PHYSICAL REVIEW VOLUME 137, NUMBER 1A 4 JANUARY 1965

Ambipolar Diffusion of Free Carriers in Insulating CdS Crystals*

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(Received 12 June 1964; revised manuscript received 25 August 1964)

A new method is described for measuring ambipolar diffusion of free carriers in insulating materials. Strongly absorbed light producing electron-hole pairs is shone on one surface of the material through a transparent noninjecting contact. These carrier pairs set up a concentration gradient extending into the interior due to ambipolar diffusion. To describe this process, the theory of ambipolar diffusion is extended to the insulator case of unequal lifetimes for electrons and holes and significant trapping of both types of carriers. Simultaneously, excess space charge of the same sign as the majority photocarriers is injected through an Ohmic contact on the opposite face and space-charge-limited current (SCLC) flow is established. The point of equality of these two charge distributions establishes an effective thickness x_0. To a good approximation, x_0 can be inserted into the SCLC density formula which, for shallow trapping, is $J=KV^2/x_0^3$ where K is a constant. The thickness x_0 depends on the illumination intensity and therefore introduces an intensity dependence into the SCLC formula. A technique is described with which the ambipolar diffusion length L_a of free carriers can be calculated from this intensity dependence. The procedure was tested with insulating CdS crystals. The results show that $L_a \approx 1\mu$ at room temperature from which the minority carrier (hole) recombination lifetime $\tau_p \approx 5\times10^{-8}$ sec is obtained. These values are in good agreement with earlier estimates.

INTRODUCTION

THE minority carrier properties of insulators are very difficult to investigate for a variety of reasons, principal among which are high impedance level, small minority carrier lifetime, and undesirable space charge effects due to trapping and poorly defined contacts. There are basically two ways by which minority carrier behavior in solids may be studied. One method makes use of the drift of carriers in an electric field. The minority carriers are usually, but not necessarily, injected at the contacts. Various modifications of the drift technique have been used to observe minority carrier motion in a variety of insulating materials, for example, CdS[1–3] and anthracene.[4] A second approach is to examine the diffusion of free carrier pairs. This latter technique has not been too successful when applied to insulators. To the author's knowledge, the only references in the literature to ambipolar diffusion[5] measurements in insulators is the photoelectromagnetic (PEM) effect[6] measurement with 10^{10} Ω cm CdS reported by Sommers, Berry, and Sochard.[7]

In view of the interest in the electronic and optic-electronic properties of insulators, it is desirable to have at one's disposal a simple experimental procedure for studying minority carrier behavior. The purpose of this paper is to present a new technique for accomplishing this by determining the ambipolar diffusion length L_a in an insulator with a simple photoelectric measurement. One surface of the insulator is illuminated with strongly absorbed light through a transparent noninjecting contact and, simultaneously, space charge is injected from the opposite side through an Ohmic contact. The illumination produces electron-hole pairs which set up a concentration gradient extending into the interior due to ambipolar diffusion and space-charge-limited current (SCLC) is established by the injected space charge. The point where the injected space-charge concentration and the photogenerated majority carrier concentration are equal defines an effective thickness x_0 which now appears in the SCLC density formula[8]:

$$J=(9/8)\theta\epsilon\mu V^2/x_0^3$$

($\epsilon\equiv$specific inductive capacity in mks units, $\mu\equiv$drift mobility, $\theta\equiv$constant ratio of free to trapped charge valid for shallow trapping). The thickness x_0 depends on the level of illumination (and also on the voltage), and therefore introduces an intensity dependence into the SCLC. A method is presented for obtaining L_a from a measurement of this dependence.

Insulating CdS crystals, whose dark resistivities exceeded 10^{10}Ω cm at room temperature, were chosen as a representative material in the realization of this technique. The results show that $L_a \simeq 1\mu$ at room temperature from which the minority carrier (hole) recombination lifetime $\tau_p \approx 5\times10^{-8}$ sec is obtained.

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* The research reported in this paper was sponsored by the U. S. Army Research Office (Durham) under Contract No. DA 31-124-ARO-(D)-84, and by RCA Laboratories, Princeton, New Jersey.

[1] R. W. Smith, Phys. Rev. **105**, 900 (1957).

[2] I. Broser and R. Broser-Warminsky, Phys. Chem. Solids **6**, 386 (1958).

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[4] R. G. Kepler, Phys. Rev. **119**, 1226 (1960).

[5] R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, 1961), Chap. 8, pp. 234–317.

[6] T. S. Moss, L. Pincherle and A. M. Woodward, Proc. Phys. Soc. (London) **B66**, 743 (1953); H. Buillard, Phys. Rev. **94**, 1564 (1954); S. W. Kurnick, A. J. Strauss and R. N. Zitter, *ibid.* **94**, 1791 (1954); R. N. Zitter, *ibid.* **112**, 852 (1958).

[7] H. S. Sommers, Jr., R. E. Berry and I. Sochard, Phys. Rev. **101**, 987 (1956).

[8] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), Chap. 5, pp. 170–173; A. Rose, Phys. Rev. **97**, 1538 (1955); *Concepts in Photoconductivity and Allied Problems* (John Wiley & Sons, Inc., New York, 1963), Chap. 4, pp. 69–81; M. A. Lampert, Proc. IRE **50**, 1781 (1962); *Reports on Progress in Physics, 1964* (The Institute of Physics and the Physical Society, London, 1964).

In the Appendix, an expression for the spacial dependence of the photogenerated majority carrier concentration is obtained from the semiconductor theory of ambipolar diffusion of free carriers[9] adapted to the insulator case of unequal lifetimes for electrons and holes and significant trapping of carriers of both signs. The self-consistence of the method is also investigated.

All calculations are based on a one-dimensional plane geometry and the equations are written in mks units.

THEORY

The purpose of this section is to present a method for determining the ambipolar diffusion length of free carrier pairs in an insulator by a simple photoelectric measurement. In order to accomplish this, it is necessary to obtain an expression for ambipolar diffusion of free carrier pairs in a representative insulator, the assumed energy band configuration of which appears in Fig. 1. This model is the simplest consistent with the results of the measurements presented here; one set of recombination centers and two discrete trapping levels, one for electrons and one for holes. Geometrically, the insulator is in the form of a slab (Fig. 2) of unit area and thickness d. The desired expression is the position dependence of the photogenerated free electron concentration $n(x)$ and free hole concentration $p(x)$ for the one-dimensional geometry of Fig. 2, when one surface of the insulator is illuminated with strongly absorbed light.

The calculation is outlined in the Appendix. At this point, only the result of the calculation is presented together with a summary of the underlying physical assumption made in the derivation. The insulator problem differs from the standard semiconductor approach[5,9] in the following significant ways. First, there is the very definition of a photoconducting insulator which is that $n(x)$ and $p(x)$ are significantly larger than the corresponding concentrations $\bar{n}$ and $\bar{p}$ in thermal equilibrium. This means that $n(x)$ and $p(x)$ cannot be treated as perturbations on $\bar{n}$ and $\bar{p}$. Second, the free carrier recombination lifetimes τ_n and τ_p for electrons and holes, respectively, are generally not equal and may differ by orders of magnitude. This is a reflection of the fact that at a given position $n(x)$ is generally different from $p(x)$. In this discussion, electrons are considered the majority carriers. Hence, $n(x) > p(x)$ and $\tau_n > \tau_p$. Third, trapping is a first-order effect since only a small fraction of the total photogenerated carriers remain in conducting states. The remaining carriers are localized in traps and recombination centers.[10]

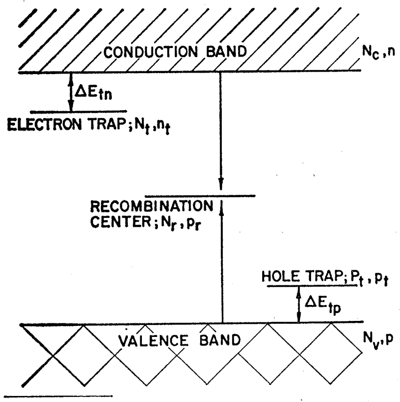

FIG. 1. Simplified energy band configuration of the representative insulator showing one shallow trapping level for electrons and one for holes, and the recombination center level. The symbols are defined in the text.

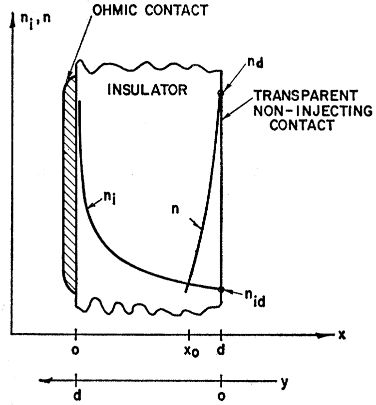

FIG. 2. Geometric arrangement of sample and free-carrier distribution in the sample. Light is incident from the right through the transparent noninjecting electrode and space charge is injected through the Ohmic contact on the left. n = photogenerated majority carrier concentration, n_i = injected carrier concentration.

These insulator conditions complicate the mathematics of the problem by requiring the simultaneous solution of a pair of nonlinear differential equations for the variables $n(x)$ and $p(x)$. In order to obtain a solution, three physical assumptions are necessary. First, at any position, $n(x)$ is proportional to $p(x): n(x)/p(x) = \rho$ and ρ is independent of x. A direct result of this assumption is that τ_n and τ_p are separately constant and that their ratio is also ρ. There is ample evidence that this assumption is physically realistic. Many insulating photoconductors display a linear relation between the photocurrent and the illumination level which is evidence that the majority carrier lifetime is constant.[10] Mathematically, this assumption reduces the problem to one involving only one dependent variable. The second physical assumption is that space-charge neutrality is maintained by the localized carriers in the traps and recombination centers. This condition leads to limiting values for the concentration N_r of recombination centers and for their recombination cross section S_n for electrons in terms of parameters which

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[9] W. van Roosbroeck, Phys. Rev. **91**, 282 (1953); **101**, 1713 (1956); **119**, 636 (1960).

[10] A. Rose, RCA Rev. **12**, 362 (1951); Phys. Rev. **97**, 322 (1955); in *Progress in Semiconductors*, edited by A. F. Gibson, P. Aigrain and R. E. Burgess; (Heywood & Company, London, 1957), Vol. II, p. 111. *Concepts in Photoconductivity and Allied Problems* (John Wiley & Sons, Inc., New York, 1963), Chap. 3, pp. 18–22; R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York), Chap. 9, p. 273.

can be measured. Thus, it is possible to investigate the validity of this assumption. The mathematical consequence of this assumption is to linearize the problem. The third assumption is that surface recombinations can be described by a surface recombination velocity σ, which is necessary as a boundary condition. This is the most difficult assumption to justify for the insulator case. It is important, however, only when surface recombination dominates. In this work, samples which display no evidence of surface recombination were deliberately chosen in an effort to eliminate complications arising from this source. Finally, there is a restriction on L_a necessary to maintain self-consistency, which is that $(L_a/\lambda)^2$ be significantly greater than unity. λ is the penetration depth of the incident illumination.

The position dependence of $n(x)$ is derived in the Appendix and is given by

$$n(x)=n_d \exp\{-(d/L_a)[1-(x/d)]\} \qquad (1)$$

when the illumination is incident on the surface $x=d$. This dependence is schematically illustrated on Fig. 2 by the curve marked "n." The coefficient n_d, which is the photogenerated free carrier concentration at the illuminated surface, is always proportional to $I\tau_n$ where I is the photon flux density of the illumination. The magnitude of n_d depends on whether or not surface recombinations are important (see Appendix). Equation (1) contains L_a in the exponent. This parameter can be measured in the following way.

Simultaneously with the illumination, excess space charge is injected through the opposite side $x=0$ which is provided with an Ohmic contact. In the case treated here, that of an n-type photoconductor, the contact at $x=0$ must be Ohmic for electrons, and it is at negative bias during the measurement. If no light were incident on the sample, the injected free electron concentration $n_i(x)$ for the case of shallow trapping would depend on x according to[8]

$$n_i(x)=n_{id}(d/x)^{1/2}. \qquad (2)$$

This function is also shown schematically on Fig. 2 by the curve marked "n_i." The factor n_{id} is the injected free carrier concentration at the anode and is given by[8]

$$n_{id}=3\epsilon\theta V/4de^2, \qquad (3)$$

where e is the elementary charge.

In the actual experiment both the light and the voltage act simultaneously. Near the anode, n decreases exponentially from the illuminated surface while n_i decreases only as a fractional power of the distance away from the cathode. To a good approximation, the total free electron concentration is n_i in the cathode space and n in the anode space. The position x_0 is now defined to be where n and n_i are equal. Because n rises exponentially on the anode side of x_0, it is assumed, subject to later examination, that only a negligibly small fraction of the applied voltage appears across the anode space. This means that the photoexcited region is considered shorted out and that the SCLC density formula can be written as

$$J=J_0(d/x_0)^3, \qquad (4)$$

where $J_0=(9/8)\theta\epsilon\mu V^2/d^3$. It is clear that x_0 depends on I as well as V. For example, increasing I will merely increase $n(x)$ by a constant factor, owing to the proportionality between n_d and I, thereby reducing x_0. Also, increasing V raises n_i through the dependence of n_{id} on V expressed by Eq. (3) and this has the effect of increasing x_0.

The dependence of x_0 on I, V, and L_a is obtained by equating Eqs. (1) and (2) for $x=x_0$. This leads to the relation

$$\eta(I,V)=(d/x_0)^{1/2}\exp\{(d/L_a)[1-(x_0/d)]\}, \qquad (5)$$

where η is defined as the ratio: $\eta=n_d/n_{id}\propto I/V$. The transcendental character of Eq. (5) requires a numerical solution. It is most advantageous to formulate the solution as $(d/x_0)^3$ versus η with d/L_a as parameter. This will give directly the ratio J/J_0 as a function of the ratio I/V. The graphical solution is shown in Fig. 3 on a logarithmic plot. For a given d/L_a, J/J_0 increases with I when V is held fixed and decreases with increasing V when I is held fixed, reflecting the previously discussed behavior of x_0. Also, J/J_0 increases with decreasing d/L_a for a given η because the smaller d/L_a, the farther $n(x)$ extends toward the injecting cathode.

To obtain L_a experimentally, the SCLC is measured over some voltage range both in the dark (J_0) and at various light levels (J). The ratio J/J_0 is plotted on a double logarithmic field as a function of I for a fixed V. By comparing the experimental curves with the theoretical curves, two parameters are independently obtained: L_a and η for a given I and V. Further, it is shown in the Appendix that if τ_n is known, for example from an independent photoconductivity measurement,[10] the ambipolar diffusion coefficient D_a can be obtained from Eq. (A12). Finally, if μ_n and μ_p (the electron and hole mobilities, respectively) are also known, the lifetime ratio τ_n/τ_p is obtained from Eq. (A9) and the Einstein relation $D=\mu kT/e$ (k is the Boltzmann constant; T is the absolute temperature.) This leads directly to a value for τ_p.

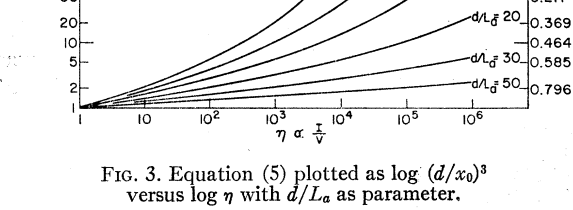

FIG. 3. Equation (5) plotted as log $(d/x_0)^3$ versus log η with d/L_a as parameter.

Clearly, the analysis is significant only when $L_a > \lambda$. Then, it follows from the calculations of the Appendix that when $(L_a/\lambda)^2 \gg 1$, $n_d = I\tau_n/L_a$ whenever $\sigma \ll D_a/L_a$, which turns out to be the case with the CdS crystals used in this investigation. Alternatively, if $L_a < \lambda$, the measurement yields λ rather than L_a because the spatial extent of $n(x)$ is set by the penetration depth of the light and not by ambipolar diffusion. If in addition $(L_a/\lambda)^2 \ll 1$, $n(x) = (I\tau_n/\lambda)\exp\{-(d/\lambda)[1-(x/d)]\}$.

The ratio of the voltage drop V_{x_0d} in the anode space $x_0 < x < d$ to the applied voltage V is:

$$V_{x_0d}/V = 1/[1+(2x_0/3L_a)].$$

The restriction imposed by the assumption that V_{x_0d}/V be small is

$$2x_0/3L_a \gg 1. \tag{6}$$

EXPERIMENTAL

The CdS crystals used in this investigation were all insulating with a dark resistivity greater than $10^{10}\Omega$ cm. They were grown from the vapor phase without the addition of any known impurity. The crystals were in the form of platelets from 20 to 30 μ thick with areal dimensions of a few square millimeters. In addition to the high dark resistivity, the crystals were also limited to those which displayed no sensitivity peak in their photoconductivity excitation spectrum, indicating that surface recombinations play only a negligible role,[11] and which were not photosensitive to red light, thus assuring that the excitation energy migrates only by ambipolar diffusion of free carriers and not by the reabsorption of fluorescence.[2,12]

The crystals were sealed over the end of a short glass capillary tube ($\frac{1}{16}$-in. i.d.) with glycolphthalate, such that both faces of the crystal remained free. The crystal face on the inside of the tube was covered with In–Ga–Sn liquid eutectic, which makes Ohmic contact to CdS, and a wire was led down the tube into the electrode to make contact to the external circuit. The end of the tube with the crystal on it was then immersed into an 0.1M KI solution which served as a noninjecting electrode.[13] Contact was made to the electrolyte with a platinum wire.

This crystal-electrode combination was positioned in such a way that light could be made incident through the electrolyte onto the crystal. The light source was a microscope illuminator in combination with Corning 7-37 and 1-69 filters which passed a band centered at 0.36μ about 40 mμ wide. This band is well to the short wavelength side of the optical absorption edge of CdS.[14] The maximum (100%) intensity of this source was 23.4μ W/cm^2 which corresponds to a flux density of 4.2×10^{13}/sec cm^2. The intensity was varied with calibrated wire mesh filters.

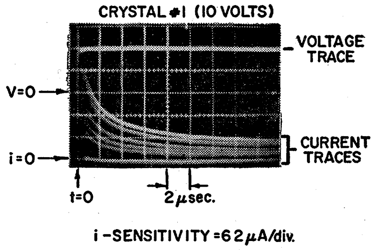

FIG. 4. CRO trace photograph of the transient SCLC flowing with the anode illuminated with strongly absorbed light. The upper trace is the voltage and the lower traces are, in descending order, the current traces corresponding to the intensities 100, 19, 4, 1.4, 0.55%, and darkness.

The simplest way to make the measurement would be to observe the steady state SCLC for various illumination intensities. This proved unfeasible with the CdS crystals available for the experiment because trapping of the injected carriers made the steady state SCLC so small at the voltages used (10–100 V) that absurdly low light levels were needed to satisfy condition Eq. (6) on x_0. Consequently, although a steady illumination was always employed to assure quasiequilibrium in the photoexcited portion of the crystal, a transient technique was used for the electrical measurement in order to work with the largest possible SCLC. It should be emphasized here that in the photoexcited space near the anode, where ambipolar diffusion occurs, the carrier concentrations are determined by the illumination and not by the magnitude of the SCLC. Even though $n_i(x)$ is time variant during the measurement, the illumination is steady so that $n(x)$ is not a function of time.

The transient SCLC technique requires the application of a fast rising voltage signal to the relatively insulating crystal and the simultaneous measurement of a current transient due to the flow of injected carriers. In order to suppress the huge capacitive current surge which accompanies the application of the voltage, a balanced circuit was used like that used by Helfrich and Mark[15] to obtain SCLC transients in anthracene. This made it possible to measure a carrier current of 1 μA about 2 μsec after the application of a 100-V signal. The rise time of the voltage signal was about 0.1 μsec.

The currents were recorded as follows. The capacitive surge was eliminated by adjusting the circuit with the crystal in the dark at reverse bias. Forward bias was then applied and, with the crystal in the dark, the current transient at various voltages was recorded on a cathode-ray oscilloscope (CRO) photograph. Between measurements, the crystal was exposed to infrared light to empty the traps which were filled during the preceding application of the voltage. If this is omitted, the trapped space charge in the crystal prevents the max-

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[11] R. H. Bube, Phys. Rev. **101**, 1668 (1956).
[12] P. Mark, Phys. Chem. Solids **25**, 911 (1964).
[13] R. Williams, Phys. Rev. **117**, 1487 (1960).
[14] D. Dutton, Phys. Rev. **112**, 785 (1958).
[15] W. Helfrich and P. Mark, Z. Physik **166**, 370 (1962).

imum possible space charge from entering at the electrode and a spuriously low SCLC results.[16] The measurement was then repeated with the anode surface under steady illumination with strongly absorbed light. At each voltage the currents transient for several light levels were recorded on one CRO photograph. An example of such a record is shown on Fig. 4. It was taken with 10 V applied to crystal No. 1. This picture shows, in descending order, the voltage trace and six current traces corresponding, respectively, to the intensities 100, 19, 4, 1.4, 0.55%, and darkness. The decaying nature of the current is caused by trapping of the injected space charge in the unexcited portion of the crystal.[8,16] In this region, where the injected space charge dominates, steady state conditions do not prevail and $n_i(x)$ is also a function of time. The voltage dependence of the SCLC was obtained by always noting the current a fixed time (in this case, 2 μsec) after the application of the voltage. This assures that $n_i(x)$ corresponds to the same degree of trap filling, i.e., the same θ, in the unexcited portion of the crystal for every measurement.[10,15] The shallow trap approximation is still valid since in darkness the time varying SCLC a fixed and short interval after the application of the voltage is proportional to the square of the voltage[15] (see Fig. 5). From the CRO photograph, it is evident that the voltage rises considerably faster than 0.5 μsec and that the capacitive current overshoot is practically absent. No cusp[15] appears in the SCLC transient because the transit time of the injected space charge is much smaller than the resolution time of the circuit.

RESULTS AND DISCUSSION

Three crystals, each taken from a different preparative run, were examined. The voltage dependence of the SCLC is shown on Fig. 5. Each graph shows the dark SCLC and the photosensitive SCLC at various levels of illumination measured 2 μsec after the application of the voltage. Figure 6 shows the data of Fig. 5 plotted as $\log J/J_0$ versus $\log I/I_0$ at 10 V. The lines connecting each set of points are the best fit of the data to the solution of Eq. (5) for the values of d/L_a and η shown on the figure. The η values correspond to the maximum intensity ($I/I_0=1$, 4.2×10^{13} photons/sec cm^2) and 10V. The high intensity point of crystal No. 1 falls off the curve drawn through the remaining points. This point is the $I=100\%$, $V=10$-V point of the preceding figure and would correspond to $x_0/d=0.4$ were it on the curve. For this small value of x_0, it is probable that a significant fraction of the applied voltage appears across the illuminated section.

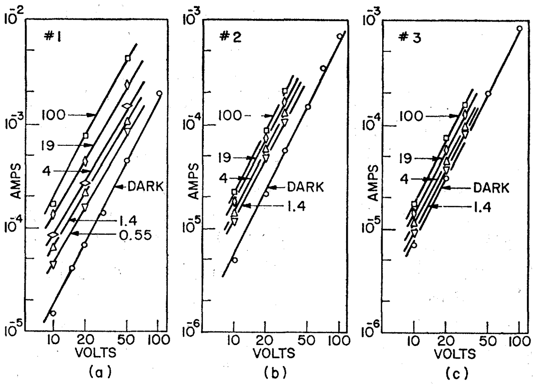

FIG. 5. Dark and photosensitive SCLC for three CdS crystals recorded 2 μsec after the application of the voltage. The intensities in percent of maximum for each measurement are shown on each graph. (a) No. 1, $d=24$ *u*; (b) No. 2, $d=27$ *u*; (c) No. 3, $d=20$ μ.

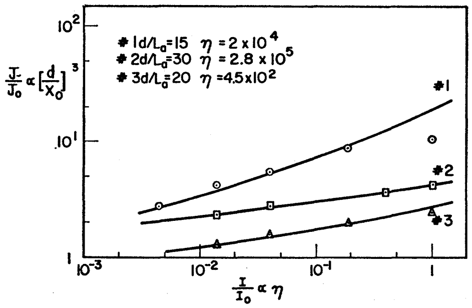

FIG. 6. Plot of the measured ratio J/J_0 versus I/I_0 on a logarithmic field at 10 V. The lines connecting each set of points are best fit of the data to the solution of Eq. (5) for the values of d/L_a and η shown on the graph.

These data were then analyzed according to the procedure outlined earlier. The results of the analysis are summarized in Table I. The first two columns list the geometric data of the crystals. Column 3 shows the θ factors obtained from the ratio of the measured dark SCLC to the ideal trap-free SCLC which is expected from the geometry using $\epsilon/\epsilon_0=10$ and $\mu_n=150$ cm^2/V sec.[17] Columns 4 and 5 list the experimental information obtained from Fig. 6 and column 6 lists the values of L_a obtained from the data of columns 1 and 4. The ratio L/λ is shown in column 7. Here the value $\lambda=1.25\times10^{-5}$ cm obtained by Dutton[14] was used. The square of this ratio is appreciably greater than unity showing that L_a as measured is indeed the ambipolar diffusion length and not λ. Column 8 shows the lifetime τ_n obtained from independent photoconductivity measurements. These showed the photocurrent varying as I^n where n was confined to the range $0.95<n<1$. Hence, τ_n is practically constant. Column 9 lists D_a as obtained from Eq. (A12) of the Appendix. Column 10 shows the ratio ρ for each crystal as computed from Eq. (A9) of the Appendix and column 11 lists the values of τ_p. The hole mobility $\mu_p=15$ cm^2/V sec[17] was used in evaluating ρ.

The values obtained for L_a and τ_p compare well with other estimates and measurements for CdS in the

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[16] P. Mark and W. Helfrich, J. Appl. Phys. **33**, 205 (1962); Z. Physik **168**, 469 (1962).

[17] W. E. Spear and J. Mort, Proc. Phys. Soc. (London) **81**, 130 (1963).

TABLE I. Tabulation of experimental results.

Crystal	1 d (u)	2 a $(\times 10^{-3}\ \mathrm{cm}^2)$	3 θ^{a} $\times 10^{-7}$	4 d/L_a	5 η	6 L_a μ	7 L_a/λ^{b}	8 $\tau_n{}^{c}$ $(\mu\mathrm{sec})$	9 $D_a{}^{d}$ $\times 10^{-4})$ cm²/sec)	10 ρ $\times 10^3$	11 τ_p (nsec)
1	24	3.8	3.66	15	2×10^4	1.6	12.5	50	5.2	1.45	35
2	27	11.4	57.5	30	2.8×10^5	0.9	7.3	170	3	2.5	69
3	20	3.15	12	20	4.5×10^2	1.25	9.2	40	3.2	2.35	18

[a] Computed using $\epsilon/\epsilon_0=10$ and $\mu_n=150$ cm²/V sec after W. E. Spear and J. Mort, Proc. Phys. Soc. (London) **81**, 130 (1963).
[b] Computed using $\lambda=1.25\times 10^{-5}$ cm after D. Dutton, Phys. Rev. **112**, 785 (1958).
[c] Obtained from an independent photoconductivity measurement.
[d] Computed with $\mu_p=15$ cm²/V sec and $b=10$ after J. Mort and W. E. Spear, Phys. Rev. Letters **8**, 314 (1962).

literature. Sommers *et al.*[7] and Smith[1] estimate $\tau_p \approx 10^{-7}$ sec, the former from PEM measurements and the latter from the observation of low voltage injection electroluminescence. Keating[18] obtains $\tau_p \approx 10^{-8}$ sec from an analysis of double injection. Mort and Spear[3,17] have found $\tau_p \approx 10^{-7}$ sec and $L_a=3.7\mu$ from drift measurements. Broser and Broser-Warminsky,[2] using the results of high field measurements, deduce the values $\tau_p \approx 10^{-8}$ sec and $L_a \approx 1.0\mu$ at room temperature. In more recent work dealing with exciton emission in CdS, Bleil and Broser[19] report that the hole lifetime must be small compared to 10^{-6} sec at room temperature.

SUMMARY

A new method is described which makes it possible to measure ambipolar diffusion of free carriers in insulating materials. Strongly absorbed light producing electron-hole pairs is shone on one surface through a transparent noninjecting contact. These carrier pairs set up a concentration gradient extending into the interior due to ambipolar diffusion. Simultaneously, excess space charge is injected through an Ohmic contact on the opposite face and SCLC is established. The point of equality of the two charge distributions, the injected carrier concentration and the photogenerated carrier concentration, establishes an effective thickness x_0 which now appears in the SCLC density formula: $J=(9/8)\theta\epsilon\mu V^2/x_0^3$. x_0 depends on the illumination and introduces an intensity dependence into the SCLC. A technique is developed for obtaining the ambipolar diffusion length from a measurement of this dependence. The procedure was realized with insulating CdS crystals as representative insulators. The results show that $L_a \approx 1\mu$ at room temperature from which $\tau_p \approx 5\times 10^{-8}$ sec is obtained.

ACKNOWLEDGMENTS

The author is indebted to Murray A. Lampert for his interest and guidance during the course of this work. Thanks are also extended to Alfred Willis for his very skillful contributions to the experimental work and to Alvin M. Goodman for his critical reading of the manuscript.

APPENDIX

A. Mathematical Formulation

The purpose here is to outline the derivation of Eq. (1) subject to the insulator conditions discussed in the body of the paper. With reference to Figs. 1 and 2, the behavior of the free and localized photogenerated carriers is governed by the equations of continuity:

$$\begin{aligned} \partial n/\partial t &= f(y)-(n/\tau_n)-(\partial j_n/\partial y)\,,\\ \partial p/\partial t &= f(y)-(p/\tau_p)-(\partial j_p/\partial y)\,; \end{aligned} \tag{A1}$$

the equations of current flow:

$$\begin{aligned} j_n &= -n\mu_n\mathcal{E}-D_n(\partial n/\partial y)\,,\\ j_p &= p\mu_p\mathcal{E}-D_p(\partial p/\partial y)\,; \end{aligned} \tag{A2}$$

the conservation of current:

$$|j_n|=|j_p|\,; \tag{A3}$$

and Poisson's equation for space charge:

$$(\epsilon/e)(\partial\mathcal{E}/\partial y)=p+p_t+p_r-\bar{p}_r-(n+n_t)\,. \tag{A4}$$

In these equations $f(y)$ is the generation rate of free carriers: $f(y)=(I/\lambda)\exp(-y/\lambda)$; j_n and j_p are the particle current densities for electrons and holes, respectively; D_n and D_p are the diffusion coefficients for electrons and holes, respectively; $\mathcal{E}$ is the local electric field; n_t and p_t are the concentrations of trapped electrons and trapped holes, respectively; p_r and $\bar{p}_r$ are the concentration of holes in the recombination centers under illumination and in thermal equilibrium, respectively. The remaining symbols have been defined earlier. The quantities n, p, n_t, p_t, and p_r are all position dependent. With the exception of $\bar{p}_r$, the carrier concentrations in thermal equilibrium do not appear in this formulation because the insulator case is under consideration.

In the steady state, the electron and hole recombination rates must be equal: $n/\tau_n=p/\tau_p$. This, together with the assumed energy level scheme, yields $\tau_n=(pS_p+nS_n)/pN_rS_nS_pv$, where S_n and S_p are the recombination cross sections of the N_r centers for electrons and holes, respectively, and v is the thermal velocity ($\simeq 10^7$ cm/sec at room temperature). An expression for τ_p can be obtained from the two previous

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[18] P. N. Keating, Phys. Chem. Solids **24**, 1101 (1963).

[19] C. E. Bleil and I. Broser, Phys. Chem. Solids **25**, 11 (1964).

equations. Thus, τ_n and τ_p are functions of both n and p. Assuming nondegenerate behavior, $n_t = nN_t/(n+N)$, $N = N_c \exp(-\Delta E_{tn}/kT)$; $p_t = pP_t/(p+P)$, $P = N_v \exp(-\Delta E_{tp}/kT)$; $p_r = pN_rS_p/(pS_p+nS_n)$; where N_t and P_t are the concentration of electron traps and hole traps, respectively; N_c and N_v are the effective densities of states in the conduction band and valence band, respectively; ΔE_{tn} and ΔE_{tp} are the electron and hole trap depths, respectively (see Fig. 2).

In the steady state, this equation system can be reduced to the following pair of nonlinear second-order differential equations in the position-dependent variables $n(y)$ and $p(y)$:

$$f(y)[p\mu_p + n\mu_n] - np[(\mu_p/\tau_n) + (\mu_n/\tau_p)] + p\mu_p D_n(d^2n/dy^2) + n\mu_n D_p(d^2p/dy^2) + \mu_n\mu_p \mathcal{E}(y)[p(dn/dy) - n(dp/dy)] = 0, \quad \text{(A5a)}$$

$$\frac{\epsilon}{e}\frac{d\mathcal{E}}{dy} = p\left\{1 + \left(\frac{P_t}{p+P}\right) + \left(\frac{N_rS_p}{pS_p+nS_n}\right)\right\} - n\{1 + [N_t/(n+N)]\} - \bar{p}_r \quad \text{(A5b)}$$

where

$$\mathcal{E}(y) = [D_p(dp/dy) - D_n(dn/dy)]/(n\mu_n + p\mu_p). \quad \text{(A6)}$$

A simultaneous solution of Eqs. (A5) with appropriate boundary conditions is required.

The first assumption, consistent with the insulator conditions,[10] which simplifies the problem is that $n(y)$ and $p(y)$ are proportional:

$$n(y)/p(y) = \rho \quad \text{(A7)}$$

and that ρ is not position-dependent. A consequence of this is that τ_n and τ_p are separately constant and that their ratio is also ρ. Constant τ_n requires a proportionality between the photocurrent and the illumination intensity which was observed. This assumption reduces the differential equation pair into equations in one unknown for which a compatible solution is required. Setting $b = \mu_n/\mu_p = D_n/D_p$, Eq. (A5a) becomes

$$f(y) - (n/\tau_n) + D_a(d^2n/dy^2) = 0, \quad \text{(A8)}$$

where D_a is the ambipolar diffusion coefficient in insulators:

$$D_a = 2b/(b\rho+1) \longrightarrow 2D_p(\tau_p/\tau_n) \text{ when } b\rho \gg 1. \quad \text{(A9)}$$

The field $\mathcal{E}(y)$ becomes

$$\mathcal{E}(y) = \frac{kT}{e}\frac{b\rho-1}{b\rho+1}\frac{1}{n}\frac{dn}{dy}. \quad \text{(A10)}$$

This is the insulator Dember field which compensates the difference in the two carrier ranges per unit field since the product $b\rho = \mu_n\tau_n/\mu_p\tau_p$. This field is generally not solenoidal.

The general solution of Eq. (A8) is

$$n(y) = A\exp\left(-\frac{y}{L_a}\right) + B\exp\left(\frac{y}{L_a}\right) + \left[\frac{IL_a^2}{\lambda D_a}\right]\left[1 - \left(\frac{L_a}{\lambda}\right)^2\right]^{-1}\exp\left(-\frac{y}{\lambda}\right), \quad \text{(A11)}$$

where A and B are constants of integration and

$$L_a = (D_a\tau_n)^{1/2} \longrightarrow (2D_p\tau_p)^{1/2} \text{ when } b\rho \gg 1. \quad \text{(A12)}$$

The boundary condition for obtaining A and B is taken from the simple semiconductor problem[9,20] in which recombination at the surface may be represented by a recombination velocity σ. The solution now reads:

$$n(y) = \left[\frac{I\tau_n}{\lambda}\right]\left[1 - \left(\frac{L_a}{\lambda}\right)^2\right]^{-1} \times\left\{\exp\left(-\frac{y}{\lambda}\right) - \left[\frac{\sigma + (D_a/\lambda)}{\sigma + (D_a/L_a)}\right]\exp\left(-\frac{y}{L_a}\right)\right\}. \quad \text{(A13)}$$

It is difficult to establish whether this solution is compatible with the solution of the nonlinear differential equation (A5b). However, a simple way of providing compatibility is to assume $\mathcal{E}$ solenoidal: $d\mathcal{E}/dy = 0$. This is an *a priori* assumption, the physical consequence of which is investigated in Appendix B. By virtue of (A10), solenoidal $\mathcal{E}$ requires that the solution for $n(y)$ be a simple exponential in y. The solution (A13) is not in this simple form. However, the two limited cases obtained by choosing either $L_a \ll \lambda$ or $L_a \gg \lambda$ are simple exponentials which satisfy the condition of solenoidal $\mathcal{E}$. When $L_a \ll \lambda$ the spatial extent of the photogenerated carriers is set by λ. The solution reduces to $n(y) = (I\tau_n/\lambda)\exp(-y/\lambda)$ which does not contain L_a and yields no information about ambipolar diffusion. When $L_a \gg \lambda$, ambipolar diffusion governs the spread of photogenerated charge away from the illuminated surface and

$$n(y) = \frac{I\tau_n}{\lambda}\left(\frac{\lambda}{L_a}\right)^2\left[\frac{\sigma + (D_a/\lambda)}{\sigma + (D_a/L_a)}\right]\exp\left(-\frac{y}{L_a}\right)$$

which contains L_a both in the coefficient and in the exponent. The coefficient can have three limiting forms depending on whether volume or surface recombinations dominate. When the former prevail, $\sigma \ll D_a/L_a$ and $n(y) = (I\tau_n/L_a)\exp(-y/L_a)$. When surface recombination is important, there are two further possibilities: When $D_a/L_a \ll \sigma \ll D_a/\lambda$, $n(y) = (I\tau_n/L_a)(D_a/\sigma L_a)\exp(-y/L_a)$ and when $D_a/\lambda \ll \sigma$, $n(y) = (I\tau_n/L_a)(\lambda/L_a)\exp(-y/L_a)$. All the solutions for $L_a \gg \lambda$ can be written in the form $n(y) = n_d\exp(-y/L_a)$ where n_d represents the photogenerated free electron concentration at the

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[20] Reference 5, p. 297.

TABLE II. Verification of results.

	1		2	3	4
Crystal	τ_n[a] (μsec)	τ_n[b] (μsec)	N_r ($\times 10^{17}$ cm^{-3})[c]	S_n ($\times 10^{-21}$ cm^2)[d]	V_{x0d}/V[e]
1	20	50	3.6	5.5	12
2	200	170	1.35	4.3	10
3	60	40	1.1	23	8.4

[a] Computed using the experimentally determined values of L_a and η.
[b] Photoconductivity lifetime (Table I, column 8).
[c] Computed from Eq. (B1) with p_r neglected using smallest I used in the investigation.
[d] Computed from Eq. (B2) with p_r neglected and N_r from column 2.
[e] Computed from Eq. (6) using the smallest valid x_0 from Fig. 3.

illuminated surface. This is just Eq. (1) of the text in the variable $y=d-x$. Note that n_d is always proportional to $I\tau_n$.

This treatment also bears on the PEM effect. The short circuit PEM current[6] is $i_s=(IeB/l)(kT/e)^{1/2}\times(\mu_0{}^3\tau_0)^{1/2}$ when surface recombinations are neglected. Here B is the magnetic field in the plane of the illuminated surface and l is the sample dimension parallel to the illuminated surface, and normal to B, along which the current is measured. The illumination I is normal to the surface. The quantities μ_0 and τ_0 have the dimensions of mobility and time, respectively. These parameters are different from their semiconductor interpretation[9] in the insulator case. If Eq. (A9) is used in the derivation of i_s, one obtains: $\mu_0=\mu_n[1+(1/b)]^{2/3}$ and $\tau_0=2\tau_n/(b\rho+1)$, and

$$\mu_0{}^3\tau_0=\mu_p{}^3\tau_p[2b\rho/(b\rho+1)][b+1]^2 \xrightarrow[b\rho,\ b\gg 1]{} 2\mu_n{}^2\mu_p\tau_p.$$

B. Self-Consistency of the Analysis

The measurement yields directly a value for η [Eq. (5)]. Knowledge of η serves to check the self-consistency of the analysis and gives information about the relative importance of surface and volume recombination processes. Recalling from Appendix A that $n_d=I\tau_n/L_a$ when $\sigma\ll D_a/L_a$, η can be written as $\eta=\eta_0\equiv 4I\tau_n ed^2/3\epsilon\theta VL_a$. The quantities d, V and I are measured directly, τ_n is obtained from the photoconductivity and θ from a comparison of the ideal trap-free SCLC with the measured dark current. The parameters η and L_a are therefore related by a proportionality constant (for a fixed I and V) all of whose factors are known. Alternatively, if the measurements show that this relation is not satisfied, the discrepancy may result from the dominance of surface recombinations. If $\sigma\gg D_a/\lambda$, $\eta=\eta_0(\lambda/L_a)$ and η and L_a are again related by a known proportionality constant. For the intermediary case $D_a/L_a\ll\sigma\ll D_a/\lambda$, $\eta=\eta_0(D_a/L_a\sigma)$. Here σ is unknown but it can be obtained from this equation since both L_a and D_a are amenable to measurement.

The assumption of solenoidal $\mathcal{E}$ in the derivation of Eq. (1) requires that [see Eq. (A4)] $(n/p)[1+(n_t/n)]=1+(p_t/p)+(p_r-\bar{p}_r)/p$. This relation is simplified by noting that the ratios n/n_t and p/p_t are much less than unity in the insulator case and that

$$p_r=N_r/[1+(\rho S_n/S_p)]\approx N_r,$$

the latter because the product $\rho S_n/S_p<1$ (see Table I and the work of Bube[21]). Also, for shallow trapping $p/p_t\approx P/P_t$. With these simplifications and Eq. (A7), the following condition on N_r is obtained:

$$N_r\leqslant(pP_t/P)+\bar{p}_r=(n/\theta)+\bar{p}_r. \tag{B1}$$

Similarly, from the relation for τ_n with constant n/p and the inequality $\rho S_n/S_p<1$, S_n becomes: $S_n\approx(\tau_n N_r v)^{-1}$. Inserting N_r from the above expression shows that the assumption of solenoidal $\mathcal{E}$ also requires that

$$S_n\geqslant\theta/v\tau_n(n+\theta\bar{p}_r). \tag{B2}$$

The measurements yield numerical values for n, θ and τ_n. If the value of $\bar{p}_r$ were known, numerical limits on N_r and S_n could be computed which would be useful in checking the assumption of solenoidal $\mathcal{E}$. Unfortunately, the magnitude of $\bar{p}_r$ cannot be measured. But $\bar{p}_r\leqslant N_r$. If $\bar{p}_r\ll N_r$, the terms involving $\bar{p}_r$ in Eqs. (B1) and (B2) can be neglected and one obtains the smallest upper limit on N_r and the largest lower limit on S_n. If $\bar{p}_r$ is appreciable, the upper limit on N_r is raised and the lower limit on S_n is reduced. Thus, neglecting $\bar{p}_r$ will give the most adverse limits on N_r and S_n.

The information in Table II demonstrates the self-consistency of the analysis. Column 1 shows the electron lifetime computed from the relation $\eta=\eta_0$, valid when surface recombinations are unimportant, as well as the photoconductivity lifetime (Table I, column 9). The agreement is very good. This not only substantiates the validity of the analysis but supports the observed absence of a sensitivity peak in the photoconductivity spectral response curves. Column 2 shows the limit on N_r computed from Eq. (B1) with $\bar{p}_r$ neglected using the free electron concentration corresponding to the lowest illumination level. Values of N_r ranging from 10^{14} to 10^{17} cm^{-3} are the generally accepted values for CdS.[10] Column 3 shows the limit on S_n computed from Eq. (B2) again with $\bar{p}_r$ neglected. These values are comparable with those estimated by Bube[21] which place S_n in the range 10^{-22} to 10^{-20} cm^2. The validity of assuming V_{x0d}/V small, as expressed by Eq. (6), is demonstrated by the data of column 4. In computing this voltage ratio, the smallest value of x_0 for each measurement was used.

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[21] R. H. Bube, J. Appl. Phys. **32**, 1707 (1961); R. H. Bube and F. Cardon, J. Appl. Phys. **35**, 2712 (1964).

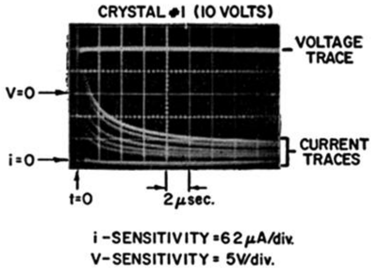

FIG. 4. CRO trace photograph of the transient SCLC flowing with the anode illuminated with strongly absorbed light. The upper trace is the voltage and the lower traces are, in descending order, the current traces corresponding to the intensities 100, 19, 4, 1.4, 0.55%, and darkness.