, it is desirable to measure the decay time at as high a light intensity as possible, and to determine the decay time from the initial decay of photocurrent after the cessation of excitation.

Data from one of the crystals which showed close agreement between measured decay times and sensitivity-ratio are shown in Fig. 8. The sensitivity-ratio for this crystal was about seven, and the ratio of decay times is also the same order of magnitude. As indicated in Fig. 8, the decay time (measured as the time for the current to decrease to 84 percent of its initial value) increases from about 8 millisec. for surface excitation to about 65 millisec. at the absorption edge, and then decreases somewhat for longer wavelengths. Similar correlations between decay times and sensitivity-ratio have been previously reported.[7,9]

Table III shows the effect of irradiation by infrared on the decay time. For these measurements, infrared was obtained from a GE 1493 incandescent lamp with an infrared filter passing over 8500A. The data show that the effect of the infrared in quenching the photocurrent excited by the primary radiation is directly explainable in terms of the decrease in lifetime caused by the infrared.

The variation of percent quenching with primary wavelength can be explained by a consideration of the effect of infrared on the lifetime of a free electron. The lifetime of a free electron in the absence of infrared will be given by:

$$t = 1/(CvS) \qquad (1)$$

where t is the lifetime, C is the number of recombination centers per unit volume, v is the thermal electron velocity, and S is the capture cross-section of a recombination center for an electron.[12] According to the postulated mechanism for infrared quenching described in a previous

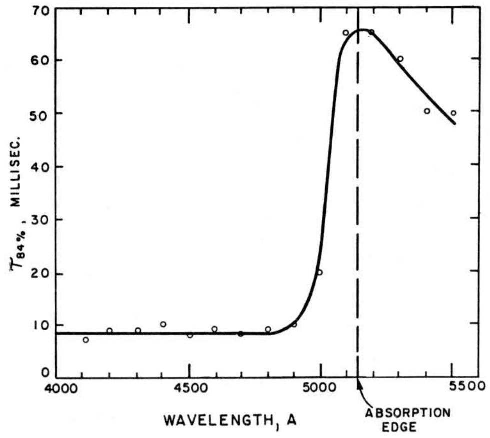

Fig. 8 – The time for the photocurrent to decay to 84 percent of its initial value as a function of the excitation wavelength for crystal 18; measured at constant voltage and constant photocurrent.

TABLE III

Infrared Quenching and Photocurrent Decay Time
(Crystal 18)

Primary Wavelength, A	Light Intensity *	Photocurrent #		Decay Time, msec. ##		Photo-current Ratio **	Decay Time Ratio **	$N_s' v S_s$	$N_v' v S_v$
		No IR	With IR	No IR	With IR				
4300	100	0.48	0.36	7	5	0.75	0.72	5.9×10^{-2}	
4800	100	0.87	0.69	6	5	0.79	0.83	3.3×10^{-2}	
5120	100	10	9.2	7	6.5	0.92	0.93		1.1×10^{-2}
	37	4.5	3.2	23	18	0.71	0.78		1.2×10^{-2}
	14	2.1	1.1	50	27	0.52	0.54		1.7×10^{-2}
5200	100	6.5	5.4	13.4	12	0.83	0.89		0.9×10^{-2}
	37	2.7	1.9	53	30	0.70	0.57		1.5×10^{-2}
	14	1.2	0.65	70	35	0.54	0.50		1.4×10^{-2}
5350	100	0.91	0.49	80	40	0.54	0.50		1.2×10^{-2}

* Light intensity of 100 represents full uncorrected monochromator output.
** Ratio of value with infrared quenching to that without infrared quenching.
\# Photocurrent in microamps measured with 100 volts applied.
\#\# Time to decay to 84% of the initial value.

publication,[16] assume that infrared quenches photoconduction by raising electrons from the filled band to fill centers with a small capture cross-section for free electrons, the holes formed by the infrared migrating to centers with a large capture cross-section for free electrons, once the hole has been captured. Then the lifetime of a free electron in the presence of infrared will be given by:

$$t' = 1/(C'vS) \qquad (2)$$

where C' is the new number of available large capture cross-section centers per unit volume.

It is possible to write:

$$C' = C + N' \qquad (3)$$

where N' is the equilibrium number of large capture cross-section centers per unit volume made available for recombination by the infrared.

By adding subscripts "s" to signify surface and "v" to signify volume, the following relationships may be set down between the lifetime with infrared and the lifetime without infrared, by combining Equations 1-3:

$$1/t_v' = 1/t_v + N_v' v S_v \qquad (4a)$$

$$1/t_s' = 1/t_s + N_s' v S_s \qquad (4b)$$

Calculated values of $N_v' v S_v$ and $N_s' v S_s$ have been listed in Table III.

If it is assumed, for the sake of calculation, that N_v' is about equal to N_s', the effective capture cross-section for centers at the surface is about two to seven times larger than that for centers in the volume. If a value of N' of about $10^{12}/\text{cm}^3$ is chosen, the effective capture cross-section for surface centers is about 3-6 x 10^{-21} cm^2, the capture cross-section for volume centers is about 0.9-1.7 x 10^{-21} cm^2, and the density of recombination centers is about 10^{15}-$10^{16}/\text{cm}^3$ for both surface and volume.

Thermally Stimulated Current

Thermally stimulated current measurements were made on several CdS crystals for both surface excitation and volume excitation. The purpose of these measurements was (1) to determine whether there were any gross differences in the thermally-stimulated-current curves for surface and volume excitation, (2) to check whether the thermally stimulated current for surface excitation was confined to only a fraction of the crystal, by determining whether it was necessary to assume a smaller effective volume for surface excitation than for volume excitation to make the trap depths (as calculated from the peak conductivity) the same for both types of excitation, and (3) to see if a correlation existed between the transition in n with increasing light intensity, illustrated in Fig. 3-b, and the location of the major traps.

Several typical examples of thermally-stimulated-current curves for both surface and volume excitation are shown in Fig. 9. There are no large differences in the location of major trap depths between surface and volume excitation. It was, however, always observed that thermally stimulated current at low temperatures, corresponding to the emptying of traps near the conduction band, was much more prominent for volume excitation. This fact is probably not caused by an actually greater density of shallow trapping centers in the volume than in the surface, but is probably associated with the accentuation of the difference in the free electron lifetimes at low temperatures for volume and surface excitation. Surface excitation might well produce a higher density of empty recombination centers in the neighborhood of the trapped electrons than volume excitation; the first electrons freed from traps during the heating after surface excitation would have a relatively shorter lifetime than electrons freed after most of the recombination centers had been refilled.

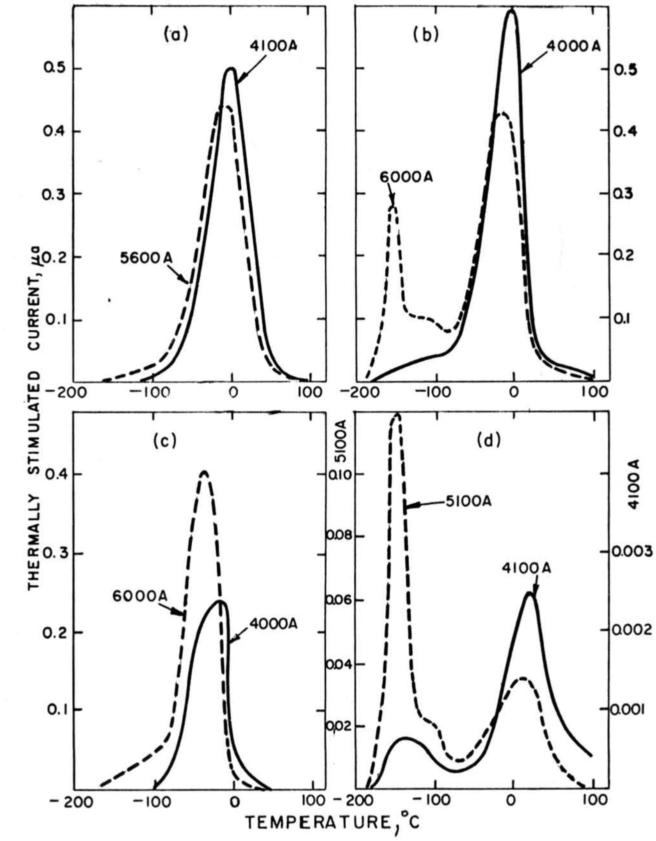

Fig. 9 – Thermally-stimulated-current curves measured at a heating rate of 0.77 degrees/sec. for (a) crystal 10 for excitation by 4100A and 5600A, (b) crystal 5 for excitation by 4000A and 6000A, (c) crystal 16 for excitation by 4000A and 6000A, and (d) crystal 8 for excitation by 4100A (right ordinate) and 5100A (left ordinate). Applied voltage was 100 volts.

Calculations of the trap depths are given in Table IV. The results, together with those of previous studies,[13,16] show that the traps with depth of about 0.4 ev are fundamentally characteristic of the CdS crystal. As has been previously reported,[16] there are some six other trap depths in the range between 0.2 and 0.8 ev commonly found in many pure CdS crystals, the most frequently found in the present investigation being those at about 0.2 and 0.7 ev. It is worth while in this connection to compare the location of these characteristic traps with the low-temperature infrared stimulation of photoconduction, after previous excitation, reported by Lambe[9] and ascribed to the presence of silver impurity. Such a comparison is made in Table V. The correlation between defect trap depths in pure crystals and experimental infrared stimulation peaks suggests that the use of the infrared stimulation data to argue specifically for a location of the silver level near the conduction band should be further investigated.

The attempt to determine whether measurements of thermally stimulated current would reveal that currents resulting from surface excitation were confined to only a fraction of the crystal resulted in the experimental finding of every shade of possible result. (1) Thermally-stimulated-current curves for surface and volume excitation were found to be practically identical for some crystals, with the same calculated trap depths assuming both currents were passed by the whole crystal, as illustrated by the curves for crystal 10 in Fig. 9-a. (2) Definite differences in the curves for surface and volume excitation were found for some crystals, but the calculated trap depths were the same assuming both currents were passed by the whole crystal, as illustrated by the curves for crystal 5 in Fig. 9-b. (3) Curves for surface and volume excitation were similar for some crystals, but in order to make the calculated trap depths the same for both types of excitation, it was necessary to assume that the surface-excited currents were confined to about 1/10 of the crystal, as illustrated for crystal 16 in Fig. 9-c. (4) Curves for surface and volume excitation differed very markedly for some crystals, and it was necessary to assume that the surface excited currents were confined to less than about 1/100 of the crystal to make the calculated trap depths the same for surface and volume excitation, as illustrated for crystal 8 in Fig. 9-d.

Another method for checking on whether surface-excited currents are effectively limited to a small fraction of the crystal is by observing the transition from low-light-n to high-light-n as the excitation wavelength is varied through the absorption edge, as illustrated for crystal 5 in Fig. 3-b. If it is assumed that this transition occurs for a critical location of the steady-state Fermi-level, it would be expected that the transition photoconductivity would increase as the excitation was changed from surface

TABLE IV

Comparison of Trapping Data with Transition in *n* for Several Crystals

Crystal	Calculated Trap Depths, ev *		Calculated Fermi-level for *n* Transition, ev **		Density of Free Electrons at *n* Transition #
	Surface	Volume	Surface	Volume	
2	0.18	0.18			
	0.42	0.42	None	0.38	4×10^{12}
10	0.45	0.44	0.50	0.48	5×10^{10}
8	0.28	0.19			
	0.56	0.46	None	None	–
5		0.19			
	0.41	0.40	0.39	0.36	2×10^{12}
11	0.43	0.42	0.49	0.47	10^{11}
16	0.47	0.43	None	0.50	3×10^{11}
17	0.48	0.44			
	0.79	0.69	None	None	–

* Obtained from a calculation of the location of the Fermi-level corresponding to the peak conductivity and temperature for the thermally-stimulated-current curves. The conductivity was calculated as if the *whole* crystal were participating in the current flow for the values given.

** Obtained from a calculation of the location of the Fermi-level corresponding to the conductivity at which the value of *n* changes with increasing light intensity at room temperature. The conductivity was calculated as if the *whole* crystal were participating in the current flow for the values given.

\# Calculated from the data for volume excitation, assuming a mobility of 100 cm^2/volt sec.

TABLE V

Comparison of Characteristic Trap Depths with Photoconductivity Photostimulation Data of Lambe[9]

Characteristic Trap Depths of Pure CdS, ev *	Photoconductivity Photostimulation Maxima of CdS:Ag (after Lambe)	
	Microns	ev
0.21	5.0	0.25
0.30	4.2	0.30
0.38		
0.42	2.8	0.44
0.52		
0.70	Begins at 1.8	Begins at 0.69
0.77		

* As indicated in this paper and reference 16, the most prominent trap depths in more sensitive crystals are often 0.2, 0.3, 0.4, and 0.7 ev.

to volume, in order that the same effective conductivity might be found in surface as in volume regions of the crystal at the *n*-transition. The data of Fig. 3-b indicate on the basis of such an analysis that the surface excitation is restricted to about 1/10 of the crystal. But as pointed out above, the thermally-stimulated-current data did not indicate any restriction of the surface-excited current for crystal 5. Thus it can only be concluded that the proportion of the crystal involved in surface-excited current flow differs from crystal to crystal and with the type of measurement performed.

Finally, the cause of the transition in *n* should be considered. Table IV shows that for almost every crystal showing a transition in *n*, the corresponding energy difference between the location of the Fermi-level and the bottom of the conduction band was about the same as, or slightly larger than, the major trap depth of 0.4 ev.[13] Table IV also shows that the density of free electrons at the conductivity corresponding to the transition in *n* for volume excitation, is of the order of 10^{10}-$10^{12}/\text{cm}^3$, and hence is much smaller than the density of trapping centers which is about 10^{15}-$10^{17}/\text{cm}^3$. These facts indicate that the transition in *n* is not occurring when the density of free electrons exceeds the density of trapping centers (thus producing bimolecular recombination), but is occurring when the Fermi-level is about to rise into the main group of traps, the transition in *n* being the result of bimolecular recombination caused by more electrons being trapped above the Fermi-level than below.[12]

Summary

The fact that the photosensitivity of most cadmium sulfice crystals is smaller for surface excitation by strongly-absorbed radiation than for volume excitation by slightly-absorbed radiation is caused by a smaller free lifetime for surface-excited electrons than for volume-excited electrons. This smaller free-electron lifetime for surface excitation is caused by a higher recombination rate at the surface than in the volume, associated with the adsorption of moist air on the surface of the cadmium sulfide crystal. The higher rate of surface recombination may be associated with a greater density of recombination centers of equal capture cross-section at the surface than in the volume (either because of surface states or because of the effect of adsorbed vapors on the shape of the band-edges at the surface), with a greater capture cross-section for surface recombination centers than for volume centers, or with a combination of both. The second possibility seems the most favored from the data previously described.

These conclusions are supported by the following experimental evidence cited in this bulletin:

(1) The larger the free electron lifetime in the volume (i.e., the greater the volume sensitivity), the larger is the sensitivity-ratio (the ratio of photocurrent at the maximum of the spectral response curve to the photocurrent for strongly-absorbed radiation). Since the free electron lifetime at the surface will be limited by the adsorption of molecules producing a high recombination rate, the ratio of volume to surface lifetime will become greater the larger the volume lifetime. The effect of surface recombination rate on the spectral response will also depend on the rate with which excited electron-hole pairs are able to diffuse away from surface regions of the crystal, which in turn will depend upon the lifetime of the minority carriers, the holes. Since the hole lifetime will be larger the less sensitive the crystal, the less sensitive crystals will be affected to a smaller extent by surface recombination than more sensitive crystals with smaller free hole lifetimes.

(2) Lower surface sensitivity because of a high density of excitation resulting in bimolecular recombination with resultant decrease in free electron lifetime (rather than because of an inherently lower surface sensitivity) is discounted because (a) the values of *n* for surface excitation have not been found to be lower than 0.8, which is considerably larger than the value of 0.5 which should result from bimolecular recombination, (b) the value of *n* for surface excitation approaches unity, at least for some crystals, as the sensitivity-ratio increases with surface treatment, and (c) some insensitive crystals with small volume lifetime have a sensitivity-ratio of unity even though the density-of-excitation effect should still be present at the surface.

(3) Measurements of the decay time itself for surface and volume excitation, under conditions which should make the decay time roughly comparable to the true lifetime, show a sharp increase in decay time as the excitation wavelength increases past the absorption edge.

(4) The interpretation of the results of infrared quenching in terms of a smaller surface than volume lifetime are able to explain (a) the rapid increase in percent quenching as the primary wavelength increases past the absorption edge in crystals with a large sensitivity-ratio, (b) the absence of a change in percent quenching at the absorption edge in crystals with a sensitivity-ratio of unity, (c) the decrease in percent quenching for excitation by primary wavelengths much longer than that of the absorption edge, excitation by such wavelengths resulting in a smaller free electron lifetime (as indicated by smaller measured decay times), because of excitation directly from bound states in which the excited hole is trapped, and (d) the decrease in percent quenching for

surface excitation after the acetone treatment which had caused a further decrease of the lifetime for free electrons near the surface.

(5) The sensitivity-ratio was reduced by heating the crystal in dry helium to free the surface from adsorbed moist air; the sensitivity-ratio was reversibly increased again by readmitting moist air to the system.

In addition to the above results, a study of thermally stimulated currents emphasized the characteristic nature of traps located at about 0.4 ev below the conduction band in pure cadmium sulfide crystals. A good correlation can be made between the principal trap depths in cadmium sulfide crystals without added impurity and the peaks of the low-temperature spectrum of the photostimulation of photoconduction for CdS:Ag crystals reported by Lambe.[9] Although Lambe ascribed these peaks to absorption by the silver, the present data indicate that they may be fundamental to cadmium sulfide itself.

A transition in *n* with increasing light intensity from a value near unity to a value near one-half was shown, for many cadmium sulfide crystals, to occur, not when the density of free electrons exceeds the density of trapped electrons, but when the Fermi-level is about to rise into the main group of characteristic traps.

Further research on surface-excited and volume-excited photoconduction might well be directed toward (1) measurements of electron mobility as a function of excitation wavelength for a crystal with a large sensitivity-ratio to determine whether the mobility for surface excitation is the same as that for volume excitation, (2) measurements of photoconduction phenomena for cadmium sulfide crystals in controlled atmospheres of other gases, and (3) measurements on cadmium selenide crystals which show a large transition from an *n* greater than unity to an *n* less than unity.[16,17]

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