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Authors

Taagepera, Rein
Williams, Ferd

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it is possible for the break from high sensitivity data to yield a different activation energy than that gotten from the break to low sensitivity. And finally, the calculated value of majority carrier density at $1/T_b=0$, gotten by extrapolating $\log n_b$ vs $1/T_b$ data, can no longer be considered to provide a reliable value for the capture cross-section ratio of the sensitizing centers since it again depends on the parameters characterizing the active thermal-quenching states.

It now seems plausible that many previously reported discrepancies between optical- and thermal-activation energy values for sensitizing centers resulted from the erroneous assumption that thermal quenching arose from the action of the sensitizing centers themselves. Apparently for stannic oxide, thermal quenching originates in one or more of the electron trapping levels. From the fact that $\log n_b$ vs $1/T_b$ data² yielded values of 0.33 eV for the break from high sensitivity and 0.47 eV for the break to low sensitivity, it seems appropriate to assume that the shallow electron trapping states are instrumental in causing the low temperature break while the deeper level is active at the higher temperatures. The involvement of the shallow electron

trapping states in the low temperature break also means that an anomalously low value of 700, previously interpreted as the capture cross-section ratio for the hole-trap sensitizing centers, is in no way indicative of this parameter.

It must be concluded that while the correlations mentioned above have not yet been established in a completely quantitative fashion, they do reflect the trends predicted by the Dussel-Bube theory. On the basis of the optical-quenching results it becomes necessary to modify the imperfection level scheme for flux-grown stannic oxide crystals to replace the 0.33-eV hole-trap sensitizing center by one at 1.3 eV above the valence band and to indicate that it takes no direct part in the thermal-quenching process.

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The authors wish to thank Professor R. H. Bube of Stanford University for bringing the superlinearity theory extension to their attention and for furnishing a preprint of the work.

Photoelectroluminescence of Single Crystals of Manganese-Activated Zinc Sulfide*

REIN TAAGEPERA† AND FERD WILLIAMS

Physics Department, University of Delaware, Newark, Delaware

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Photoelectroluminescence, which involves the control of electroluminescence by electromagnetic radiation, is reported for single crystals of manganese-activated zinc sulfide. Both plane-parallel and point-contact electrode structures were used. The latter resulted in greater homogeneity of luminescent emission with the applied voltage mainly across the spreading resistance regions. The field distribution was probed. The observations are explained with essentially the same basic theory as was earlier used to explain observations on vapor-deposited films. However, from the analysis of the data on single crystals we deduce that carrier multiplication is occurring in the cathode region and to a lesser extent in the anode region, and also obtain values for the local fields for acceleration of carriers and for collision excitation.

I. INTRODUCTION

PHOTOELECTROLUMINESCENCE (PEL), which is defined as the control of electroluminescence (EL) by incident electromagnetic radiation, was first observed by Cusano¹ and considered theoretically by Williams.² The effect was found with ultraviolet

radiation incident on thin films of zinc sulfide activated with manganese, arsenic, phosphorous, or antimony and co-activated with chlorine.^{3,4} The observations clearly involved PEL rather than electrophotoluminescence (EPL), which is the control of photoluminescence (PL) by an electric field, because the emitted visible light energy exceeded the incident ultraviolet (uv) energy by as much as a factor of 10 and therefore the electric field was clearly the main source of energy. In contrast to the EL and EPL of phosphor powders, reported by

* Supported by U. S. Army Engineer Research and Development Laboratories under contract DA-44-009 Eng. 5044. Based on a Ph.D. dissertation submitted to the University of Delaware by R. T. (June 1965). Presented in part at the Meeting of the American Physical Society, Philadelphia, March 1964 [Bull. Am. Phys. Soc. 9, 222 (1964)].

† Present address: Pioneering Research Laboratory, E. I. DuPont de Nemours & Company, Inc., Wilmington, Delaware.

¹ D. A. Cusano, Phys. Rev. 98, 546 (1955).

² F. E. Williams, Phys. Rev. 98, 547 (1955).

³ F. J. Studer and D. A. Cusano, J. Opt. Soc. Am. 45, 493 (1955).

⁴ D. A. Cusano, Ph.D. dissertation, Rensselaer Polytechnic Institute (1959); Dissert. Abstr. 20, No. 2 (1959).

Destriau^{5,6} which require alternating current, the PEL of thin films of ZnS:Mn, Cl occurs with direct current as well. The EL was negligible unless the film was simultaneously exposed to uv. The PEL intensity was as much as 80 times greater than the PL intensity with the same uv.

The explanation of PEL has been based on the photo-creation of charge carriers by uv in a high-field region, followed by acceleration and multiplication of carriers which excite luminescence by collision excitation of activator impurities.² In addition, an increase in electron injection has been emphasized as part of the PEL mechanism.^{7,8} This arises from the narrowing of the contact barrier due to the space charge created by photoionization. In the thin films it is not possible to separate spatially the injection, carrier acceleration and multiplication, and collision-excitation stages of PEL.

We initiated a program to study PEL in single crystals. Depending on electrode configuration, for example, plane parallel or point contacts, the investigations with single crystals can be made with controlled and measurable electric field distributions and with some separation of the sequential steps occurring in PEL. Our work involved 365 nm uv and dc voltages on single crystals of ZnS:Mn, Cl.

II. GROWTH, STRUCTURE, AND PHOTO-LUMINESCENT PROPERTIES OF ZnS:Mn,Cl CRYSTALS

Single crystals of ZnS were grown in this laboratory from the vapor phase according to the sublimation technique developed by Piper and Polich.⁹ MnCl₂ was mixed into the ZnS powder. Crystals were approximately 5 mm long and 5 mm in diameter. Manganese content of different crystals varied from 0.1 to 10% by weight. Optical absorption measurements indicated some variation in concentration throughout each crystal; however, microscopic observations revealed no separation into different phases and no gross differences in manganese concentration.

The x-ray diffraction pattern and birefringence under polarized light indicate that the crystals were hexagonal, with strongest growth along the *c* axis. Lattice parameters were $a_0=3.822$ and $c_0=12.530$. Electron spin resonance spectrum confirmed that an appreciable fraction of the manganese was in the ⁶S state of the $3d^5$ configuration at the zinc sites.

At room temperature the orange PL emission characteristic of manganese-activated ZnS was observed with uv excitation for crystals with manganese concentration

less than 3%. Excitation by mercury lines at 365 to 366 nm gave an asymmetrical emission spectrum with a peak at 583 nm. This agreed well with earlier reports on thin films (585 nm)⁴ and powders (584 nm)¹⁰ of hexagonal ZnS:Mn, Cl. At liquid-nitrogen temperature red-orange emission was observed even with manganese concentrations higher than 5%; at low concentrations the blue self-activated ($V_{Zn}+Cl$) emission predominated in some crystals.

For the PL emission in the 565 to 600 nm range the maxima in the excitation spectrum are shown in Table I, together with previous results on films and powders. Powders and single crystals give the same peak positions for the four bands which are due to the direct excitation of manganese centers, and which are insensitive to changes of the lattice constant.¹¹ The shortest wavelength peak corresponds to the excitation of a center formed by a zinc vacancy combined with a substitutional Cl ion ($V_{Zn}+Cl$).¹² The excitation of this center is sensitive to changes of the lattice constant¹¹ and leads to photoconductivity.¹⁰ The corresponding excitation peak tended to lie at longer wavelengths for single crystals than for powders. Resistivity of the crystals decreased from approximately $10^{10} \Omega \cdot \text{cm}$ in the dark to approximately $10^7 \Omega \cdot \text{cm}$ with uv excitation.

The PL rise and decay curves were not simply exponential, probably because of filling and thermal emptying of deep traps. The steepness of the PL rise curve depended on the time elapsed since, and duration of, previous exposures to uv. There is a detectable influence after more than 10 days in darkness. The relative intensities of the excitation bands for manganese emission also depend to some extent on previous conditions of excitation. This is understandable on the basis of the shorter wavelength excitation involving perturbed band-to-band transitions followed by energy transfer to the manganese and transfer to saturable traps competing with excitation of the manganese.¹³ In addition, a decrease in quantum efficiency of PL at low uv intensities shown in Fig. 1 indicates a competing radiationless de-excitation which is saturated at higher excitation intensities.

TABLE I. PL excitation maxima in ZnS:Mn, Cl.

	Excitation of ($V_{Zn}+Cl$) centers	Excitation of manganese centers			
		I	II	III	IV
Single crystals	358	397	430	466	494
Thin films ⁴	367
Powders ^{10,11}	340	397	432	476	506
	348	395	430	...	490

⁵ G. Destriau, *J. Chim. Phys.* **34**, 117 (1937); *Phil. Mag.* **35**, 700 (1947).

⁶ G. Destriau, *Compt. Rend.* **238**, 2298 (1954).

⁷ D. A. Cusano and F. E. Williams, *J. Phys. Radium* **17**, 742 (1956).

⁸ D. A. Cusano, *Luminescence of Organic and Inorganic Materials*, H. P. Kallmann and G. M. Spruch, Eds. (John Wiley & Sons, Inc., New York, 1962), pp. 494-522.

⁹ W. W. Piper and S. J. Polich, *J. Appl. Phys.* **32**, 1278 (1961).

¹⁰ R. H. Bube, *Phys. Rev.* **90**, 70 (1953).

¹¹ H. Treptow, *Z. Phys. Chem. Kristallphosphore II* (D. Ak. Wiss., Berlin, 1962).

¹² J. S. Prener and F. E. Williams, *J. Phys. Radium* **17**, 667 (1956).

¹³ L. Acchione and F. E. Williams (unpublished data).

III. EXPERIMENTAL STUDIES OF PHOTOELECTROLUMINESCENCE

A. Investigations with Large-Area Electrodes

The first tests were conducted with electrode structures similar to the sandwich-like geometry of the thin-film PEL cells⁴ [Fig. 2(a)]. The extended transparent electrodes were obtained by mechanically pressing two pieces of tin oxide-coated glass against opposite faces of a polished slice of ZnS: Mn, Cl crystal about 1 mm thick. Although the electrode structure is plane-parallel, the field distribution is not strictly laminar because of non-uniform contact to the crystal surfaces. The photomultipliers were EMI 9524B and RCA 7102. Ultraviolet from a GE H-100 BL 38-4 mercury lamp initiated PEL. A yellow filter transmitted the visible output from the crystal to the photomultiplier but eliminated the uv.

Without previous or concurrent uv incident on the crystal no EL was detected with up to 1500 V dc or ac. With uv and at least 500 V dc or ac an increase in luminescent intensity above the PL level was obtained. With 1500 V dc this increase became about seven times the PL intensity. Since the PL quantum efficiency of ZnS: Mn is well known to be close to unity,¹⁴ except at low excitation intensities, the electric field is clearly the main energy source for additional luminescence.

The PEL emission shifted towards wavelengths shorter than for the PL emission, similar to the PEL emission in ZnS: Mn, Cl films.⁴ The same effect has been reported for dc EL in ZnS: Mn, Cu, Cl films where no uv is needed to obtain EL.¹⁵

The quantum efficiency of the PEL, i.e., the ratio of the PEL intensity to the uv intensity, increased with voltage but decreased with increasing uv intensity. PEL intensity is defined here as the extra luminescent intensity in excess of the PL intensity.

The PEL emission with the large-area electrode structure [Fig. 2(a)] came from bright spots near the cathode and sometimes also at the anode. These spots

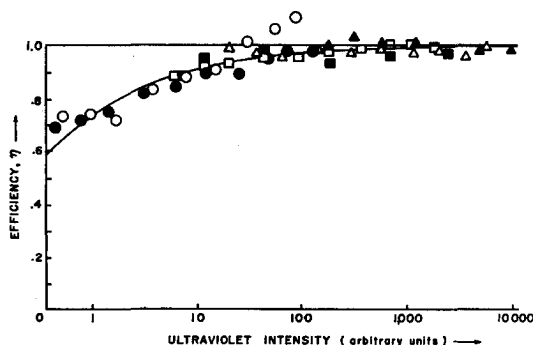


FIG. 1. Photoluminescent efficiency η vs intensity of excitation in arbitrary units.

¹⁴ D. Curie, *Luminescence in Crystals*, translated by G. F. J. Garlick (John Wiley & Sons, Inc., New York, 1963), p. 272.

¹⁵ P. Goldberg and J. W. Nickerson, *J. Appl. Phys.* 34, 1601 (1963).

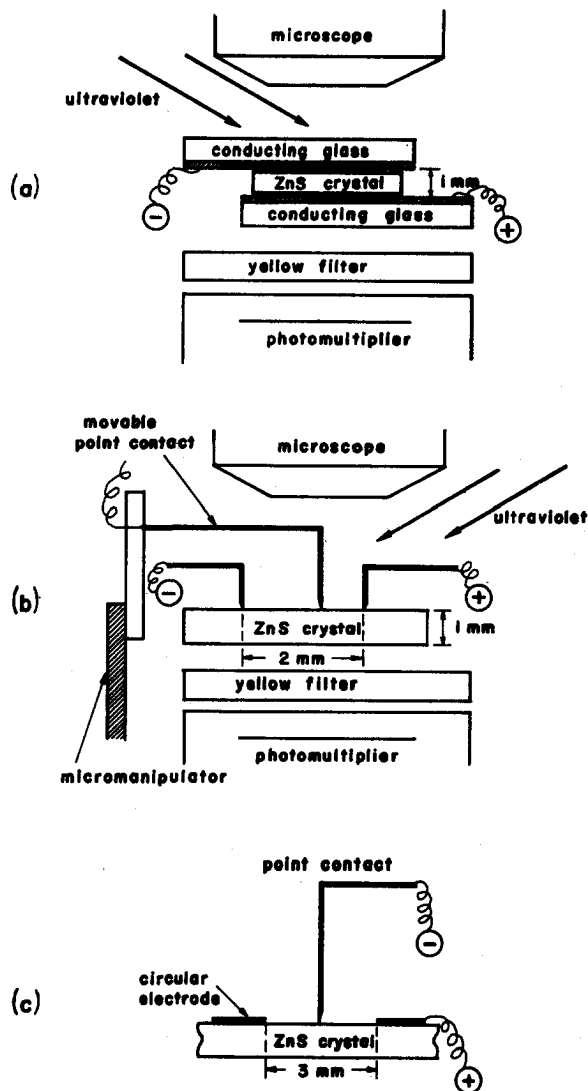


FIG. 2. Photoelectroluminescent cells: (a) plane-parallel transparent electrode structure, (b) point-contact electrodes plus probe; (c) combination of non-transparent extended electrode and point contact.

were 10 μ or less in diameter and became brighter and more numerous with increasing voltage. A difference in PEL was observed depending on whether uv entered the crystal through the cathode or the anode, being up to eight times more intense for irradiation through the cathode. Crystals with more than 5% manganese which did not show any PL at room temperature did not show any PEL either. With ac the PEL emission intensity varied little with frequency in the range from 50 to 500 cps. Above 500 cps the emission intensity decreased rapidly.

Phosphorescence due to previous uv irradiation was also enhanced by the electric field, and this sometimes gave the erroneous impression of simple EL, since the PL afterglow itself was already below the detection level. The PEL afterglow, that is, emission after re-

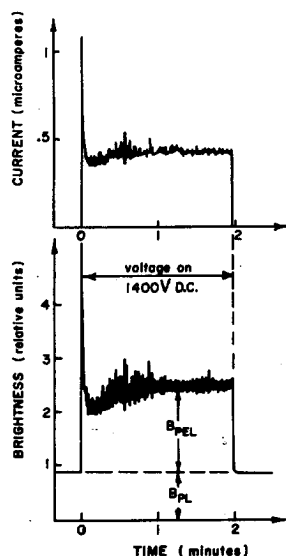


FIG. 3. Transient PEL effects for cell with one point contact.

moving the uv but leaving the field on, tended to last longer for the cathode spots than for the anode spots.

B. Investigations with Point Contacts

For further experiments, point contacts were used [Fig. 2(b)]. The radius of the area of contact between copper points and the ZnS:Mn, Cl crystal was approximately 0.04 mm. In relatively homogeneous crystals and with applied voltages in excess of 500 V, PEL emission occurred near the electrodes. In some cases a visible effect was detectable with 100 V. The minimum distance between point contacts was limited to about 0.5 mm because of discharges in the air.

With the two contacts at 2 mm from each other, with moderate uv intensity and with 1500 V dc a bright disk with a radius of 0.2 to 0.3 mm appeared around the cathode. Viewing through different thicknesses of gray filters indicated that the brightness was almost uniform throughout the bright region and decreased rapidly at its borders. The radius of the PEL disk increased when the interelectrode distance was decreased.

In addition to the PEL emission at the cathode a very small but bright spot was sometimes observed at the anode. When the contacts were displaced both spots moved smoothly along. However, the cathode PEL region became oblong and its center preceded the contact points in the direction of motion by about 0.1 mm. With uv turned off a similar phosphorescent region preceded the cathode as long as it was kept in motion over previously undepleted areas. This observation offers the possibility of separating the Gudden-Pohl effect from the photoelectroluminescence.

If the field were applied with uv already on, a time constant for the rise of PEL could be measured. This time constant was found to decrease rapidly with increasing voltage. With voltages higher than about 1000 V an initial transient often occurred, as shown in

Fig. 3. There is a close correlation between changes in current and in PEL intensity. When the field was turned off (with uv still on) the PEL intensity decreased with a time constant of less than 0.2 sec.

In more inhomogeneous crystals the PEL emission occurred mainly in the form of bright lines and dots at the crystal surface, in between the contacts. Most of these regions corresponded to visible crystal defects which may be built-in point contacts between regions of high conductivity or scattering regions for light generated elsewhere.

Measurements were made on several slices of three crystals which had large, relatively homogeneous regions. The potential distribution at the surface of one such crystal exposed to uv was probed as shown in Fig. 2(b). In the regions around the contacts where a voltage drop was detectable the equipotential lines were circular. The distribution along the lines joining the two contacts is shown in Fig. 4. Independent of which contact was negative, the total voltage drop across the spreading resistance region at the anode was 840 V, while the total voltage drop across the contact barrier and the spreading resistance region at the cathode was 660 V. Less than 300 V, and probably less than 100 V, were across the barrier region. Hence, the spreading resistance at the cathode amounted to 70% to 80% of the anode spreading resistance. PEL emission occurred near the cathode in the region where the local fields were stronger than approximately 5×10^8 V/cm. No PEL at the anode was observed in this particular experiment, although the local field near the anode was approximately 3×10^4 V/cm.

The cell shown in Fig. 2(c) was used to measure the electric current and the luminescence brightness as functions of voltage and uv intensity. When the central electrode was made negative the PEL emission took place in the central spreading resistance region. When the circular electrode was negative the current was high and the PEL emission occurred mainly at imper-

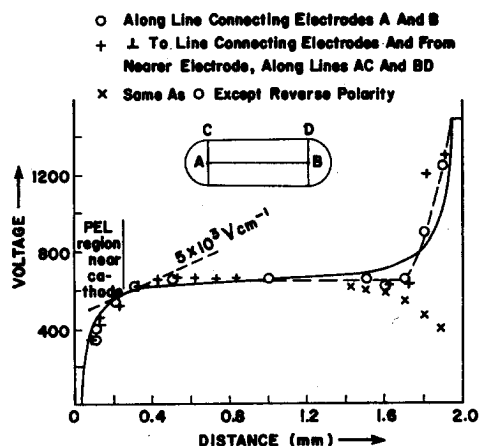


FIG. 4. Voltage distribution between two point contacts with moderate uv intensity and current of $0.1 \mu\text{A}$. Dashed line is best fit to data; solid line is based on $V \propto r^{-1}$.

fections adjacent to this electrode. Current-voltage relations were similar in both cases and are shown in Fig. 5. At low voltages the current was proportional to voltage, as indicated by straight lines of slope one on the log-log scale. The onset of PEL emission was found to coincide with departure from Ohmic behavior. The PEL intensity was approximately proportional to the square of the current, as shown in Fig. 6, which in turn depended on the voltage and the uv intensity. Different combinations of voltages and uv intensities which produced the same current also resulted in approximately the same PEL intensity. Therefore, the analysis of Roberts, as reported in Ref. 4, applied to these data would not rule out electroluminescent-photoconductive effects.

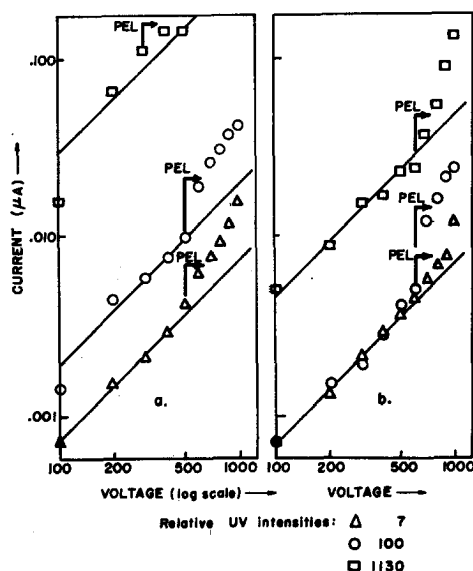


FIG. 5. Current vs voltage in a cell with concentric electrodes as in Fig. 2(c): (a) central electrode positive; (b) central electrode negative.

IV. DISCUSSION

A. Barrier Characteristics for Photoelectroluminescence

Experimental probing of the voltage distribution as shown in Fig. 4 indicates that with point contacts the largest part of the applied voltage occurs in the spreading resistance regions, rather than at the cathode barrier as is believed to be the case in thin-film PEL cells. However, the current through the crystal, therefore the PEL, is still regulated by the barrier width.

Many of the qualitative features of the mechanisms proposed for the PEL of thin films^{2,7,8} can be applied to the PEL of single crystals. At the metal-semiconductor interface the difference in work functions is compensated by an accumulation of positive space charge in the semiconductor which is assumed to be *n*-type, resulting in a potential barrier [Fig. 7(a)]. In accord-

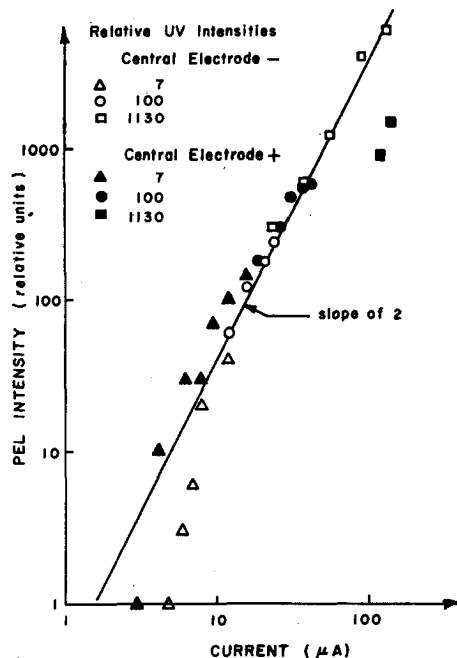


FIG. 6. Photoelectroluminescent intensity versus current.

ance with this interpretation metal electrodes with different work functions have earlier been shown to result in different barriers.¹⁶ The space-charge density, however, is limited by the concentration of ionizable defects, and consequently the barrier is relatively wide. On exposing the contact to uv, conduction electrons are created in the high field region near the contact and the barrier width is reduced [Fig. 7(b)]. When an external potential is applied with the metal negative, injection of electrons from the metal into the semiconductor crystal occurs if the potential barrier is sufficiently narrowed to permit tunneling [Fig. 7(c)]. When in-

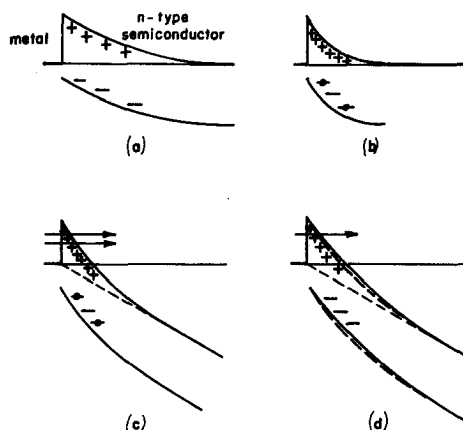


FIG. 7. Effects of ultraviolet radiation uv and applied voltage V on electron injection: (a) no uv, no V; (b) uv, no V; (c) uv, V (transient state); (d) uv, V (steady state).

¹⁶ W. W. Piper and F. E. Williams, Phys. Rev. 87, 151 (1952).

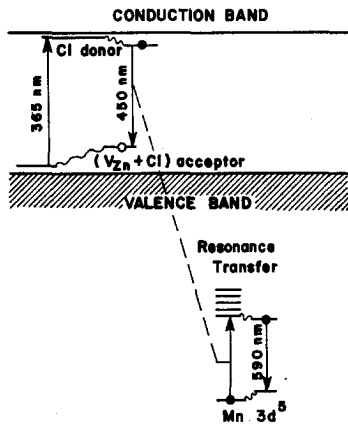


FIG. 8. Band theory model of luminescent centers and transitions in ZnS:Mn, Cl.

jection occurs, the concentration of conduction band electrons at the contact increases so that the probability of capture by ionized defects increases, therefore the potential barrier is somewhat widened by the injection [Fig. 7(d)]. When the voltage is applied the barrier is still narrow, and the initial injection rate is higher than during the following steady state. The observed current burst (Fig. 3) is in accord with the assumed time constants.

B. Electroluminescence in the Spreading Resistance Region

The conduction electrons photogenerated in the high-field region or injected through the barrier are accelerated in the cathode spreading resistance region where the field strength is approximately proportional to $1/r^2$, as indicated by Fig. 4. The local conductivity is less than 2×10^{-8} mho/cm everywhere in the region where PEL emission occurs; the average conductivity (corresponding to exact proportionality of the field to $1/r^2$) in this region is 6×10^{-9} mho/cm. These figures are based on the assumption that the diffusion current can be neglected.

The general model of luminescence centers in ZnS:Mn, Cl is shown in Fig. 8. The energy of the $6S$ state of the $3d^5$ configuration of substitutional manganese relative to the band structure of ZnS is shown based on a tight-binding calculation.¹⁷ In principle uv-controlled EL emission could result from the impact excitation of both Mn and $(V_{Zn}+Cl)$ centers in the high-field region. However, it has been thought that in thin-film PEL the excitation of the Mn by inelastic collisions predominates.⁸ Since the excitation of $(V_{Zn}+Cl)$ centers leads to carrier multiplication while the excitation of Mn centers does not, the voltage distribution between two symmetrical point contacts on a single crystal would be different for the two cases.

If there is no carrier multiplication the spreading resistance would be the same at the cathode and at the anode, provided that the diffusion current can be

¹⁷ H. Gumlich, R. L. Pfrogner, J. C. Shaffer, and F. E. Williams, *J. Chem. Phys.* **44**, 3929 (1966).

neglected and that the mobilities are the same. Because of collisions with luminescence centers in the cathode region where most of the PEL emission occurs the electron mobility is expected to be less than at the anode, leading to a higher voltage drop across the cathode spreading resistance region. On the other hand, if there is carrier multiplication connected with the PEL emission in the cathode region, the resistivity in this region is reduced. If little or no impact excitation occurs at the anode, the voltage drop at the cathode could then be less than the voltage drop at the anode. This is the case for the experimentally probed voltage distribution, as shown in Fig. 4, and, therefore, carrier multiplication must occur in the cathode region.

Carrier multiplication could occur by collision excitation of the $(V_{Zn}+Cl)$ center or by band-to-band collision excitation, depending on relative cross sections for these processes. In the latter case the effects of nonradiative recombination through the trapping levels should be included in view of the explanation of the PL efficiency shown in Fig. 1. Collision excitation of $(V_{Zn}+Cl)$ centers accounts for the concurrence of carrier multiplication and PEL.

C. Theoretical Basis for Carrier Acceleration

The local PEL emission intensity depends on the number of electrons that the photogeneration and injection through the barrier make available for acceleration, and on the average distance Λ an electron has to travel before it attains sufficient energy for impact excitation. This distance Λ is determined by the rates at which electrons gain energy from the electric field and lose it by lattice collisions. In polar crystals the low-energy scattering peak occurs at approximately 0.1 eV.¹⁸ Thus an electron with an energy above this

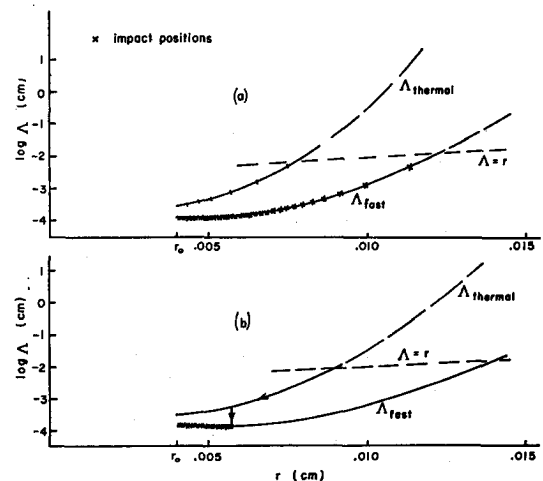


FIG. 9. Average distances between successive collision excitations in spreading resistance region: (a) cathode region; (b) anode region.

¹⁸ F. Seitz, *Phys. Rev.* **76**, 1376 (1949).

critical value can be accelerated by a field which would be too low for a thermal electron. For regions with nonuniform field strength $E(r)$ it is difficult to calculate Λ exactly. However, if $E \approx K/r^2$, and if Λ is much smaller than the coordinate r_1 of the point where the acceleration process starts, then the Taylor expansion of $E(r_1 + \Lambda)$ about r_1 converges:

$$E(r_1 + \Lambda) = E(r_1) [1 - 2(\Lambda/r_1) + 3(\Lambda/r_1)^2 - \dots]. \quad (1)$$

To the zeroth approximation (i.e., E constant over the short distance Λ) we can use a function $\Lambda(E)$ determined for regions of uniform field strength¹⁸:

$$\Lambda = AE(\epsilon_2/\epsilon_1)^{B/E}, \quad (2)$$

where ϵ_2 is the energy required for the impact excitation, ϵ_1 is the initial energy of the electron, and A and B are constants for a given crystal.

If we assume that only the $(V_{zn} + Cl)$ centers are excited, the minimum excitation energy ϵ_{ex} is 3.4 eV. The average energy reached when the collision actually occurs is 1.1 to 1.3 times higher than this minimum energy.¹⁸ The ϵ_2 is accordingly taken as $1.2\epsilon_{ex}$ or 4.1 eV. When an electron starts from "rest," its initial energy ϵ_1 is of the order of the thermal energy kT (0.025 eV at room temperature). However, after the first collision, the resulting two electrons have a total average energy of $0.2\epsilon_{ex}$ left. This means that for further collisions $\epsilon_1 = kT$ must be replaced by $\epsilon_1 = 0.1\epsilon_{ex} = 0.34$ eV, which is above the critical energy.

Figure 4 gives $E \approx 2.7/r^2$ near the cathode, r being in cm and E in V/cm. The resulting $\Lambda(r)$ curves are shown in Fig. 9(a) for $\epsilon_1 = kT$ and for $\epsilon_1 = 0.34$ eV, with parameters A and B chosen arbitrarily (but not in conflict with the estimates of Seitz for impurity atom excitation¹⁸) as $A = 4 \times 10^{-10}$ cm²/V and $B = 5 \times 10^4$ V/cm. Electrons injected through the cathode barrier enter the spreading resistance region with higher than thermal energies and create new fast electrons by impact excitation of $(V_{zn} + Cl)$ centers. Successive average impact excitation positions are indicated on the Λ_{fast} curve by crosses. The average distance between successive excitations increases rapidly for r larger than 0.010 cm (corresponding to fields lower than 25 000 V/cm). The assumption that fast electrons remain at higher than thermal energies after collisions loses its validity at low fields strengths; the assumption $\Lambda \ll r$ also breaks down for $r > 0.012$ cm. Therefore, Λ increases even faster than indicated by the Λ_{fast} curve and hardly any impact excitations should occur for $\Lambda > 0.012$ cm. Actually PEL emission is observed at twice this distance. This result could be obtained by altering the values of the parameters A and B . Because of the approximative nature of these calculations no exact numerical fit is attempted.

Near the anode $E = 3.5/r^2$ experimentally (Fig. 4) and the $\Lambda(r)$ curves [Fig. 9(b)] differ only slightly from those of the cathode region. However, here all the electrons start from the bulk of the crystal and move toward the point contact at thermal energies. On the average, the first collision excitation occurs at less than 0.002 cm before the metal contact is reached. Therefore, only 12 generations of secondary electrons are produced at the anode, while 29 generations are produced at the cathode. Thus the total PEL output as well as the emission area are smaller at the anode than at the cathode. However, since the fast electrons are converging at the anode and diverging at the cathode, the local PEL intensity at the anode (if it occurs) can be higher than anywhere in the cathode region. These semiquantitative differences between the PEL emission at the two electrodes agree with experimental observations.

Starting from the basic equations used by Seitz, Λ can also be calculated when the first correction term in Eq. (1) is taken into account (i.e., dE/dr is considered constant over the distance Λ), provided that the condition

$$E \gg [(\epsilon_2)^{\frac{1}{2}} - (\epsilon_1)^{\frac{1}{2}}] [(2/e)(dE/dr)]^{\frac{1}{2}} \quad (3)$$

is satisfied. Then Eq. (2) is replaced by

$$\Lambda = AE(\epsilon_2/\epsilon_1)^{B/E} [1 + (\epsilon_2/eE^2)(dE/dr)]^{-B/E}. \quad (4)$$

Condition (3) is satisfied in our experimental conditions if $r \ll 0.25$ cm. For r varying from $r_0 = 0.004$ cm to 0.015 cm the value of $\log \Lambda$ calculated from Eq. (2) varies by at least 2. The correction for $\log \Lambda$ introduced by using Eq. (4) instead is less than 0.03 and can thus be neglected in this range.

V. CONCLUSIONS

The phenomenon of photoelectroluminescence has been found to occur in single crystals of manganese-activated zinc sulfide. Homogeneous excitation is attained in the spreading resistance regions near point contacts where the local fields are controllable and measurable. Charge-carrier multiplication in the region of the cathode is deduced from the field distribution between electrodes. The local field necessary for acceleration of injected carriers is less than for acceleration of thermally created carriers. The concurrence of photoelectroluminescence and carrier multiplication is in accord with collision excitation of self-activated centers, which transfer energy to the manganese, as the dominant impact ionization process.

ACKNOWLEDGMENTS

We wish to thank Miss Chava Fischler for preparing the crystals used in these investigations.