

to T^{-1} . Rough calculations show that, in a temperature interval in which the intervalley scattering causes the elastoresistance to have a temperature dependence much stronger than T^{-1} , the mobility should show marked deviations from a $T^{-3/2}$ variation. In the temperature interval considered, the mobility variation is not greatly different from $T^{-3/2}$.⁴ Thus, even though the phonon energy $\hbar\omega$ is not known, the observed temperature variation of the elastoresistance is to be expected.

⁴ F. Morin, *Phys. Rev.* **93**, 62 (1953).

We can conclude that the elastoresistance varies with temperature in a manner consistent with the theory described above.

IV. ACKNOWLEDGMENTS

The author is indebted to Dr. E. N. Adams for calling the importance of the elastoresistance effects to his attention and for discussions of their interpretation, and to J. P. McKelvey, J. W. Faust, and A. J. Bennett for supplying the samples.

Electroluminescence of Zinc Sulfide Single Crystals

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Quantitative measurements of the electroluminescent emission from synthetic single crystals of zinc sulfide with silver paint contacts under 60-cycle half-wave voltage excitation have been carried out at several temperatures. Other workers have shown that the emission intensity has two major peaks per cycle, the first coincident with the voltage maximum and the second as the voltage is falling to zero. These peaks have the same color, and both appear to originate throughout the crystals, but they have different voltage dependencies. The second peak is the larger at low-voltage amplitudes, but the first peak grows the more rapidly with increasing voltage amplitude. Emission intensities of the order of 10^{12} photons per second, with energy efficiency of the order of 10^{-5} , were obtained. The total current consists of a displacement current which is linear with voltage and a conduction current which is roughly exponential with voltage. No evidence of space-charge polarization was detected. It is tentatively suggested that excitation occurs by impact of conduction electrons accelerated through internal barriers, that the two emission peaks result, respectively, from immediate recombination and from recombination delayed by trapping of the excited electron, and that the electric field tends to hold the electron in the trap state.

INTRODUCTION

ELECTROLUMINESCENCE may be defined as the emission of visible radiation by a solid at subincandescent temperatures when subjected to an electric field without previous excitation. The latter restriction distinguishes true electroluminescence from a variety of related phenomena which may occur when a field is applied to a phosphor during or after excitation by x-rays, ultraviolet light, etc.

Electroluminescence in silicon carbide was described by Lossew.¹ Other workers²⁻¹⁰ more recently have studied the phenomenon in a variety of powder phosphors, the powder being suspended in a dielectric between condenser plates. Of the types of phosphors studied, those based on zinc sulfide have received by

far the greatest emphasis and have been developed to commercially practical brightness levels.⁷

Electroluminescence of zinc sulfide single crystals has been reported by Piper and Williams¹¹ (denoted PW below) and by Watson, Dropkin, and Halpin¹² (denoted WDH below). They have shown the emission intensity under sinusoidal exciting voltage to contain two peaks per half cycle, the first in phase with the voltage peak and the second as the voltage is falling to zero. Both PW and WDH attribute the excitation of luminescence to impact on the luminescent centers of fast conduction electrons, the acceleration of these electrons taking place in a macroscopic barrier. PW believe the barrier to be at the cathode, while WDH believe it to lie within the crystal. As for the peaks in emission intensity, PW attribute the in-phase peak to electrons tunneling through the cathode barrier and the out-of-phase peak to electrons released from deep donor levels in the barrier, while WDH attribute these peaks respectively to immediate and delayed recombination with ionized centers, the delay being ascribed

¹ O. Lossew, *Wireless World and Radio Review* **271**, 93 (1924).

² G. Destriau, *Phil. Mag.* **38**, 700 (1947).

³ Payne, Mager, and Jerome, *Illum. Eng.* **45**, 688 (1950).

⁴ S. Roberts, *J. Opt. Soc. Am.* **42**, 850 (1952).

⁵ C. W. Jerome and W. C. Gungle, *J. Electrochem. Soc.* **100**, 34 (1953).

⁶ J. F. Waymouth, *J. Electrochem. Soc.* **100**, 81 (1953).

⁷ Homer, Rulon, and Butler, *J. Electrochem. Soc.* **100**, 566 (1953).

⁸ Zalm, Diemer, and Klasens, *Philips Research Repts.* **9**, 81 (1954).

⁹ S. Nudelman and F. Matossi, *J. Electrochem. Soc.* **101**, 546 (1954).

¹⁰ J. F. Waymouth and F. Bitter, *Phys. Rev.* **95**, 941 (1954).

¹¹ W. W. Piper and F. F. Williams, *Phys. Rev.* **81**, 151 (1952); *Brit. J. Appl. Phys., Supplement No. 4*, 39 (1955).

¹² Watson, Dropkin, and Halpin, *Phys. Rev.* **94**, 777(A) (1954); *Enlarged Abstracts of the Electrochemical Society Spring Meeting*, (1954).

to the removal of the electron from the vicinity of the center. However, our results disagree in several respects with both of these mechanisms, as will be discussed below.

EXPERIMENTAL METHODS

Crystals

The specimens used in this work were synthetic zinc sulfide single crystals grown by Kremheller of our laboratories by deposition from the vapor phase.¹³ The crystals obtained to date have shown wide variations in morphology, impurity content, and luminescence characteristics. Rod-shaped crystals of uniform color and uniform blue fluorescence under 3650 Å excitation with rapid decay were selected for the present study. Nearly all such crystals are electroluminescent, whereas crystals showing green or orange fluorescence are rarely electroluminescent.

Synthetic zinc sulfide crystals have been shown¹⁴ to be quite complex in structure, containing both cubic and hexagonal regions, and random and periodic stacking faults. The crystals used in the present work covered a wide range of structures, from nearly pure cubic through faulted structures to nearly pure hexagonal. All those whose structure was determined were oriented with the long axis in the (110) direction referred to the hexagonal coordinate system. The crystals used ranged in length from about 3 to 10 mm and in width from about 0.1 to 0.7 mm, usually having irregular polygonal cross sections.

Emission Intensity Measurements

The crystal is excited to luminescence by the application of a time-varying voltage across its length. In most of the present work, a half-wave-rectified 60-cycle sine wave (denoted "half-wave" below) was used. The light emitted by the crystal was detected by means of a calibrated Type 1P28 photomultiplier tube whose output was displayed on a cathode-ray oscilloscope.

Since the light output is generally too dim for conventional spectroradiometry, the measurement of emitted intensity was carried out in a series of narrow wavelength bands, isolated by means of interference filters. The rate of photon emission in the j th such band is given approximately by

$$n(\lambda_j) = C_j i_j \text{ photons/sec-}\mu, \quad (1)$$

where

$$C_j = \frac{10^7 4\pi R^2 \lambda_j}{hc A \Delta\lambda_j T_j S_j} \quad (1a)$$

R = distance from crystal to cathode of photomultiplier;

A = area of cathode of photomultiplier; λ_j = peak transmission wavelength of filter; $\Delta\lambda_j$ = integrated bandwidth of filter; T_j = peak transmission of filter; S_j = sensitivity of photomultiplier at wavelength λ_j , in amps/watt; i_j = photomultiplier anode current, in amps; and c = velocity of light, 3×10^{17} m μ /sec. Because of various uncertainties in calibration and geometry, the results have only order-of-magnitude precision.

Physical Arrangements

Figure 1 shows the apparatus used for measurements over a range of temperatures. The crystal is cemented by dots of conductive silver paint at its end to a slab of crystalline quartz which provides excellent electrical insulation and good thermal conduction. The silver paint is extended from the crystal so as to hold two small coil springs carrying copper plugs, to which contact is made by quartz-insulated tungsten probes. The slab, together with a copper plate carrying a copper-constantan thermocouple, is bolted to a copper block brazed to the brass base of the chamber. The thermocouple is taken out through one of two tubes through which predried nitrogen can be circulated for prevention of condensation at low temperatures, and the photomultiplier is inserted through a snug-fitting hole in the top of the chamber. Temperature control is provided by an appropriate bath surrounding the lower part of the apparatus.

Some of the work was done in a simpler apparatus, limited to room temperature, but providing more efficient geometry in that the light path was unobstructed. The filter constants C_j of Eq. (1a) were determined for this apparatus, and results obtained in the variable temperature apparatus were corrected by an empirical factor.

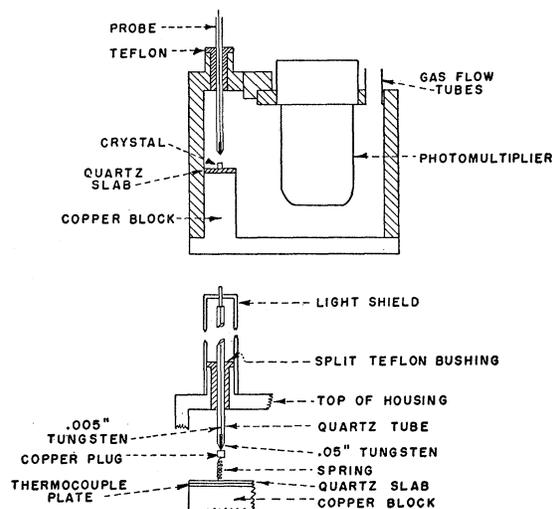


FIG. 1. Apparatus for light and current measurement over a range of temperatures. Top, elevation cross section. Bottom, detail of contacting arrangement, not to scale.

¹³ A. Kremheller, Electrochemical Society Spring Meeting, Chicago, Illinois (May 2-6, 1954); *Sylvania Technologist* 8, 11 (1955).

¹⁴ L. W. Strock and V. A. Brophy, *Am. Mineralogist* 40, 94 (1955).

Current Measurement

A novel feature of the present work is the measurement of the current passing through the crystal under the half-wave voltage. For this purpose, a variable capacitor was used as one arm of a bridge to balance out the displacement current in the crystal and the quartz slab. The crystal and quartz slab formed the second arm, and the other two arms consisted of equal resistors across the inputs of the differential preamplifier of the oscilloscope used as detector. Since the time derivative of the voltage changes abruptly twice in the cycle, balance of the displacement current could readily be detected by the absence of corresponding discontinuities in the net current displayed on the oscilloscope. The capacitor was adjusted under fairly low voltage (a few hundred peak volts) until this condition was achieved, and was thereafter left untouched. Since the two circuits to be balanced actually contain distributed resistance and inductance as well as capacitance, perfect balance cannot be achieved, but the unbalance current is negligible in comparison with the crystal currents obtained under the higher working voltages.

EXPERIMENTAL RESULTS

General Behavior

The steady-state light output from electroluminescent ZnS crystals under 60-cycle half-wave excitation has been described by WDH. Oscillograms are shown in Fig. 2 for a typical crystal at various voltage amplitudes. At low voltages, the emission comes to a peak at about 150 degrees phase,¹⁵ and decays during the second half-cycle. As the voltage is increased, this "150-degree peak" increases in intensity and a new peak at 90 degrees phase emerges. With further increase of voltage, the 90-degree peak grows the more rapidly. In most experiments, the voltage was increased until there was discernible instability in the 90-degree peak, taken as a sign of incipient breakdown. In some crystals, the 150-degree peak contains a 180-degree component, and, more rarely, a small peak at about 130 degrees. These "fine structure" peaks vary in prominence from crystal to crystal, and have not yet been investigated in detail.

The relative colors of the two major peaks have been investigated by measuring the emission through blue and green filters. In general there was no significant color difference between the peaks in a given crystal, although some crystals showed small deviations in either direction. This result contradicts WDH, who found the 90-degree peak to be distinctly bluer than the 150. Subsequent examination of one of their crystals by the writer, however, disclosed that the 90-degree peak contained appreciable ultraviolet due to arcing

¹⁵ It is convenient to refer to the brightness peaks by the location of their maxima in phase degrees with respect to zero phase of the exciting voltage.

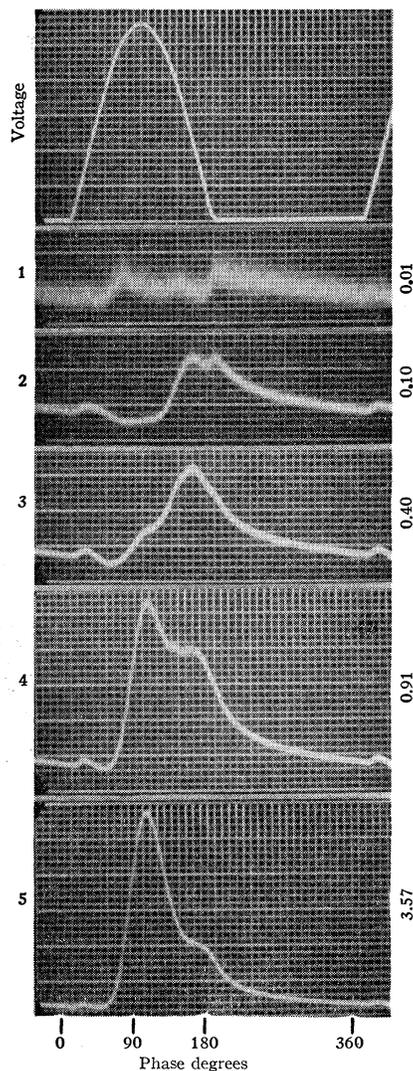


FIG. 2. Half-wave voltage wave form (at top) and oscillograms of electroluminescence of crystal with Ag paint electrodes. Figures at left give voltage amplitudes in kv. Figures at right give scale factors, emission intensity (arbitrary units) per scale division.

in an internal void. This ultraviolet was transmitted by their "blue" filter, giving a spurious result.

Many crystals have been examined microscopically to determine the spatial distribution of the emission. In air, the high refractive index of ZnS results in multiple internal reflection, and the light often appears to originate at the ends or at surface or internal flaws. However, it is significant that in no case was there any appreciable change of distribution with polarity. Furthermore, microscopic observation through a synchronous shutter showed that the spatial distributions of both major peaks were, within limits of visibility, the same. By immersing the crystal in a fluid of refractive index $n_D = 2.0$,¹⁶ the critical angle is increased

¹⁶ "High Series Index of Refraction Liquid 2.0," R. P. Cargille Laboratories, Inc., New York, New York.

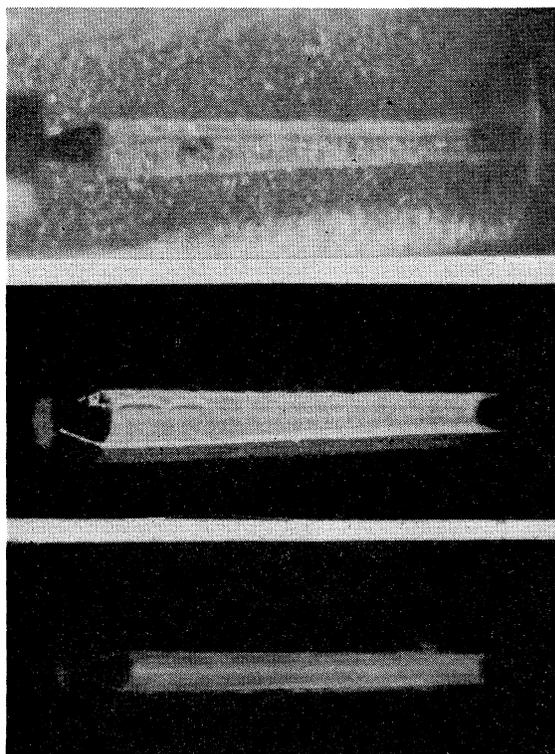


FIG. 3. Photomicrographs of an electroluminescent ZnS crystal. Top, external illumination. Middle, electroluminescence in air. Bottom, electroluminescence in high-index fluid.

to about 60° , and observations under these conditions indicate the emission to be generally uniform throughout the crystal. In a few crystals, poorly resolved bright transverse striations or rows of dots were discernible. These observations are illustrated in Fig. 3.

Approach to Steady State

The first few cycles of emission after sudden application of the half-wave voltage were observed by photographing a triggered single sweep of the oscilloscope. The steady state was reached after some five to ten cycles, during which the residual intensity at the end of the cycle increased while the peak heights usually increased but sometimes decreased slightly. Both infrared irradiation and long resting in the dark failed to give reproducibility in the transient behavior of the peak heights. However, the total change was usually less than twenty percent of the steady-state height; an example is shown in Fig. 4(a). With full-wave excitation, on the other hand, there was a marked build-up in the peaks in the first few cycles, as shown in Fig. 4(b). Presumably this is due to the accumulation of electrons in the conduction band or in traps, since the absence of a zero-field interval such as exists in the half-wave cycles does not give the excitation opportunity to decay. From this comparison of 60-cycle full-wave and half-wave excitation, we may conclude that each cycle of the

latter starts with the crystal "nearly" in its ground state, and we may therefore hope to correlate the resulting emission with other physical properties of the "unexcited" crystal.

Steady-State Results

Emission Intensity

Figure 5 shows approximate spectral distributions of the emission from a typical crystal. It is noteworthy that all three curves have about the same shape, confirming the above-mentioned result that there is no appreciable difference in spectral distribution between the two major peaks. The emission is seen to consist mainly of a broad band centered at about $470 \text{ m}\mu$, similar to that of a blue-electroluminescent ZnS:Cu powder phosphor.⁶

From the total emission intensities (areas under curves of Fig. 5), we obtain a calibration factor for conversion of the unfiltered photomultiplier response to absolute intensity in photons/sec. This factor should, strictly speaking, be separately determined for each crystal. In view of the many other errors in these measurements, however, the amount of labor involved seemed unwarranted, and the factor used was the average of the values obtained from two crystals.

Figure 6 shows the absolute intensities of the 90-degree peak and the time-average emission from a typical crystal as functions of the voltage amplitude at temperatures of 25° , 0° , and -78°C . All crystals observed to date have shown a progressive deterioration in brightness during the course of a series of measurements. These data were taken after the crystals had been "aged" beyond the initial rapid deterioration.

Current

After balancing out the displacement current under low voltage, as described above, the system remained in balance under all voltages, showing that the displacement current amplitude in the crystal is linear with voltage. The instantaneous net current as function of the instantaneous voltage in the half-wave cycle is shown in Fig. 7. The current is roughly exponential

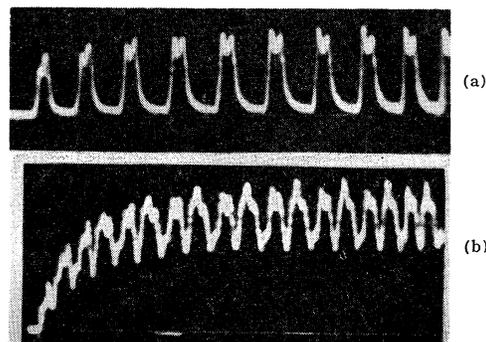


FIG. 4. Initial cycles of electroluminescence of a ZnS single crystal. Top, half-wave excitation. Bottom, full-wave excitation.

with voltage. The falling current is somewhat greater than the rising current, showing that the conductivity of the crystal is temporarily increased by exposure to the peak voltage. It is particularly to be noted that there is no reverse current detected in any part of the cycle. The small current close to 180 degrees cannot be measured due to the unbalance current mentioned above. However, there is no doubt whatever about the existence of forward current at the time of the 150-degree peak.

Efficiency

From the measured light output, current, and voltage, we compute the average efficiency $\bar{\eta}$ of the over-all cycle as

$$\bar{\eta} = h\bar{\nu} \int_0^T L dt / \int_0^T i V dt, \quad (2)$$

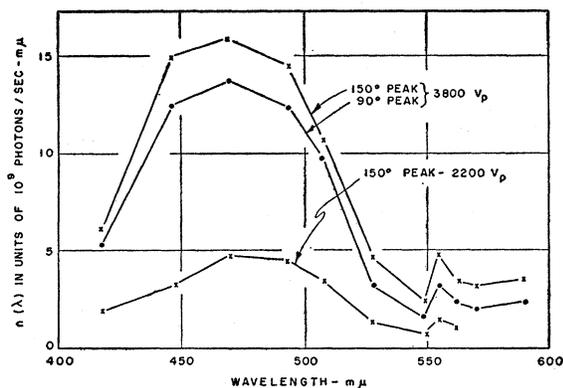


FIG. 5. Photon distributions in electroluminescent emission from a ZnS single crystal.

where

$$L = \int_0^\infty n(\lambda) d\lambda \quad (2a)$$

= instantaneous rate of photon emission,

$$h\bar{\nu} = \frac{1}{L} \int_0^\infty n(\lambda) \frac{hc}{\lambda} d\lambda \quad (2b)$$

= average quantum energy of emitted light.

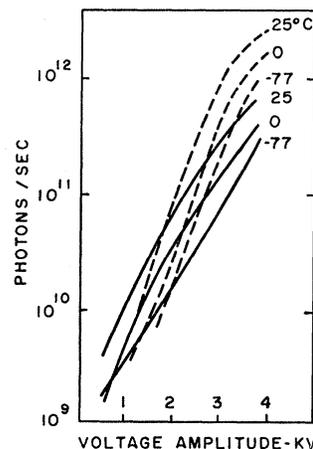
The value of $h\bar{\nu}$ was obtained by graphical integration of the data of Fig. 5. Values of L , i , and V were scaled off the oscillograms, and the integrations in Eq. (2) were performed numerically.

We may also compute the instantaneous efficiency η_{90} of the 90-degree peak since L , V , and i are all stationary at this instant:

$$\eta_{90} = h\bar{\nu} [L/iV]_{90^\circ}. \quad (3)$$

Also of interest are the photon-electron ratios $\bar{\xi}$ and ξ_{90} for the over-all cycle and the 90-degree peak, given

FIG. 6. Absolute intensities of 90-degree peak (broken curves) and time-average (solid curves) electroluminescent emission from a ZnS single crystal.



respectively by

$$\bar{\xi} = \int_0^T L dt / \int_0^T i dt / e, \quad (4)$$

$$\xi_{90} = e[L/i]_{90^\circ}. \quad (5)$$

The meaning of these ratios requires some discussion. The denominators, current divided by electronic charge, give the total number of electrons per second passing any given transverse plane in the crystal. In general, both free and bound electrons would be included, but the absence of space charge polarization means that only the former are involved here. Now we may *formally* define a reaction cross section in the usual manner,¹⁷ viz.,

$$\sigma = \frac{\text{No. of reactions per second}}{\text{Incident flux} \times \text{No. of reacting centers}}. \quad (6)$$

Thus, we find that

$$\xi = \sigma N / A, \quad (6a)$$

where σ = cross section of a luminescent center, N = total number of centers in the crystal, and A = cross-sectional

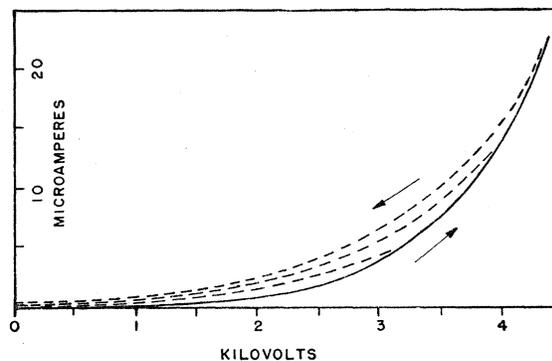


FIG. 7. Instantaneous current vs voltage in half-wave cycle for three voltage amplitudes.

¹⁷ See for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 97.

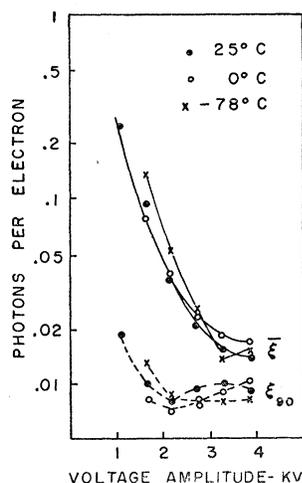


FIG. 8. Photon-electron ratios in 90-degree peak and time-average electroluminescent emission from a ZnS single crystal.

area of crystal. It must be emphasized that σ is purely a formal quantity. But if it can later be shown that excitation occurs by electron impact, then σ will have the physical significance of a collision cross section multiplied by an emission probability.

Figures 8 and 9 show η and ξ for one of the three crystals on which these data were measured. Despite considerable variation among the crystals, certain features seem to be common:

1. ξ_{90} is roughly independent of temperature and increases slowly with voltage.
2. Within a factor of three, $\xi_{90} \cong 0.01$, i.e., the 90-degree peak amounts to about 1 photon per 100 electrons traversing the crystal.
3. η_{90} is also roughly independent of temperature and is roughly constant or a slowly decreasing function of voltage.
4. Within a factor of two, $\eta_{90} \cong 10^{-5}$.
5. Both ξ and η decrease with increasing voltage, since the 150-degree peak increases less rapidly than the current.

DISCUSSION

Excitation Processes

Various authors have recognized that there are at least three possible mechanisms for the excitation of electroluminescence, viz., (a) direct field excitation of luminescent centers, analogous to the Zener effect, (b) injection of holes, and trapping of the latter in the ground state of the centers, and (c) impact of fast electrons on the centers. We shall consider these in turn. With regard to direct field excitation, PW have estimated the required field strength in ZnS:Cu to be 2×10^7 v/cm, while Burns,¹⁸ by a different approach, obtains 3×10^6 v/cm. In view of the high estimated field strengths, these and other authors reject this mechanism. We concur in this conclusion, but for a different reason, since it is entirely conceivable that sufficiently

¹⁸ L. Burns, J. Electrochem. Soc. **100**, 572 (1953).

high fields exist in localized regions of a crystal. However, under this mechanism one would expect ξ to be of the order of unity at all voltages, since each conduction electron would arise from excitation of a luminescent center. It is hardly conceivable that only a few percent of the electrons arise through this mechanism, since the required high-field regions could not exist in the presence of a parallel conduction mechanism.

Excitation by hole injection through a *p-n* junction has been observed¹⁹ in silicon carbide crystals. The strongest reason for rejecting this mechanism in zinc sulfide is that it provides no simple way of accounting for the out-of-phase emission peak. This peak is, indeed, absent in the emission oscillograms presented in reference 19. A second reason is that the voltage required in zinc sulfide crystals seems much too high.

Impact excitation was considered in some detail by Curie.²⁰ Although neither the theory of high-field phenomena in crystals nor our knowledge of the structural details of zinc sulfide is sufficiently advanced for a quantitative evaluation, Curie's considerations make impact excitation seem plausible, and we shall base the subsequent discussion on it. The observed slight increase of ξ_{90} with voltage seems concordant with this mechanism, but the decrease of ξ is not readily understandable.

PW also accept the impact excitation mechanism, but limit its region of occurrence to an exhaustion layer at the cathode, where the field is concentrated by space charge. In support of their hypothesis, they find that the intensity of the in-phase emission peak under ac excitation depends upon the work function of the cathode material. However, one would also then expect the emission of light to be localized near the cathode. As described above, we have never observed such localized emission. WDH propose that impact *ionization*

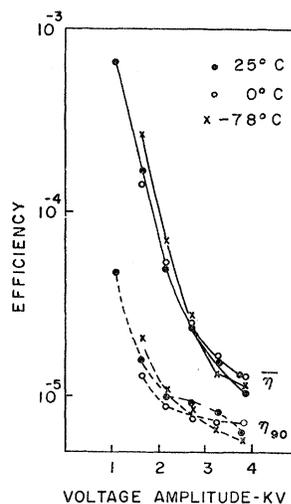


FIG. 9. Efficiency of 90-degree peak and time-average electroluminescent emission from a ZnS single crystal.

¹⁹ Lehovc, Accardo, and Jamgochian, Phys. Rev. **83**, 603 (1951); **89**, 20 (1953).

²⁰ D. Curie, J. phys. radium **14**, 510 (1953).

occurs in macroscopic barriers within the crystal. Indeed, they found such barriers by a probe method under low dc voltages, and claimed that when the emission is localized its maximum coincides with the barrier. This coincidence, however, may well have been the result of internal reflection in crystals containing macroscopic flaws. Our own observations have disclosed no correlation between the emission and the barriers found by probing.

On the other hand, it seems highly plausible that *microscopic* barriers may play a key role. Ince²¹ has found that extremely high magnetic fields fail to quench electroluminescence, showing that the excitation must be localized in small regions. These regions might well be associated with rectifying junctions between regions of different conductivity type, such as *n*- and *p*-type or all *n*-type but with different donor concentrations. The voltage drop would then be concentrated across the alternate junctions which were biased in their reverse direction, and the rapidly increasing current-voltage characteristic would correspond to "breakdown" of the barriers. If there are of the order of 10^3 to 10^4 barriers per cm along the crystal, the emission would appear uniform under any microscopic resolution that it has yet been possible to employ.

Emission Processes

PW attribute the in-phase emission peak to electrons which enter the crystal from the cathode and the out-of-phase peak to electrons released from donor centers in the exhaustion barrier, the emission in both peaks being supposed to occur immediately following excitation. However, in a given half-cycle, the out-of-phase emission would occur *first*; thus, under half-wave excitation there would be a peak near zero rather than near 180 degrees. WDH postulate that the center is ionized and the electron swept away by the field and subsequently trapped. They then attribute the in-phase peak to capture of conduction electrons and the out-of-phase peak to the return of the trapped electrons under the influence of the space-charge field. The critical objection to this mechanism is the absence of reverse current coincident with this peak. The observed height of the 150-degree peak would require readily measurable reverse currents if the electron range is an appreciable fraction of the crystal length. Instead, there is a measurable *forward* current at the time when this peak reaches its maximum.

The observations can be explained by attributing both peaks to excitation which occurs principally during the short time interval about the 90-degree phase when high current flows. The 90-degree peak then arises from

"immediate" emission, while the 150-degree peak is delayed by trapping of the excited electron in or near the center. The relative voltage dependencies of the two peaks are then understandable, since a given center could undergo several successive 90-degree processes, but only one 150-degree process in one cycle.

In the 150-degree process, the return of the electron to the ground state is delayed until the applied field is reduced. The delay must be a direct effect of the field rather than simply a result of a long lifetime of the trap, since the phase of the peak remains constant over a wide temperature range, hence over a wide range of trap lifetimes. It appears, therefore, that the electron is in some way held in the trap by the field. This does not imply that the thermal depth of the trap is necessarily increased, but only that the over-all probability of transition from trap to ground state is decreased. If we accept the hypothesis²² that the luminescent center is a large complex, then the polarization of an excited metastable state might lead to this effect. As a crude picture, the electron would be drawn to the edge of the large center and there could not recombine with the activator atom.

The idea of trap stabilization is consistent with the quenching of emission usually observed when an electric field is applied to a phosphor during or after ultraviolet excitation. The temporary stimulation also observed in such experiments may be a true electroluminescence effect, i.e., excitation of additional centers. However, it must be admitted that these phenomena are extremely complicated, and that quite different ideas which have been advanced to explain them²³ may well turn out to be correct.

Summary of Conclusions

Impact of fast electrons, accelerated through microscopic barriers, appears to be the most plausible mechanism for excitation of the luminescent centers. The excited electron may return to the ground state immediately, or may become trapped in a metastable excited state of the center. In the latter case, the presence of the electric field tends to hold the electron in the trap.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to his Sylvania colleagues and to Professor J. J. Dropkin for many helpful and stimulating discussions. Especial gratitude is due to Dr. A. Kremheller for the crystals and information relating to them; to Mr. V. A. Brophy for the x-ray diffraction studies; and to W. S. Romito and S. R. Kellner for assistance in the experimental work.

²² G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, London, 1949), p. 119.

²³ See, for example, F. Matossi, *Phys. Rev.* **94**, 1151 (1954).

²¹ A. N. Ince, *Proc. Phys. Soc. (London)* **B67**, 870 (1954).

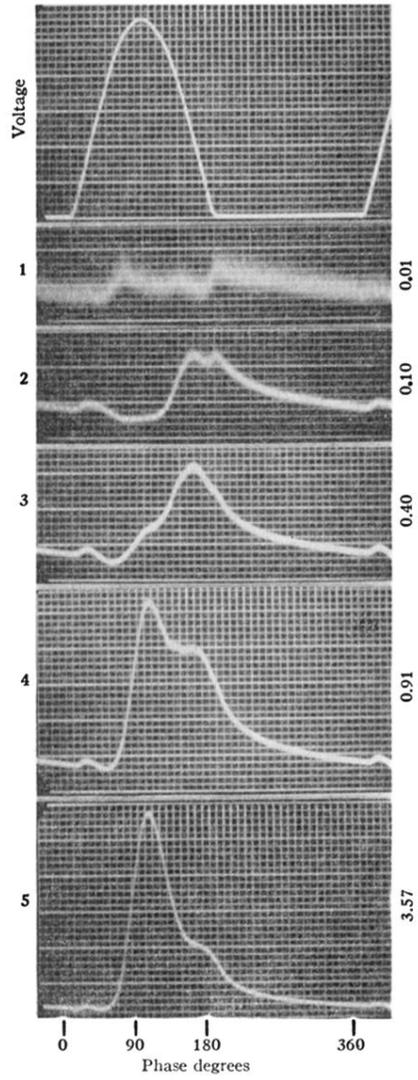


FIG. 2. Half-wave voltage wave form (at top) and oscillograms of electroluminescence of crystal with Ag paint electrodes. Figures at left give voltage amplitudes in kv. Figures at right give scale factors, emission intensity (arbitrary units) per scale division.

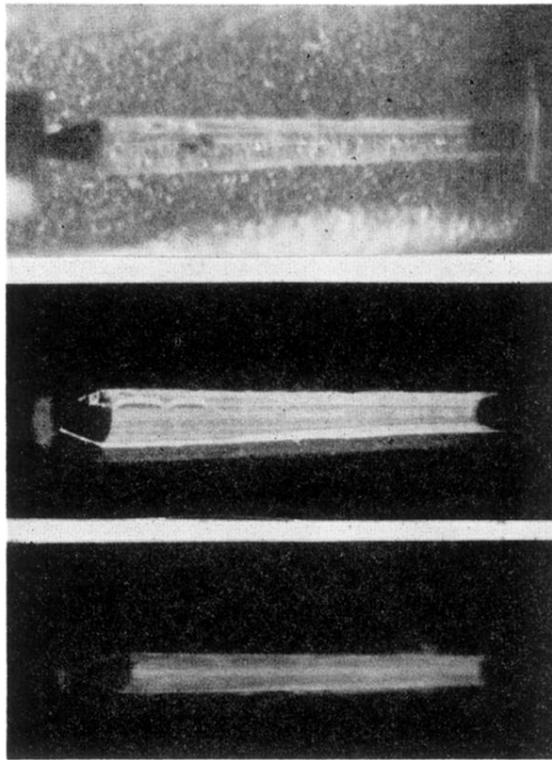


FIG. 3. Photomicrographs of an electroluminescent ZnS crystal. Top, external illumination. Middle, electroluminescence in air. Bottom, electroluminescence in high-index fluid.

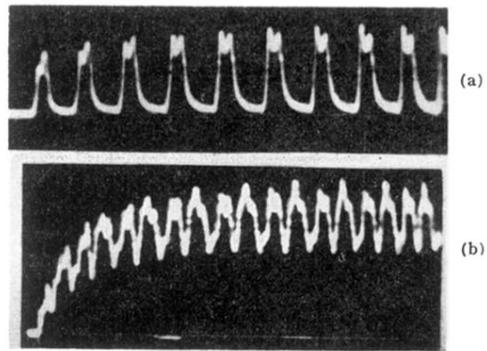


FIG. 4. Initial cycles of electroluminescence of a ZnS single crystal. Top, half-wave excitation. Bottom, full-wave excitation.