Positive Hole Motion and Photovoltaic Effects in Zinc Cadmium Sulfide Phosphors*

Hartmut Kallmann, Bernard Kramer,† Frank Spagnolo,‡ and Grace Marmor Spruch
Department of Physics, New York University, New York, New York
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Information was gained about the free carriers in activated and unactivated ZnCdS phosphors through a study of the photovoltaic effect in these materials. The photovoltages produced in activated ZnCdS phosphors by illumination with various wavelengths parallel the absorption spectra of these materials and do not depend strongly upon the type of activation. The photovoltages are brought about by a diffusion of electrons from the excited region into the interior of the sample. The addition of lead as a coactivator reduces the voltage because it increases the recombination rate. In unactivated ZnS the size of the photovoltage again parallels the absorption spectrum but its sign is reversed, indicating that positive charges are the more mobile carriers. Unactivated CdS exhibits voltages similar to the activated materials. Insulating one electrode affects the size of the photovoltage appreciably only for the unactivated materials, showing that charge exchange at the electrode is important for them and not for the activated materials.

INTRODUCTION

PHOTOVOLTAGES have their origin either in the excitation of a material and the diffusion of the excited charges into the interior, or in an injection of charge from one type of material into another.[1] In the first case one type of carrier should have a considerably greater mobility than the other, and the diffusion voltage within the electrode must be small. This case occurs primarily when a material is inhomogeneously excited. The second case occurs in organic materials, when positive holes are injected into the organic materials,[2] in CuO-coated CdS, where electrons are injected into the CdS,[3] and at p-n junctions.[4] Thus the measurement of such voltages provides information about the motion and type of carrier involved in the conduction process.

Photovoltages in various ZnCdS phosphors were studied as functions of the cadmium content and activation, as well as the wavelength of excitation. It was necessary to work with powdered materials since single crystals of definite ZnCd content and specific activation cannot readily be produced. In order to discriminate between the voltages produced in the bulk of the material and those originating in charge exchange at the electrode, the phosphors were studied when electrodes were applied to them directly, and when Mylar insulators separated them from the electrodes. The materials investigated were unactivated ZnS; unactivated CdS; ZnS:Cu; ZnS:Ag; ZnCdS:Ag (20% Cd); ZnCdS:Ag (70% Cd); ZnCdS:Cu, Ni;

ZnS:Cu, Pb; and ZnS:Mn. The percentage of cadmium is the percentage by weight.

EXPERIMENTAL PROCEDURE

Thin phosphor layers, about 20 mg/cm² in thickness, were deposited with very little binder between two conductive glass electrodes, and the edges of the arrangement sealed with epoxy resin to keep out moisture. The binder did not interfere with the conductivity of the sample.

In those experiments where the phosphor was insulated from the electrode, a sheet of clear Mylar 7×10^{-4} cm in thickness was placed between the phosphor and one of the glass plates.

The source of excitation was a General Electric 100 w H4AB mercury lamp. Interference and cutoff filters were used rather than a monochromator to isolate different regions of the spectrum, in order to keep the intensity high. The apparatus was so constructed that both surfaces of the sample could be illuminated. The other light source was a General Electric BMG 100 w tungsten lamp, which was used in conjunction with filters.

The photovoltages were transient. Transient photovoltages had been observed earlier[5] in experiments on CdS crystals when the crystals were insulated with Mylar. One might conclude, then, that in the present case the grain-to-grain and grain-to-electrode barriers play the role of the Mylar in the case of the crystals. There is, however, another explanation for the transient character of the photovoltage. Since the photovoltage is due primarily to inhomogeneous excitation, it will decrease as the sample becomes more uniformly excited owing to the absorption of its own fluorescence radiation. This absorption will be more pronounced in a powder than in a crystal because the scattering is more extensive in the former.

The voltages were measured with an electrometer circuit and a Sanborn model 151 recorder. The elec-

† Also with Physics Department, Hunter College, New York, New York.
‡ Now associated with Research Department, Grumman Aircraft Engineering Corporation, Bethpage, New York.
[1] For a bibliography on the photovoltaic effect see J. Tauc, Revs. Modern Phys. **29**, 308 (1957).
[2] H. Kallmann and M. Pope, J. Chem. Phys. **32**, 300 (1960).
[3] D. C. Reynolds, G. Leies, L. L. Antes, and R. E. Marburger, Phys. Rev. **96**, 533 (1954), A. E. Middleton, D. A. Gorski, and F. A. Shirland, Amercan Rocket Society Space Power Systems Conference, Santa Monica, California, Sept. 27–30, 1960 (unpublished).
[4] L. P. Hunter, *Handbook of Semiconductor Electronics* (McGraw-Hill Book Company, Inc., New York, 1956).

[5] H. Kallmann, B. Kramer, J. Shain, and G. M. Spruch, Phys. Rev. **117**, 1482 (1960).

trometer grid resistance could be varied from 10^8 to 10^{11} ohms. Because of the transient character of the photovoltage, it was found convenient to make the excitation one second in duration. The intensity of excitation was measured with a calibrated thermopile at the position of the sample, with absorption in the glass plates taken into account.

In some samples without Mylar a contact potential of up to 50 mv was observed. This was not due to residual excitation as it was independent of the direction of previous illumination. Even after long periods without excitation the potentials were of the same magnitude. Since the resistance of the samples was smaller than that of the electrometer, this contact voltage should not change with illumination of the sample, the illumination causing reduction of the sample resistance. In order to make certain that no appreciable fraction of the measured photovoltage was due to a change in contact voltage the sample was illuminated on each side, so that in one instance the photovoltage added to the contact voltage and in the other it was counter to it. The change in voltage observed upon illumination was only slightly different for different directions of illumination.

DEPENDENCE OF PHOTOVOLTAGE UPON ACTIVATION AND WAVELENGTH OF EXCITATION

A. Activated Materials

The results obtained are given in Table I. The first column gives the sample and its thickness. The second and third columns give the wavelengths and intensities incident on the phosphor surface from the mercury lamp. The fourth and fifth columns give the wavelengths and intensities incident on the other phosphor surface from the incandescent lamp. The last column gives the photovoltage; this is the peak height of the transient pulse. A positive polarity means that the side illuminated by the mercury lamp is positive with respect to the other.

The thicknesses being comparable, it is valid to compare the photovoltages for the different samples.

The results for ZnS:Ag and ZnS:Cu show that the photovoltages are produced primarily by radiation in the wavelength region below 3200 A. Relatively low intensities in this wavelength region produce larger photovoltages than radiation of 3600 A at a much higher intensity, though 3600 A produces the stronger fluorescence. Radiation of 3200 A is absorbed in a thin layer consisting of a few grains, while radiation of 3600 A is almost uniformly absorbed throughout the sample. This would indicate that photovoltages originate in a few grains in which there are large charge concentration gradients, and the reason for low photovoltages with excitation by radiation of 3600 A is that much smaller charge concentration gradients result from the more uniformly absorbed radiation. Excitation

by the entire mercury spectrum increases the photovoltage slightly in ZnS:Cu and reduces it in ZnS:Ag, compared with that produced by 3130 A. Again this can be interpreted in the same manner as above. Copper shifts the absorption edge of ZnS to longer wavelengths than does Ag, the consequence being to make a larger portion of the spectrum more inhomogeneously absorbed in the ZnS:Cu than in the ZnS:Ag. This argument is given support by the fact that illumination of the other side of the sample by light from the incandescent lamp, which is absorbed relatively homogeneously throughout the sample, reduces the photovoltage in ZnS:Cu because the inhomogeneity of the excitation has been reduced, while the photovoltage in ZnS:Ag is hardly affected, excitation in it having been more homogeneously absorbed in the first instance.

When the radiation is quite inhomogeneously absorbed in both ZnS:Ag and ZnS:Cu, 3130 A for example, then the silver activated sample gives the higher photovoltage.

In both ZnS:Ag and ZnS:Cu small photovoltages of negative polarity were induced by 4340 A. No satisfactory explanation can be offered at this time. Lempicki[6] reported similar reversals at 3300 and 3500 A in ZnS single crystals.

The results obtained using ZnCdS:Ag (20% Cd) and (70% Cd) support the interpretation given above. The addition of cadmium shifts the absorption spectrum of ZnS toward the visible. As a consequence, large photovoltages are produced in the 20% Cd sample by 3600 A but not by 4340 A, since the latter wavelength is outside the range of absorption. In the 70% Cd sample, however, even 4340 A yields sizable photovoltages since it falls in the absorption range of that material. The photovoltages are generally larger with cadmium than without, because more of the exciting radiation is inhomogeneously absorbed. This will be discussed further in the last section.

The last three entries in Table I give the results of investigations of the influence of co-activators and quenchers. Nickel, which is a strong quencher of fluorescence,[7] does not have a noticeable effect on the photovoltage. Apparently it increases the number of radiationless transitions but does not decrease the number of excited electrons appreciably.

The addition of lead as a second activator decreases the photovoltage considerably. It is known that the addition of lead decreases quenching and increases the probability of radiative transitions,[7] thus decreasing the concentration of excited electrons. The low photovoltage compared to Cu-activated samples without Pb is further evidence that this is the case.

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[6] A. Lempicki, Phys. Rev. 113, 1204 (1959).

[7] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

TABLE I. Photovoltage of activated ZnCdS phosphors as a function of wavelength.

Sample	Excitation left (mercury lamp)		Excitation right (incandescent lamp)		Photovoltage (volts)
	λ transmitted	Intensity (μ w/cm^2)	λ transmitted	Intensity (μ w/cm^2)	
ZnS:Cu	Hg spectrum >2900 A	1900	...	...	+0.060
thickness 0.013 cm	Hg spectrum >2900 A	1900	incandescent spectrum	10 000	+0.045
	3130 A	<5	...	...	+0.025
	3130 A	<5	>6400 A	8000	+0.030
	3600 A	65	...	...	+0.010
	4340 A	35	...	...	−0.007
ZnS:Ag	Hg spectrum >2900 A	1900	...	...	+0.035
thickness 0.011 cm	Hg spectrum >2900 A	1900	incandescent spectrum	10 000	+0.030
	3130 A	<5	...	...	+0.070
	3130 A	<5	>6400 A	8000	+0.055
	3600 A	65	...	...	+0.015
	4340 A	35	...	...	−0.010
ZnCdS:Ag (20% Cd)	Hg spectrum >2900 A	1900	...	...	+0.120
	Hg spectrum >2900 A	1900	incandescent spectrum	10 000	+0.100
thickness 0.014 cm	3130 A	<5	...	...	+0.120
	3130 A	<5	>6400 A	8000	+0.080
	3600 A	65	...	...	+0.115
	4340 A	35	...	...	0.0
ZnCdS:Ag (70% Cd)	Hg spectrum >2900 A	1900	...	...	+0.180
	Hg spectrum >2900 A	1900	incandescent spectrum	10 000	+0.130
thickness 0.012 cm	3130 A	<5	...	...	+0.050
	3130 A	<5	>6400 A	8000	+0.040
	3600 A	65	...	...	+0.195
	4340 A	35	...	...	+0.150
ZnCdS:Cu, Ni (56% Cd) thickness 0.007 cm	Hg spectrum >2900 A	1900	...	...	+0.140
	3130 A	<5	...	...	+0.050
	>3700 A	1200	...	...	+0.080
ZnS:Cu, Pb	Hg spectrum >2900 A	1900	...	...	+0.025
thickness 0.013 cm	3130 A	< 5	...	...	+0.005
	>3700 A	1200	...	...	0.0
ZnS:Mn	Hg spectrum >2900 A	1900	...	...	+0.017
thickness 0.037 cm	3130 A	<5	...	...	+0.040
	>3700 A	1200	...	...	0.0

B. Unactivated Phosphors

The essential distinction between unactivated and activated phosphors is that in the former there are decidedly fewer sites where positive holes and excited electrons can be trapped. As a consequence, the rate of recombination of excited electrons with free holes is greater, and one would expect, therefore, that the density of excited free electrons would be smaller. Conductivity measurements on unactivated CdS crystals had shown this previously,[8] and it was found to be the case in the present measurements as well. The

photovoltages were smaller than in activated samples in spite of the fact that a lamp with greater intensity in the ultraviolet region had been used. Table II lists results for unactivated ZnS and CdS.

The most significant result for unactivated ZnS is that the sign of the photovoltage is negative for all wavelengths. That is, the illuminated side becomes negative rather than positive, as was the case with all the other phosphor samples and with CdS crystals.[5] Since the magnitude of the photovoltage seems to parallel the absorption spectrum the photovoltage must be interpreted to be due to a diffusion of carriers from the excited region into the interior. Since the sign of

[8] H. Kallmann and R. Warminsky, Ann. Physik 4, 57 (1948).

TABLE II. Photovoltage of unactivated phosphors as a function of wavelength.

Sample	Excitation (mercury lamp)[a] λ transmitted	Intensity (μ w/cm^2)	Photo-voltage (volts)
ZnS (unactivated)	Hg spectrum >2900 A	2200	−0.055
thickness 0.018 cm	3130 A	15	−0.030
	3600 A	130	−0.015
	4340 A	35	0.0
CdS (unactivated)	Hg spectrum >2900 A	2200	+0.120
thickness 0.015 cm	3130 A	15	+0.075
	3600 A	130	+0.120
	4340 A	35	+0.055

[a] Note that the intensity of excitation is greater here than in Table I.

the photovoltage is negative, which means that the interior of the sample is positively charged, one is led to the conclusion that in unactivated ZnS the positive holes have a greater mobility than the electrons. In order to verify that the negative photovoltage was a characteristic of unactivated ZnS the experiments were repeated with several samples of "luminescent purity" from different sources. The results were always the same. Photovoltages in unactivated CdS, however, were of the same sign and magnitude as in activated phosphors. This is interpreted to mean that in CdS the electrons have a considerably higher mobility than the positive holes.

When both holes and electrons have noticeable mobilities in the interior of a sample, the photovoltage due to the concentration gradient is given by

$$V_{ph} = \frac{kT}{e}\left[\int_{n_1^+}^{n_2^+} \frac{\omega^+ dn^+}{\omega^+ n^+ + \omega^- n^-} - \int_{n_1^-}^{n_2^-} \frac{\omega^- dn^-}{\omega^+ n^+ + \omega^- n^-}\right],$$

where n^+ and n^- are the densities of holes and electrons, respectively, ω^+ and ω^- are the mobilities, and the index 1 refers to the excited side of the sample and 2 to the unexcited side. If the concentrations of holes and electrons are equal or comparable in the region of high excitation as well as in the interior, then the photovoltage is essentially given by the mobilities. When the concentrations are not comparable because of trapping or absorption at the electrode then the value of the integrals will be determined by the limits, and these in turn will determine the sign of the photovoltage. If one assumes that the concentrations of holes and electrons are comparable in ZnS, one must conclude that the mobility of the holes is greater than that of the electrons in that material. If the concentrations are not comparable one can conclude that the holes have a considerable mobility but not necessarily greater than that of the electrons. The above considerations apply to CdS as well, with the conclusion that in that case it is the electrons which have the greater mobility.

C. Charge Exchange at the Electrodes

In the discussions above, the influence of the electrodes has been neglected. One would expect that their contribution to the voltage would be minimal since the electrodes are not excited and have a very high conductivity compared to that of ZnCdS. This expectation is supported by the fact that with strong homogeneously absorbed excitation the photovoltage is small. But in order to determine more exactly the effect of charge exchange at the electrodes, experiments similar to those described above were performed, except that the phosphors were separated by a sheet of clear Mylar 7×10^{-4} cm thick from one of the conductive glass plates which made up the sandwich arrangement. The samples were illuminated both through the Mylar and through the other electrode. The transmission of the Mylar is 20% at 3100 A, 50% at 3130 A, and greater than 80% for wavelengths longer than 3340 A. Since photovoltages are weakly dependent upon intensity, this loss in intensity will have only a relatively small effect on the voltage except possibly when the voltage is quite low.

The results are given in Table III. For ZnS:Cu there is no difference between the voltages obtained when illumination was through the Mylar and those when illumination was from the other side. This indicates that the electrode has indeed very little influence on the photovoltage for that material. In ZnS:Ag the difference was about 30%. For the unactivated materials, however, there was a considerable difference. In unactivated ZnS the illuminated side was again negative, whether it was the Mylar side or the other, showing clearly that the reversal is not due to any special electrode effect. But the difference between the magnitudes of the photovoltages for illumination through the Mylar, and from the other side, a factor of five, indicates that insulating the electrode hampers the carriers from moving out of the sample or reduces the concentration of carriers at the surface by absorption at the Mylar. For unactivated CdS the reduction in photovoltage caused by the Mylar was a factor of about 4. The polarity was the usual positive.

The question arises as to why in the activated materials the electrodes have so little effect on the photovoltage. If the positive holes are immobile no photovoltage should develop when there is a Maxwellian distribution of the electrons in the phosphor and in the electrode near the top of barrier formed at the phosphor electrode contact.[9]

The condition for the Maxwellian distribution is that at the contact the conduction band lie several kT/e above the Fermi level, a condition which very likely has been met. What then is the source of the photovoltage? There are two possibilities one can envisage:

[9] L. Landau and E. Lifshitz, Physik Z. Sowjetunion 9, 477 (1936).

TABLE III. Effect of the electrode on the photovoltage of various phosphors. One of the electrodes has been insulated from the phosphor by a sheet of transparent Mylar.

Sample	Excitation[a] (mercury lamp) λ transmitted	Intensity (μ w/cm²)	(a) Illumination through Mylar Photo-voltage (volts)	(b) Illumination on phosphor surface Photo-voltage (volts)
ZnS:Cu	Hg spectrum >2900 A	2200	+0.140	+0.140
	3130 A	15	+0.150	+0.150
	4340 A	35	0.0[b]	0.0[b]
ZnS:Ag	Hg spectrum >2900 A	2200	+0.130	+0.180
	3130 A	15	+0.150	+0.210
	4340 A	35	0.0[b]	0.0[b]
ZnS (unactivated)	Hg spectrum >2900 A	2200	−0.010	−0.050
	3130 A	15	−0.008	−0.050
	4340 A	35	0.0[b]	0.0[b]
CdS (unactivated)	Hg spectrum >2900 A	2200	+0.025	+0.140
	3130 A	15	+0.020	+0.070
	4340 A	35	+0.010	+0.040

[a] Note that the intensity of excitation is greater here than in Table I.
[b] These values were sometimes negative by a small amount which was within the limits of experimental uncertainty.

(1) There is poor contact between the electrode and the phosphor and hence there is little charge exchange. The relation between the electrons in the electrode and those in the phosphor is not the Maxwell-Boltzmann $e^{-eV/kT}$, and consequently it is possible for a photovoltage to develop.

(2) The positive carriers participate in the charge exchange at the electrode and/or contribute to the motion in the region of direct excitation. As a consequence, a particle current exists at the interface and in the region of direct excitation without there being an electric current. (In an open circuit measurement the negative and positive currents must be equal.) The opposing effects of the positive and negative charges may reduce the photovoltage in the metal and in the region of direct excitation. If the voltage in this region were not reduced, it would compensate exactly the voltage which arises from the diffusion of electrons out of the region of excitation into the interior of the phosphor. The possibility of positive hole motion is strongly supported by the results obtained with pure ZnS, where the motion of the positive holes was demonstrated directly. One should note that those wavelengths which produce the largest photovoltages always create free holes (absorption in the valence band) which recombine with activators or traps only after some time.

DIFFERENCE BETWEEN MEASURED AND ACTUAL PHOTOVOLTAGE

The photovoltage which is measured is different from the actual photovoltage at the sample when the latter extends only over several grain layers while the rest of the sample remains unexcited. If V_{ph} is the photovoltage across the sample, and V_m the measured voltage, the following relationship obtains:

$$V_{ph} = V_m\left(1 + \frac{C_{el}}{C_s} \times \frac{d-\delta}{d}\right),$$

where C_{el} and C_s are the capacitances of the electrometer and the sample, respectively, d is the thickness of the sample and δ is the thickness over which the photovoltage extends. C_{el} is about three times larger than C_s. Therefore, for small δ the difference between the actual photovoltage and the measured value can be close to a factor of 4. This may be the reason that the ZnCdS (70% Cd) sample exhibited a smaller photovoltage than the sample with 20% Cd when excited by 3130 A. In the former the absorption is greater, and so the difference between the actual and measured value is greater.