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Hole-Trap Depletion-Layer Formation in CdS*

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The formation of a depletion layer associated with a hole trap in sensitive CdS platelet crystals with blocking contacts has been studied. By monitoring the current associated with the emptying of optically filled traps in the depletion region as a function of applied voltage and temperature, only one trap species was observed, the properties of which are a density of at least $4.5\times10^{16}/\text{cm}^3$; ionization energy, 0.14 ± 0.02 eV; frequency factor, 2×10^7/sec; capture cross section, 5×10^{-18} cm^2. The carrier range was 5×10^{-7} cm^2/V, and this was determined to be the recombination range. The zero-voltage Schottky-barrier width at the gold contact is found to be 0.20 μ. It is argued that the trap is a hole trap, and it is shown to be similar to the trap level postulated to explain the CdS green emission.

I. INTRODUCTION

DEPLETION–LAYER polarization at a blocking contact has been used previously[1,2] to study such processes as carrier release from bound states in the forbidden gap, trapping and transport characteristics, and contact breakdown. Matthews and Warter[2] have performed such experiments on CdS single crystals to investigate electron trapping. The usefulness of depletion-layer polarization with blocking contacts in investigating trap parameters lies in its less ambiguous determination of the thermal ionization energy as compared to thermal release heating-rate experiments and in the possibility of determining the carrier range and charge distribution in the sample.

In the present work, the depletion-layer polarization associated with a 0.14-eV trap of very low capture cross section in CdS is reported. The effect of the built-in field at the metal-insulator contact (the Schottky barrier) is evident in the data. A means of obtaining the carrier range (Schubweg/field) from polarization experiments is given. Further, it is argued that the investigated trap level is a hole trapping level, and it is shown to have properties similar to those of a trap postulated to explain the CdS green emission (0.15 eV less than band gap).

The CdS crystals studied in the present work are of higher sensitivity than those of Matthews and Warter.[2] In their paper, the undoped crystals are described as midway in sensitivity between the extreme values for undoped CdS. The same type of crystals (from the same source[3]) were also studied by Mark.[4] In Mark's paper, the electron lifetime is reported to be 10^{-4} sec for which $\mu_n\tau_n=1.5\times10^{-2}$ cm^2/V for $\mu=150$ cm^2/V sec. Mark finds that the hole lifetime is $\approx10^{-8}$ sec, which results in $\mu_p\tau_p\approx1.5\times10^{-7}$ cm^2/V for $\mu_p=15$ cm^2/V sec.[5] The range measured in the Matthews-Warter paper (7×10^{-7} cm^2/V) was found to be the range for retrapping by the same centers which released the carriers. Thus, the carrier involved must be the electron since the recombination lifetime of the hole is too short to allow significant retrapping with a range of 7×10^{-7} cm^2/V.

The CdS crystals in the present work were doped with copper. Independent measurements[6,7] of the electron lifetime give about 5×10^{-3} sec or $\mu_n\tau_n=7.5\times10^{-1}$ cm^2/V, which is about 50 times higher than the crystals of Mark[4] or of Matthews and Warter.[2] As will be discussed later, the range measured (5×10^{-7} cm^2/V) for the carriers in the present case is the recombination range. Thus, the depletion-layer polarization reported here is associated with the minority carrier, and the trapping level is a hole trap.

II. PHYSICAL DISCUSSION OF DEPLETION-LAYER POLARIZATION

Let us consider an insulator with blocking contacts (which present a barrier to injection of at least one sign of carrier). For convenience, we assume that there exists a discrete energy level in the forbidden gap which acts as a trapping state and that this state is populated, perhaps by optical pre-excitation. If a voltage is applied to such a sample with blocking contacts then the charge carriers, upon release from the trap level to the conducting states drift a certain average distance (Schubweg) due to the field before recapture or recombination. For the case of electron release, in the region adjacent to

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[1] A. Von Hippel, E. P. Gross, J. G. Jelatis, and M. Geller, Phys. Rev. **91**, 568 (1953).
[2] N. F. J. Matthews and Peter J. Warter, Jr., Phys. Rev. **144**, 610 (1966).
[3] RCA Laboratories, Princeton, N. J.
[4] Peter Mark, Phys. Rev. **137**, A203 (1965).
[5] W. E. Spear and J. Mort, Proc. Phys. Soc. (London) **81**, 130 (1963).
[6] A. B. Dreeben and R. H. Bube, J. Electrochem. Soc. **110**, 456 (1963).
[7] R. H. Bube, J. Appl. Phys. **34**, 3309 (1963).

the negative electrode, electrons are being swept away toward the anode and none are entering through the blocking cathode contact to replenish them. Initially then, upon application of voltage, a region about one Schubweg wide acquires a net positive charge; for hole release the charge would be negative. By Poisson's equation, the magnitude of the field must increase in this region; this causes more sweep-out of charge and a further increase in charge density and field. Thus, a space charge region forms across which a progressively larger fraction of the applied voltage appears. This charge-depletion region we call a sheath.

The model to be used in the present analysis is the long carrier range (range is Schubweg per unit field) or contracting sheath model as discussed by Matthews and Warter.[2] It is assumed that at some time after the voltage application a sheath has formed of sufficient width and charge density to absorb essentially all the applied voltage. The time at which this occurs is called the "sheath formation time," and in the contracting model this time is less than the time required to exhaust the available trapped charge. Thus, as more charge carriers are released from the traps, the sheath width must decrease since the voltage drop across the sheath cannot exceed the applied voltage (ignoring diffusion effects). The sheath shrinks by charge carrier capture at its edge; the carriers not captured here are either captured in the bulk neutral region, pass out of the sample, or form a dipole layer of negligible voltage drop at the anode.

III. SAMPLES AND EQUIPMENT

The single-crystal CdS platelets were several millimeters on a side and about 50 μ thick. They were grown by Dreeben and Bube[6] from the vapor phase under a pressure of 330–380 Torr H_2S between 800 and 830°C. The crystals used were obtained from the lowest-temperature segment (800°C); 1% copper impurity was present in the initial charge, and this impurity preferentially segregated in the higher-temperature growth segment.

The platelets were etched in 25% HCl, 75% distilled water and then washed in distilled water. After air drying, a transparent gold electrode was evaporated on one surface. Aquadag was used to fasten the sample to a sapphire disk and the Aquadag served also as the opposite electrode. The final form was a parallel plate capacitor 50 μ thick, of area 2.5×10^{-3} cm^2, one electrode of gold, one of Aquadag. Both electrodes were observed to be blocking.

The sapphire sample-mounting disk was attached to a copper heating block inside a nitrogen Dewar. A flange on top of the Dewar allowed pumping on the liquid nitrogen. With this apparatus, stable temperatures (to 0.1°K) could be obtained from 75°K up. A thermocouple on the copper block measured sample temperature. Windows in the Dewar allowed illumination by an Osram Hg lamp.

One lead from the sample went to a voltage source through an RC circuit which provided a gradual voltage application ($RC\approx1$ sec) to avoid overloading the electrometer and to permit an accurate measurement of the total charge transported, including the initial capacitive charge. The other lead went to an electrometer, either of the conventional or vibrating-reed type depending on the current level being measured. The electrometer output was fed both to a chart recorder and to a digital voltmeter, whose output was recorded on IBM cards for computer analysis.

The data presented were obtained from one sample. Three CdS samples from the same batch were investigated in some detail, and all showed similar behavior. The one discussed here is the sample for which most data were obtained before mechanical failure of the sample contacts due to thermal cycling.

IV. CHARGE-VOLTAGE DEPENDENCE

A. Theory

In deriving the dependence of charge upon voltage, we shall assume that (a) charges of only one sign move during the polarization of the sample, (b) the contacts are perfectly blocking, (c) the density of mobile carriers has a negligible effect on the fields in the sample, (d) the charge density is nonzero in the sheath region only and it is uniform there, and (e) all the applied voltage appears across the sheath region. The second assumption allows us to equate the total integrated current to the charge stored in the sheath, and the last assumption limits the validity of any result to times after the sheath formation time. We assume, also, that there exists at each electrode a region of width $\frac{1}{2}\delta$ where no charge release from traps occurs and, consequently, no additional net depletion charge can form during the voltage application. This region represents the Schottky barrier at the metal-insulator contact. For a depletion sheath of uniform charge density $\rho(t)$ and width $b(t)$, Poisson's equation yields

$$V_0=\rho(t)b^2(t)/2\epsilon+\rho(t)b(t)\delta/\epsilon, \qquad (1)$$

where V_0 is the applied voltage, ϵ is the permittivity (1.03×10^{-12} F/cm). The first term on the right represents the voltage drop across the sheath, while the second term is the sum of the voltage across the two contact barriers. For release from a discrete energy trap with initial carrier population N and average time before release τ,

$$\rho(t)=Ne[1-\exp(-t/\tau)]. \qquad (2)$$

The charge per unit area stored in the sheath is

$$q(t)=\rho(t)b(t)+\delta\rho(t)\{[1+b_0^2(t)/\delta^2]^{1/2}-1\}, \qquad (3)$$

where

$$b_0^2(t)=2\epsilon V_0/\rho(t). \tag{4}$$

When the sample is fully polarized ($t\gg\tau$),

$$q(t\gg\tau)=q_0=Ne\delta[(1+2\epsilon V_0/Ne\delta^2)^{1/2}-1]. \tag{5}$$

Note that the total charge transported varies as the square root of applied voltage for $\delta^2\ll 2\epsilon V_0/Ne$ and linearly with voltage for $\delta^2\gg 2\epsilon V_0/Ne$. For intermediate cases, the slope of a $\log_{10}q_0$-versus-$\log_{10}V_0$ plot will be between $\frac{1}{2}$ and 1 and will be given by

$$m=d(\ln q_0)/d(\ln V_0)=\gamma/\{2(\gamma+1)^{1/2}[(\gamma+1)^{1/2}-1]\}, \tag{6}$$

where

$$\gamma=b_0^2(t\gg\tau)/\delta^2=2\epsilon V_0/Ne\delta^2. \tag{7}$$

B. Experiment

Current measurements were made as a function of voltage at constant temperature with and without pre-excitation. The data shown below are for one particular temperature (78°K). Without pre-excitation, the charge transported during each voltage application varied linearly with voltage and was approximately given by the geometrical capacitance. With pre-excitation (by the Hg lamp) for 10 min (followed by a 5-min dark period before voltage application), the currents were much larger and lasted for very long times, up to 1000 sec. The final current was negligibly small, $\leq 10^{-16}$ A, suggesting that there was no appreciable contact leakage current.

The current curves with pre-excitation were integrated and the total charge transported was obtained as a function of voltage from 0.5 to 6.0 V, as shown in Fig. 1. The slope of the $\log_{10}Q$-versus-$\log_{10}V_0$ plot is about 0.62 at higher voltages, while it may be as large as 0.7 or 0.8 at lower voltages. The form of the larger than square-root dependence of charge upon voltage is in agreement with the uniform sheath plus Schottky-barrier model discussed previously. For a slope of 0.62, Eq. (6) yields $\gamma=15$ for voltages above 2 V. From (5) and (6), using $\gamma=15$, the following values were obtained:

$N=2.21\times10^{15}/\text{cm}^3$ trapped carrier density at time of application of the voltage,
$\delta/2=0.20\,\mu$, insulating width at each electrode,
$b(t\gg\tau)=1.20\,\mu$, sheath width at 4 V.

The solid line in Fig. 1 is the calculated charge versus voltage using the above values.

V. TRANSIENT CURRENTS AND TRAP-RELEASE TIME CONSTANT

A. Theory

If we ignore the Schottky barrier, (1) has the simple form

$$V_0=\rho(t)b^2(t)/2\epsilon. \tag{8}$$

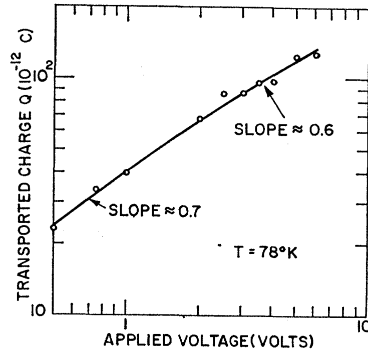

FIG. 1. Dependence of polarization charge on voltage.

The conduction current per unit area is

$$j(t)=d[\rho(t)b(t)]/dt=[\epsilon V_0/2\rho(t)]^{1/2}d\rho(t)/dt, \tag{9}$$

where the time t is measured from the voltage application. The displacement current may be ignored if the sample length is much larger than the sheath width $b(t)$, which is true for the present samples.

We assume that the dominant carrier release is by thermal excitation from a single discrete trap level with release time τ, and that deeper levels contribute a very small release of carriers which we assume to be constant on our time scale. The charge density has the form

$$\rho(t)=At+Ne[1-\exp(-t/\tau)], \tag{10}$$

where N is the initial trap population and A is the rate of release from any deeper states.

We previously postulated the existence of a built-in field at the electrodes to account for the greater than square-root dependence on voltage. This built-in field would alter the simple current dependence of (9); however, in the fitting region, which is after the time for the sheath to be well formed, the only appreciable effect is to change the fitted value of the initial trapped electron density. Accordingly, (9) was used in the fitting and A and N were adjusted afterwards to account for the Schottky barrier.

B. Experiment

A series of polarization current measurements was made on pre-excited samples at several voltages for each of a number of temperatures at approximately 1° intervals between 72 and 85°K. *This was the only temperature interval between 72 and 300°K where significant polarization currents were observed with these samples.* During each run, the temperature was held constant within 0.1°K. A typical current curve at 1.0 V is shown in Fig. 2. Note the nonexponential decay and the much larger current with pre-excitation as compared to no pre-excitation. As will be discussed later, the time region in which the simple model as expressed in (9) is valid was determined. (Note that the simple model discussed

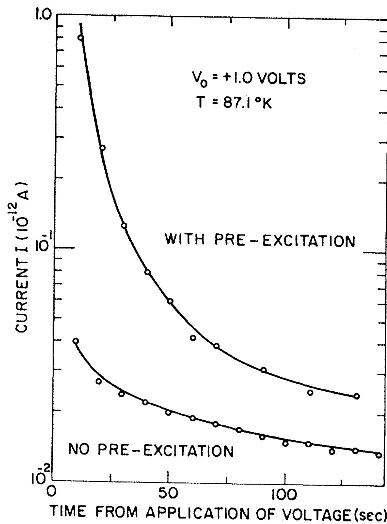

FIG. 2. Current at 1.0 V, with and without pre-excitation.

previously holds only when the sheath is well formed.) In the proper time region (9) was fitted to the data with the expression for charge density given by (10). A, N, and τ were adjusted for the best fit. Fig. 3 shows typical current data in the fitting region and the line of best fit, which is quite good.

At each temperature, values of A, N, and τ were obtained from the fitting procedure. The best-fitted values of A and N varied little with temperature, while τ was an exponential in temperature. Values of A and N averaged over the different runs and adjusted to account for the Schottky barrier were

$$A = 10^{-7}\ \mathrm{C/cm^3\ sec},$$

$$N = 1.8 \pm 0.3 \times 10^{15}/\mathrm{cm}^3.$$

The initial trapped carrier density as obtained from current fitting compares well with that obtained from the charge-voltage dependence. The constant-release-rate term A contributes a very small current to the total current measured. This may represent some other effect, such as contact leakage, noise, or drift, which we account for in the fitting procedure by assuming a small constant release. Thus, the fact that we use this constant release rate in our fitting to the data is *not* evidence for deeper traps. Indeed, the fitting could be done without this term in the release rate and reasonable matching to the data was obtained, though not as good as with the constant term.

Time in this experiment is measured from the application of voltage. There was a significant decay of the trap population in the 5 min between the end of the pre-excitation and the application of the voltage. Since the retrapping probability is low as evidenced by the low capture cross section and the results of a voltage reversal as described below, the trap population at the end of pre-excitation can be estimated using N and τ and projecting back 5 min. This gives an occupied trap density at the end of pre-excitation of $4.5 \times 10^{16}/\mathrm{cm}^3$ which is a lower limit on the trap density. The trap population at the termination of illumination appears to be an increasing function of temperature since the measured trap population 5 min after illumination is terminated varies much less than one would expect from a constant initial population decreased by 5-min decay and since no retrapping appears to occur. This suggests that the measurements may underestimate the true trap density.

The trap time constant τ is plotted in Fig. 4 as a function of inverse temperature. The slope of the line of least-squares best fit gives the thermal activation energy of the trap,

$$E = 0.14 \pm 0.02\ \mathrm{eV}.$$

The error limits on the energy are the 90% confidence limits. The intercept gives the trap frequency factor,

$$\nu^* \approx 2 \times 10^7/\mathrm{sec},$$

which for CdS, assuming an effective-mass ratio of 0.2, results in 5×10^{-18} cm^2 for the capture cross section.

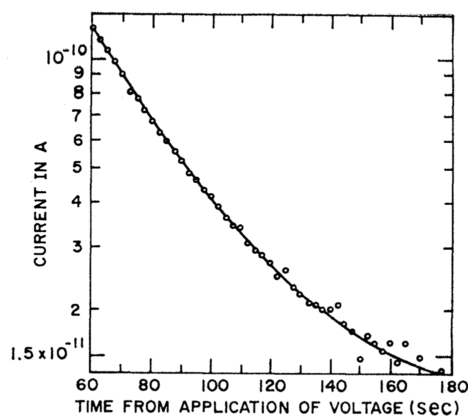

FIG. 3. Plot of current data and fitted function.

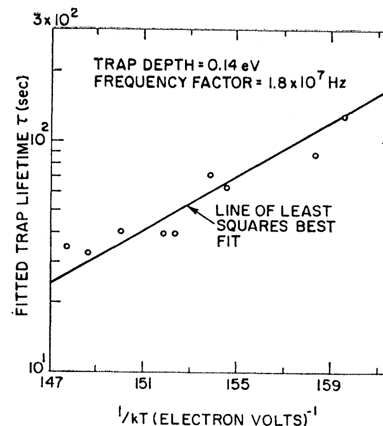

FIG. 4. Time constant as function of temperature.

VI. CARRIER RANGE

A. Theory

In discussing the measurement of carrier range, it is convenient to consider a function $F(t)$ defined to be the product of current at time t and total charge transported up to time t. Thus,

$$F(t)=q(t)j(t)\ \mathrm{A\ C/cm^4}. \tag{11}$$

In the simple model previously considered, this results in

$$F(t)=\epsilon V_0 d\rho(t)/dt, \tag{12}$$

i.e., it is proportional to the release rate $d\rho(t)/dt$. For release from a single discrete trap level, the $F(t)$ function is a simple exponential in time since

$$d\rho(t)/dt=(Ne/\tau)e^{-t/\tau}.$$

Thus, from the experimental data $F(t)$ can be evaluated and the straight-line portion of the $F(t)$ curve on a $\log_{10}F(t)$-versus-time plot defines the region where the simple model applies.

In the usual experiment $F(t)$ has a time dependence as shown in Fig. 5; the important point is that $F(t)$ has a peak before the straight-line portion of the simple model. In the simple model previously discussed, the key assumption is that the field is totally concentrated in the depletion region; for this reason $F(t)$ is simply proportional to the release rate. The assumption of zero field in the bulk, neutral region is equivalent to the assumption of infinite bulk conductivity, i.e., infinite range. Thus, the inclusion of the electron carrier range (or bulk field) in the analysis will result in a peaking of the $F(t)$ function, and perhaps allow the determination of the range.

The range may be introduced into the analysis in the following way. The total charge observed in the external circuit is the charge in the sheath plus the charge stored on the electrode at the end of the crystal away from the sheath. In terms of the field in the bulk region, $E_b(t)$, this is

$$q(t)=q_s(t)-\epsilon E_b(t)$$

or

$$q(t)=q_s(t)+\epsilon[dq_s(t)/dt]/[erR_0(t)], \tag{13}$$

where

$$q_s(t)=\rho(t)b(t). \tag{14}$$

Equation (13) is obtained by equating $E_b(t)$ to the bulk conduction current $-dq_s(t)/dt$ divided by the bulk region conductivity $erR_0(t)$, where $R_0(t)$ is the release rate in the bulk. We have assumed that the current in the bulk is given by the total rate of charge release in the sheath region. A constant release rate in the bulk is used to define the bulk conductivity, which assumes that the releasing states in the bulk essentially recapture at the same rate that they release. If this is not the case, the release rate and hence the bulk conductivity will be time-dependent. However, the changes

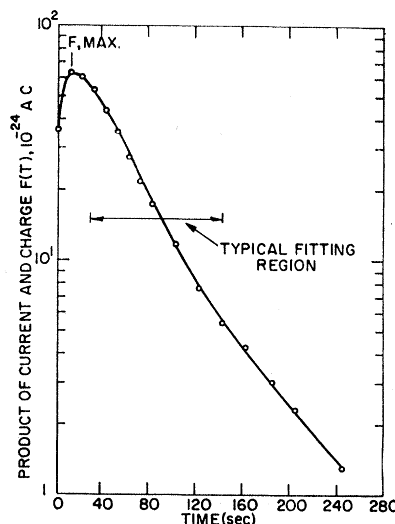

Fig. 5. Plot of $F(t)$ showing fitting region.

which occur during the sheath formation time [the time of the $F(t)$ peak] will be comparatively small and will not affect grossly the analysis made using a constant bulk release rate. The approach of Matthews and Warter[2] was to computer integrate (13) (with constant bulk release) and choose the range to give a best fit to the data. They also defined a sheath formation time and equated it to the time of the $F(t)$ peak. The approach here will be similar to the latter procedure.

Since the experimental $F(t)$ function has a peak (at a time we call T_m), the time derivative of $F(t)$ must vanish there.

Thus, at $t=T_m$ we have

$$\frac{dF(T_m)}{dt}=\left(\frac{dq(T_m)}{dt}\right)^2+\frac{q(T_m)d^2q(T_m)}{dt^2}=0. \tag{15}$$

Experimentally, T_m is near the region of validity of the simple model so that we may use the simple model value for the charge stored in the sheath,

$$q_s(t)=[2\epsilon V_0\rho(t)]^{1/2}$$

in (13). Then, substituting (13) in (15), one obtains an expression for the range in terms of the initial trap population N, the trap time constant τ, and the time T_m. For a time-dependent release rate, the result is extremely complex; however, since $T_m<\tau$, the bulk release rate has not changed much from its initial value N/τ. With this approximation, the following expression for range is obtained:

$$r=\epsilon\{1+[1+\lambda(\lambda^2-3\lambda+4)/(1-\lambda)^3]^{1/2}\}/2Ne, \tag{16}$$

where

$$\lambda=e^{-T_m/\tau}.$$

The range may also be obtained from the initial current per unit area,

$$j(0)=NerV_0/\tau L, \tag{17}$$

where the conductivity is the product of initial release rate N/τ, range, and electronic charge. Note that $r=\mu\tau_c$.

B. Experiment

The initial currents ranged from 10^{-11} to 10^{-9} A/cm^2, depending on voltage and time constant τ as given by (17). Inserting experimentally measured initial current densities and best-fit release times τ and densities N in (17), values of the range were obtained, most of which were within 20% of each other. The average value of the range calculated in this manner is 5×10^{-7} cm^2/V.

Using the best-fit values of N and the measured T_m in Eq. (16), values of the range were obtained all of which were within a factor of 2 of each other. The average value is 2×10^{-7} cm^2/V, in reasonable agreement with the initial conductivity value. The range may also be calculated by equating T_m to the sheath formation time as given by Matthews and Warter.[2] This also results in $r=5\times10^{-7}$ cm^2/V.

VII. NATURE OF TRAPPING LEVEL

Experiments were performed in which, after initial application of a voltage following pre-excitation, a reverse voltage of equal magnitude was applied. On the first voltage application, a large polarization charge was transported (about 23 times CV at 4 V). Upon voltage reversal, the charge transported was just $2CV$, and, upon reversal again, only $2CV$ was transported. This indicates that no charge was available in the 0.14-eV trap after the initial voltage application. Therefore, the 0.14-eV trap did not recapture the carriers, and the range measured is the range for capture by some other process. For a discussion of voltage reversal in bulk polarization, see Matthews and Warter.[2]

We have seen that the trap level energy is 0.14 ± 0.02 eV and that the range is about 5×10^{-7} cm^2/V. Also, voltage-reversal experiments indicate that retrapping by this level does not occur and that the carrier, once it leaves the 0.14-eV level, is either captured by some deeper trap or recombines.

The energy level of the trap correlates with an assumed trapping level postulated to explain the low-temperature emission from excited CdS crystals (insulating at room temperature) of green light of energy 0.16 eV less than the band gap energy.[8] The activation energy of the green emission has also been measured to be about 0.15–0.16 eV.[9,10] In insulating, photoconducting crystals of the type studied in the present work, the emission of this light is assigned to the recombination of a free electron and a trapped hole.[8]

The following considerations suggest that the trap studied in the present work is a hole trap. We have already seen that the range measured is not the range for retrapping by the same centers responsible for the polarization. Furthermore, experiments made between 85°K and room temperature showed no evidence of polarization currents. We may then infer that no traps deeper than 0.14 eV were active in capturing charge carriers; if there were such traps, we would certainly have been able to fill them with pre-excitation and should have observed polarization at higher temperatures. Also, even if such traps *were* present, we would expect them to be filled after optical excitation at 80°K. Thus, the range measured at 80°K is the intrinsic or recombination range. The recombination range for holes measured by Tabak and Warter[11] for sensitive CdS was approximately 7.5×10^{-7} cm^2/V, which compares well with that found in the present work, 5×10^{-7} cm^2/V.

In the same paper, Tabak and Warter report that the electron free lifetime is of the order of 10^{-2}–10^{-3} sec. With a mobility of 150 cm^2/V sec, the recombination range for electrons becomes 1.5–0.15 cm^2/V. Thus, on the basis of the range measurement and the indication that the range measured is the recombination range, it may be argued that the polarization currents observed in the present work were hole currents and that the 0.14-eV trap investigated is a hole trap.

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[8] R. E. Halstead, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley–Interscience, Inc., New York, 1967).

[9] A. N. Rushby and J. Woods, Brit. J. Appl. Phys. **17**, 1187 (1966).

[10] K. Maeda, J. Phys. Chem. Solids **26**, 1419 (1965).

[11] Mark D. Tabak and Peter J. Warter, Jr., Phys. Rev. **148**, 982 (1966).