

Oscillations in Current and in Electroluminescence in ZnS:Mn Single Crystals*

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Oscillations with time of the current and electroluminescence have been observed for single crystals of manganese-activated zinc sulfide exposed to dc voltages and ultraviolet radiation. The oscillations are correlated with saturation in the current-voltage characteristics. These observations are accounted for on the basis of assuming quenching of the conductivity at a threshold field and of applying the principle of minimum entropy production to the steady-state solutions. From the threshold fields obtained on fitting the theory to the data and from the concurrence of electroluminescence, consideration is given to the origin of field quenching.

I. INTRODUCTION

CURRENT oscillations as a function of time have been reported by Böer¹ in CdS, Ridley and Pratt² in Ge, and Barraud³ in GaAs. These oscillations were shown to result from the formation of high field regions inside the crystal, which move from cathode to anode, causing the current to be lower during the existence of that region inside the crystal, i.e., between formation at the cathode and disappearance at the anode. These high field regions are a result of field quenching of the conductivity.

Böer⁴ has applied kinetic analysis to a dielectric with field-quenching conductivity and has thus provided a kinetic basis for steady-state inhomogeneous field distributions, whereas Ridley⁵ has considered solids with differential negative resistances and by the application of the principle of minimum entropy production has shown the formation of high field domains is favored. He notes that the speed of movement of the high field region inside the crystal can be considered to be proportional to the effective mobility of the carriers including trapping. Kiess and Stöckmann⁶ have interpreted saturated photocurrents on the basis of field quenching of the conductivity and also using the principle of minimum entropy production.

Electroluminescence in some materials can be initiated by ultraviolet radiation while an applied field is, of course, present and is often called photoelectroluminescence.⁷ Taagepera and Williams⁸ reported photoelectroluminescence in single crystals of ZnS:Mn.

In this paper we report the observation of simul-

taneous oscillations in the current and in the electroluminescent emission of ZnS:Mn crystals, the correlation of these oscillations with the current-voltage characteristics, and the interpretation of these observations in terms of a simple model. The measurements were made with irradiation by ultraviolet (uv) so that the current is photoconductive and the electroluminescence (EL) could be described as photoelectroluminescence.

II. EXPERIMENTAL OBSERVATIONS

During the investigation of EL in ZnS:Mn single crystals⁹ with high applied voltages, oscillations as a function of time were observed in both the EL and the accompanying current. The crystals were 0.3 to 1.0 mm thick, with silver-gold alloy electrodes on opposite faces; the electrodes were evaporated onto the polished crystal faces in high vacuum, and were semitransparent (approximately 40% transmission). Direct-current voltages up to a few thousand volts were applied between the electrodes, while the crystal was illuminated with uv (3650 Å). With these conditions of excitation, the emission includes both orange electroluminescence characteristic of the manganese activator and the orange plus some green photoluminescence. The EL and the accompanying current were measured for the different applied voltages. The current increased approximately linearly with the voltage at low voltages; saturated and remained constant with voltage at intermediate voltages; and increased again at higher voltages. The current-voltage function is dependent on ultraviolet intensity. These effects are shown in Fig. 1 for a typical crystal.

The EL-voltage curves were either parallel to the above, or rose faster, sometimes having an inflection point instead of a plateau. At all voltages on the current plateau, both current and EL oscillated as a function of time, in phase with each other, as shown in Fig. 2. With higher uv intensities, the plateau shifted to higher voltages, and the frequency of oscillations increased, as shown in Fig. 3. The observed periods of oscillation were from a fraction of a minute up to about 10 min. Some

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¹ K. W. Böer and W. E. Wilhelm, *Phys. Status Solidi* **4**, 237 (1964).

² B. K. Ridley and R. G. Pratt, *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 487.

³ A. Barraud, *Compt. Rend.* **256**, 3632 (1963).

⁴ K. W. Böer and W. E. Wilhelm, *Phys. Status Solidi* **3**, 1704 (1963).

⁵ B. K. Ridley, *Proc. Phys. Soc. (London)* **82**, 954 (1963).

⁶ H. Kiess and F. Stöckmann, *Phys. Status Solidi* **4**, 117 (1964).

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

⁸ R. Taagepera and F. E. Williams, *Bull. Am. Phys. Soc.* **9**, 222 (1964).

⁹ Different crystals contain between 0.1 and 1% Mn; spectrographic analysis indicates 10⁻³ to 10⁻²% Cu.

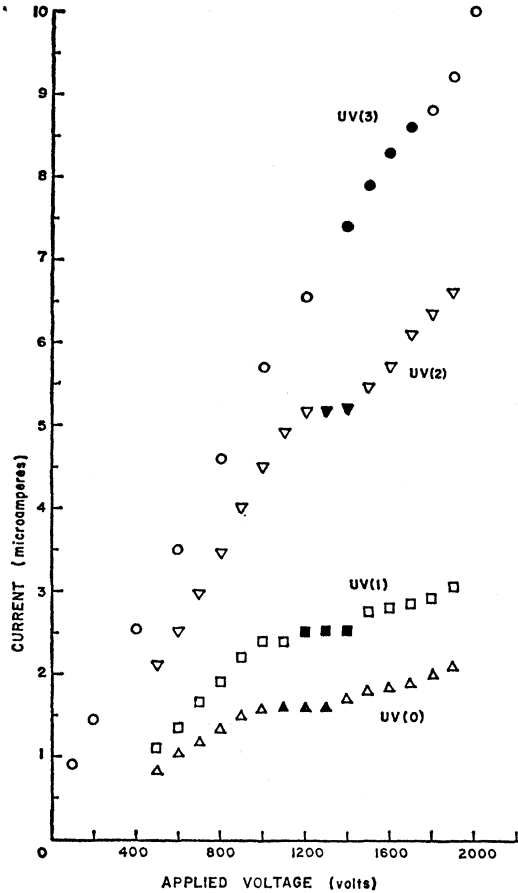


FIG. 1. Current as a function of voltage for different uv intensities. Filled symbols denote points at which oscillations of current with time were clearly observed.

crystals had a plateau, but no recorded oscillations, which might have been because the frequency was either too high or too low. Some crystals showed more than one plateau.

With the addition of infrared radiation peaking at approximately $750 \text{ m}\mu$ the current and EL are reduced, as is the case for low-voltage photoconductivity of these crystals, and the oscillations are enhanced and their frequency increased.

In order to determine whether the oscillations might arise from photoconductive response to the electroluminescent emission, crystals were irradiated from an external source with orange light. Although a greater intensity than the electroluminescent intensity was used, no change in current or in electroluminescence was observed.

All measurements were made at room temperature.

III. PROPOSED MODEL

In our analysis we assume a simple form for the conductivity σ versus local field E , use the principle of minimum entropy production to determine the steady-

state current versus applied voltage, and consider the existence of laminar high field regions as prerequisite for current and electroluminescent oscillations. In Fig. 4 is shown the assumed functional dependence of σ on E . This approximate form is consistent with the change in concentration of conduction electrons expected from the field-dependent release of trapped positive holes discussed in Sec. IV. The lifetime of the trapped holes and the concentration of conduction electrons are thus decreased at the critical field E_t .

For applied voltages $V < E_t D$, the crystal might be expected to either have a homogeneous field distribution with $E < E_t$, $\sigma = \sigma_h$, or else if the voltage is above a certain threshold, break up into two regions: one, of thickness d , with low conductivity σ_l and a field $E > E_t$, and the remainder of the crystal with the high conductivity σ_h and field $E < E_t$, as shown in Fig. 5. Since the applied voltage is the same in both cases, and the total resistance R higher in the second, the rate of entropy production will be lower in the second case:

$$\dot{S} = \dot{Q}/T = (1/T) \times (V^2/R) \quad (1)$$

as a result of which the second case will be favored. As far as our analysis is concerned the region of high field could consist of many laminae, rather than a single layer, the sum of whose thicknesses equals d .

Since \dot{Q} also equals VJ and V is constant, the minimum current is favored. The current density J equals $\sigma_l E_t$; therefore, region 1 will take the minimum field that is high enough to reduce the conductivity to σ_l , so that E_1 equals E_t , that is,

$$J = \sigma_l E_t = \text{const} \quad (2)$$

the current remains at the above constant value as long as the applied voltage is within the range to be derived.

To calculate the thickness d of the high field region we write the following:

$$J_1 = J_2 \quad (\text{div } J = 0);$$

therefore

$$J = \sigma_l E_t = \sigma_h [(V - E_t d)/(D - d)]$$

and

$$d = \{(\sigma_h/\sigma_l)V - E_t D\} / \{(\sigma_h/\sigma_l) - 1\} E_t; \quad (3)$$

from Eq. (3) we notice that

$$\begin{aligned} d < 0 & \text{ for } V < E_t D \sigma_l / \sigma_h \equiv V_t \\ d > D & \text{ for } V > E_t D \equiv V_c. \end{aligned} \quad (4)$$

Physically, $0 < d < D$, which means that the inhomogeneous distribution can occur only for $V_t < V < V_c$; for the "allowed voltages," d grows linearly with V , thus maintaining E_1 at the constant value E_t . When the voltages are below or above the plateau region we expect:

$$\begin{aligned} J &= \sigma_h V/D & \text{for } V < V_t \\ J &= \sigma_l V/D & \text{for } V > V_c, \end{aligned} \quad (5)$$

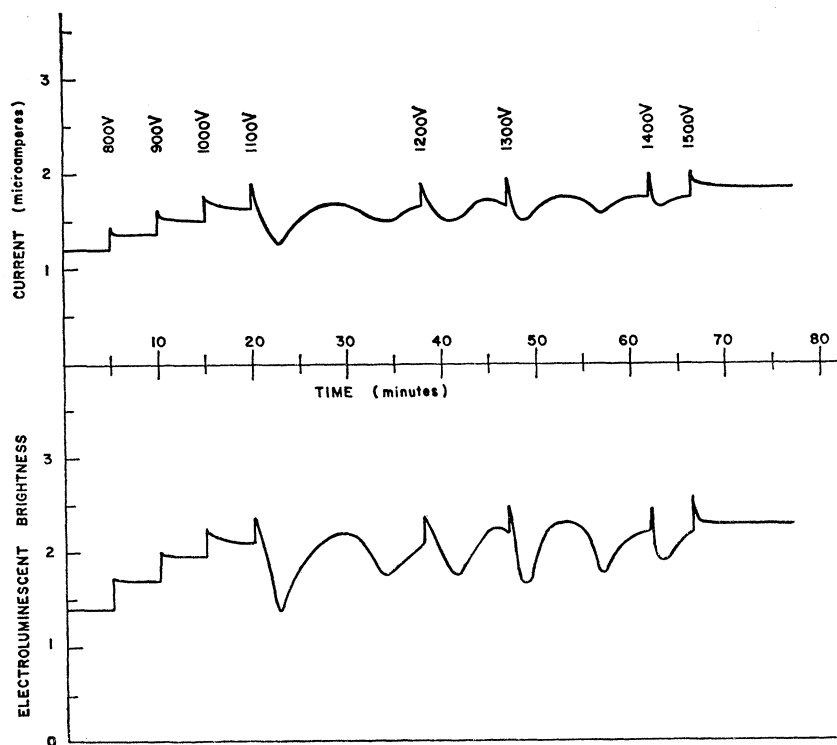


FIG. 2. Current and electro-luminescence as a function of time of observation including changes in applied voltage, for uv(0) of Fig. 1.

because below V_t the crystal is homogeneously in the high-conductivity state, and above V_e the whole crystal is in the low-conductivity state. The $J(V)$ function to be expected from a substance with the field-dependent conductivity of Fig. 4 is shown in Fig. 6.

IV. APPLICATION TO EXPERIMENTAL DATA AND DISCUSSION

Equations (2) and (5) were fitted to the experimental data and the parameters σ_h/σ_l and E_t were thus evaluated. These parameters are presented in Table I for the data in Fig. 1. For this case the electrode areas and crystal thickness are $6.1 \pm 0.5 \text{ mm}^2$ and $0.35 \pm 0.02 \text{ mm}$, respectively. The numbers for uv intensity refer to the different curves on Fig. 1.

From the values of E_t and σ_h/σ_l it is possible to make some suggestions regarding the mechanism of field quenching responsible for the change in conductivity shown in Fig. 4. From the understanding of photoconductivity of these materials we assume that there are

TABLE I. Parameters for the data in Fig. 1.

Ultraviolet intensity	E_t (volts/cm) ($\times 10^4$)	σ_h/σ_l	Plateau current (amperes) ($\times 10^{-6}$)
high uv (3)	(5.1 ± 0.4)	1.19 ± 0.05	(8.0 ± 0.5)
uv (2)	(4.2 ± 0.3)	1.20 ± 0.05	(5.2 ± 0.2)
uv (1)	(4.2 ± 0.3)	1.34 ± 0.10	(2.5 ± 0.2)
low uv (0)	(4.0 ± 0.3)	1.37 ± 0.10	(1.6 ± 0.1)

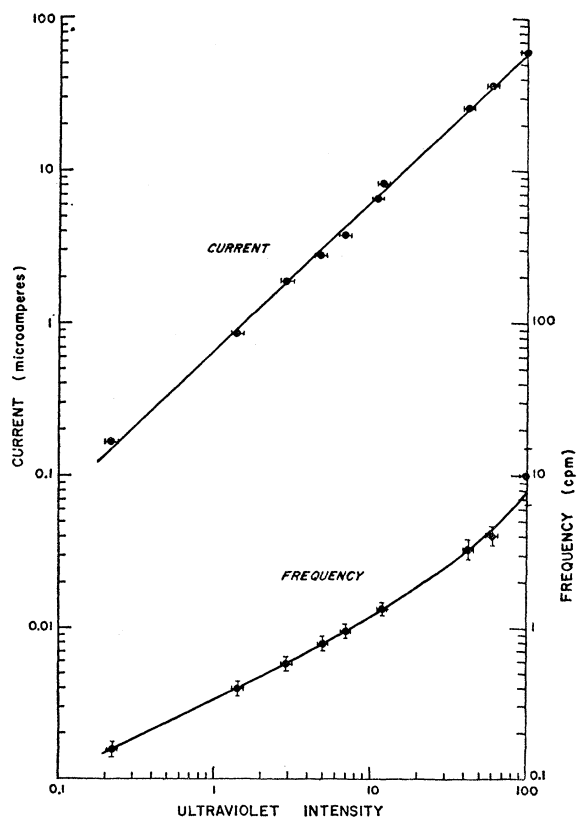


FIG. 3. Current and frequency of current oscillations as a function of uv intensity, for a fixed applied voltage.

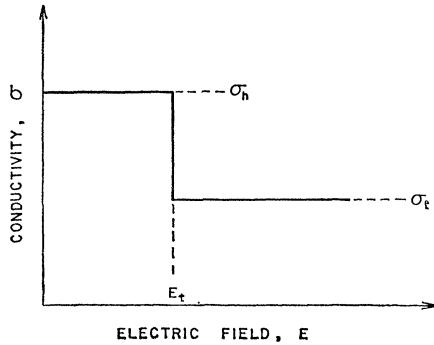


FIG. 4. The conductivity σ versus field E for proposed model.

trapped positive holes which are approximately equal in concentration to that of the conduction electrons responsible for the photocurrent. In other words, the concentration of free holes is assumed to be small. The field E_t in some way must reduce the lifetime and therefore the concentration of trapped holes.

In Fig. 7 is shown the band model without applied field (A) and with field (B). We are concerned with steady-state conditions with ultraviolet excitation in each case. For A the concentration of trapped holes is determined by the balance between α plus γ and β . The α process is determined by the specific rate constant for thermal ionization k' and given by $s \exp(-\mathcal{E}/kT)$, where \mathcal{E} is the thermal depth; the γ process is given by $nv_t\sigma_t$ where n is the concentration of conduction electrons, v_t is their thermal velocity, and σ_t is the capture cross section of thermal electrons by trapped holes. As shown in Fig. 8, α is the dominant process for annihilation of trapped holes for $\mathcal{E} \leq 0.7$ eV for the values of parameters used. We obtain n equal to $4 \times 10^7 \text{ cm}^{-3}$ for $uv(0)$ of Fig. 1, from the conductivity, assuming a mobility of $100 \text{ V}^{-1} \text{ sec}^{-1} \text{ cm}^2$.

In order to explain the field quenching of Fig. 4 we consider what field-dependent processes can compete with or enhance the above zero-field processes for annihilation of trapped holes of different \mathcal{E} . We propose three possibilities:

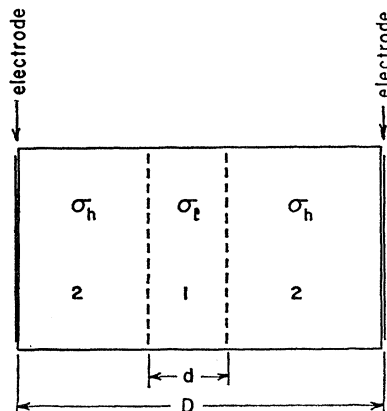


FIG. 5. The crystal with its regions of high and low conductivity.

1. Direct field ionization or tunneling, for which the probability $P_1(E)$ for Coulombic states of depth \mathcal{E} in a field E is¹⁰:

$$P_1(E) = 17 \times 10^{12} (E/K^5)^{1/4} \exp[-7 \times 10^7 \mathcal{E}^{3/2}/E] \quad (6)$$

assuming that the effective mass of trapped holes is equal in magnitude to the free electron mass and K is the static dielectric constant. This is plotted in Fig. 8 as a function of \mathcal{E} for the field E_t . Field ionization competes with thermal ionization only for $\mathcal{E} < 0.01$ eV.

2. Collision ionization by energetic conduction electrons which is given by

$$P_2(E) = nv_e\sigma_e \exp[-\mathcal{E}/E\lambda], \quad (7)$$

where v_e and σ_e are the velocity and collision cross section of the energetic electron and λ is the mean free path of conduction electrons in the field E . As shown in Fig. 8 even assuming $\sigma_e/\sigma_t \approx 10$, $P_2(E_t)$ competes with thermal ionization only for $\mathcal{E} > 1.3$ eV.

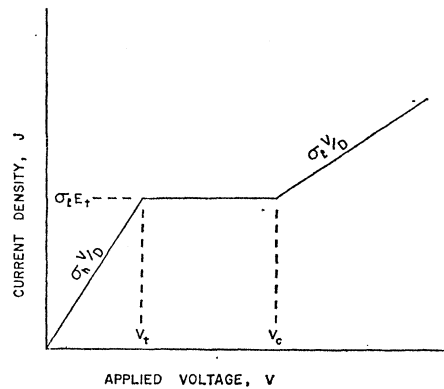


FIG. 6. The $J(V)$ dependence to be expected for a crystal with the $\sigma(E)$ characteristic of Fig. 4.

3. Field enhanced thermal ionization of trapped holes which is given by

$$P_3(E) = s e^{-(\mathcal{E}-\varphi)/kT}, \quad (8)$$

where φ is the change in height of the thermal barrier due to the applied field E . We consider the hole traps to be acceptors and estimate φ on the basis of effective mass acceptor states. The effective mass potential is therefore

$$V = -(e/Kr) - Ez, \quad (9)$$

from which φ is readily obtained and equals $2(eE/K)^{1/2}$. This process is also shown in Fig. 8. It is evident that all three mechanisms contribute in a material with a broad spectrum of hole traps; however, the field-enhanced thermal ionization appears to dominate for most of the traps present in these materials.

We have also considered a decrease of σ through a

¹⁰ W. W. Piper and F. E. Williams, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 95.

decrease in mobility μ , as has been reported for Si and Ge. In such a case the current does not decrease with the field, but only saturates (μ does not decrease sharply enough); therefore, this effect does not account for our experimental results.

The electroluminescence is assumed to be a result of either direct collision excitation of the Mn atoms, or collision excitation of forbidden-gap states from which occurs transfer of energy to the Mn atoms. In both cases we can write

$$EL \propto J \exp(-\mathcal{E}/E\lambda), \quad (10)$$

where the exponential is the same as in Eq. (7), except that \mathcal{E} here is the energy necessary for the EL excitation process; J is the current density.

The EL could originate either in the bulk of the crystal, or, at least partly, in a thin high-field layer (such as an exhaustion layer) at the cathode. Because of light scattering, we could not determine experi-

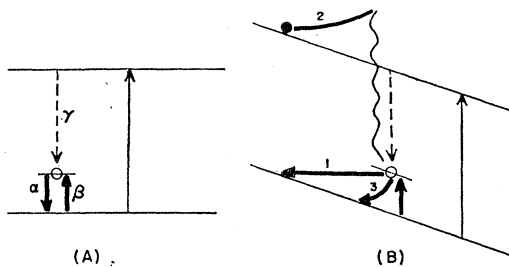


FIG. 7. The different transition processes involving trapped holes in the steady state for: (A) without applied field, (B) with applied field.

mentally which was the case. In the first case, we have to insert the average E values into Eq. (10) in order to get the voltage dependence. Using $\lambda \sim 10^{-6}$ cm, however, gives a marked voltage dependence in the exponential, which does not fit those of our data showing a parallel voltage dependence of EL and J . The fitting can be gotten only for $\lambda > 5 \times 10^{-5}$ cm, which is unexpectedly large. In the second case, a much higher E can be assumed for the cathode layer, so that (10) can fit the data even for low λ . Even in this case J is determined by the bulk characteristic. In both cases, however, the linear relation between EL and J manifests itself in the close correspondence between the EL and J oscillations.

The uv dependence of period of oscillation can be explained by changes in effective mobility of carriers, since trapping is less probable per carrier with high uv intensities. The effect of infrared can be explained in part by the increased occupational probability of shallow hole traps and the increased effective mobility

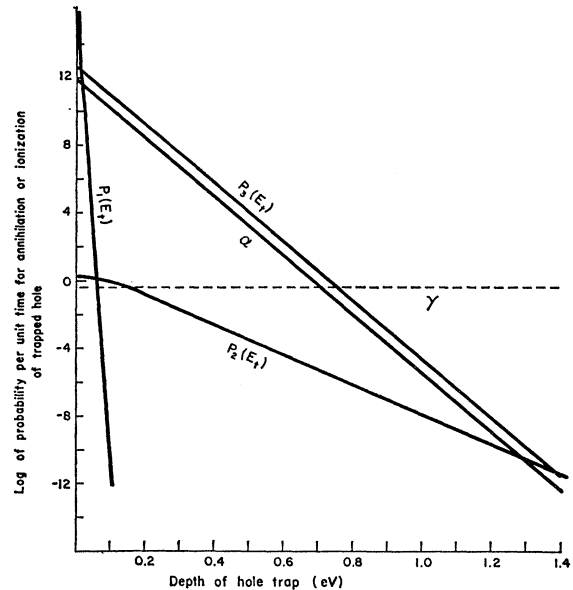


FIG. 8. Probability per unit time for the different processes of Fig. 7, with $E = E_t = 4 \times 10^4$ V/cm, as a function of depth of hole trap. The parameters used are: $s = 10^{12}$ sec $^{-1}$ for α ; $v_t = 10^7$ cm sec $^{-1}$, $\sigma_t = 10^{-16}$ cm 2 for γ ; $v_e = 5\mathcal{E}^{1/2}v_t$, $\sigma_e = 10^{-14}$ cm 2 and $\lambda = 10^{-6}$ cm for $P_2(E)$.

of positive holes, both resulting from depleting the deep-hole traps by the infrared. The deep-hole states are expected from the presence of copper acceptors.

V. CONCLUSIONS

We have found for ZnS:Mn single crystals, current saturation and, in the same voltage range, current and electroluminescence oscillations. These effects are accounted for and correlated on the basis of a simple model of conductivity versus field involving an abrupt decrease in conductivity at a critical field and on the basis of the principle of minimum entropy production. Field inhomogeneities which are prerequisite for oscillations are found to arise in the steady-state solution within a voltage range where the current is shown to be constant. Direct field ionization, collision excitation by energetic conduction electrons, and field enhanced thermal ionization have been considered and shown to contribute to changes in trapped hole concentrations and therefore to the field-dependent conductivity to different extents depending on energies of the trapped holes.

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