

Electroluminescence of Zinc Sulfide Single Crystals

I. T. STEINBERGER, V. BAR, AND E. ALEXANDER

Department of Physics, The Hebrew University, Jerusalem, Israel

(Received August 3, 1960)

In a series of experiments designed to distinguish between ionization and recombination processes during electroluminescence, rectangular voltage pulses were applied to single crystals of zinc sulfide. During the "on" period, the emission gradually increased to a stationary level. Removal of the voltage resulted in a burst of emission, which decayed slowly. This behavior is explained by the assumption of three field-dependent processes, namely: (a) ionization of centers in barrier regions; (b) sweeping out of the liberated electrons from the vicinity of the centers; (c) tunnelling of electrons into the barrier regions. It was found that for a considerable voltage range the product of the light-sum (measured during the "off" period) by the current was proportional to the stationary emission level during the "on" period. This proportionality strongly supports the model suggested.

In many cases the current was found to be more strongly dependent on the voltage than the light sum. This result favors an ionization mechanism which is independent of the current.

The model suggests furthermore an alternative explanation for the Neumark-effect, i.e., the enhancement of the thermal glow by electric fields. The explanation does not involve an impact-ionization mechanism.

I. INTRODUCTION

THE processes governing the electroluminescence ("EL") of ZnS crystals and powders have been studied and discussed for several years.

Most authors assume that during EL the luminescence centers are excited (or ionized) as a result of the impact of accelerated electrons. However, no clear-cut evidence has yet been found for the validity of this assumption.

A controversy exists over the question whether delayed recombination (of liberated electrons and ionized centers) is an important process in EL.

Electroluminescent ZnS (both crystals and powders) behaves differently in alternating fields than in direct ones. The explanation of this fact has not yet been supported adequately by experiment.

We shall discuss each of these problems in some detail.

A. Impact Ionization

An impact ionization mechanism for EL excitation was proposed by Curie¹ and, independently, by Piper and Williams.² The latter authors suggested that the excitation is confined to the exhaustion barrier at the contact with the negative electrode. According to their model, some of the electrons in the barrier region are accelerated to energies sufficient for impact-ionization. Several modifications of the Piper-Williams theory were suggested.³⁻⁷ In all these models it was assumed that EL is excited by impact-ionization in regions of high local fields. The fact⁸ that strong magnetic fields did not in-

fluence the EL showed conclusively that if impact ionization does take place, then it has to be confined to regions of high local fields. All the models mentioned above account well for the voltage and frequency dependence of EL. The observed temperature dependence has also been accounted for.^{3,4}

The experiments which seem to offer the most direct proofs for impact ionization are those of Neumark⁹ and of Steinberger.¹⁰ Neumark showed that the thermal glow of ZnS single crystals was considerably enhanced by an electric field acting during the "warming up" period. Enhancement ratios up to 10 were observed with 1000 volts dc applied to the crystal. Neumark interpreted her results by assuming that the electrons which are thermally released from traps can serve as "heads of avalanches," i.e., they are accelerated and generate secondary electrons by impact ionization. Steinberger's experiments seemed to demonstrate that the concentration of free carriers increases considerably with applied voltage in ZnS crystals showing ac EL.

On the other hand, Thornton's recent experiments¹¹ lead him to strong arguments against the impact ionization model. He found that the EL emission spectrum did not change with voltage even at the lowest voltages applied. In fact he observed EL emission in activated ZnS thin films at 1.5 volts rms, i.e., at a voltage corresponding to an energy smaller than the mean energy of the photons emitted. Thornton concludes from these results that EL does not depend on impact ionization.

B. Delayed Recombination

Waymouth and Bitter¹² applied rectangular pulses to a ZnS(Cu,Pb) powder layer. The behavior of the light

¹ D. Curie, *J. phys. radium* **14**, 510, 672 (1953).

² W. W. Piper and F. E. Williams, *Phys. Rev.* **87**, 151 (1952); *Brit. J. Appl. Phys., Suppl.* **4**, 39 (1954); and *Phys. Rev.* **98**, 1809 (1955).

³ P. Zalm, *Philips Research Repts.* **11**, 353, 417 (1956).

⁴ G. F. Alfrey and J. B. Taylor, *Proc. Phys. Soc. (London)* **B68**, 775 (1955).

⁵ E. Nagy, *Acta Phys. Acad. Sci. Hung.* **6**, 153 (1956).

⁶ W. Lehmann, *J. Opt. Soc. Am.* **48**, 647 (1958).

⁷ C. H. Haake, *J. Opt. Soc. Am.* **47**, 881 (1957).

⁸ A. N. Ince, *Proc. Phys. Soc. (London)* **B67**, 870 (1954).

⁹ G. F. Neumark, *Phys. Rev.* **103**, 41 (1956); and *Sylvania Technologist* **10**, No. 2, (1957).

¹⁰ I. T. Steinberger, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 4, p. 646.

¹¹ W. A. Thornton, *Phys. Rev.* **116**, 893 (1959).

¹² J. Waymouth and F. Bitter, *Phys. Rev.* **95**, 941 (1954).

pulses observed when the voltage was switched on and off led these authors to the conclusion that generally the recombination of the freed electrons with the ionized centers is delayed. The delay is caused by the field which "sweeps out" the liberated electrons from the vicinity of the ionized centers. Only after the removal of the external fields can the electrons return to the centers. This assumption is supported by the observation that the "waves of brightness"—under sinusoidal excitation—are much simpler for phosphors with excited activator centers (e.g., in phosphors containing manganese) than for phosphors where the centers are ionized.¹³ Further arguments for the delayed-recombination model were brought forward by Zalm,³ who applied voltages of various waveforms to phosphor powder layers, binderless or immersed in slightly conducting tricresyl phosphate.

Similar results on ZnS powders have led Matossi¹⁴ to different assumptions. He emphasized the different dependence of the green and of the blue emission bands on time. Furthermore he observed—with other authors—a decaying light pulse during the "on" period and a somewhat similar pulse during the "off" period. According to his model, these two pulses are caused by separate excitations of the centers. The high field necessary for the excitation during the "off" period is created by the polarization charges which had piled up during the "on" period. In contradistinction, the light pulse at the switching on of the voltage is determined primarily by the external field. By taking into account these two, almost independent excitation processes, Matossi explained a large number of experimental facts without using the hypothesis of delayed recombination.

All the results on powders showed^{3,14-17} that even the light pulse which is observed during the "on" period does decay with time. It is natural therefore to assume the buildup of a polarization field during the "on" period. Consequently it seems that it is rather difficult to choose between the explanations of Zalm and Matossi if the experimental evidence available was obtained on powders.

Experiments published on rectangular pulses applied to single crystals gave a simpler picture. Frankl and his co-workers¹⁸ reported that the emission of single crystals rises to a steady level during the "on" period. When the voltage is switched off, there appears a sudden burst of emission, followed by a decay. Narita's experiments¹⁹ essentially confirm these results. Frankl *et al.* explained their results by assuming the delayed-recombination mechanism.

C. Electroluminescence in Alternating and in Direct Fields

It is well known that EL in alternating fields often appears under conditions where no EL in a direct field is observed. This fact is not discussed in detail in the literature. Most authors, however, seem to agree that it is essential for the production of dc EL, that electrons reach the excited region from the cathode side. This means tunnelling of electrons through the barrier. For ac EL, however, tunnelling is not a necessary condition. Zalm³ pointed out that the tunnelling electrons can serve as the source for the impact ionization. Assuming tunnelling into an exhaustion barrier at the metal-semiconductor interface, he showed that the number of tunnelling electrons should increase proportionally to $\exp(-\alpha/\sqrt{V})$, where V is the applied voltage and α a constant. The probability for an electron in the barrier region to be accelerated to a given energy is also proportional to $\exp(-\beta/\sqrt{V})$, where β is another constant. The probability for an electron to tunnel through a barrier and to ionize subsequently a center should thus be proportional to $\exp(-\alpha'/\sqrt{V})$ where $\alpha' = \alpha + \beta$. This means that for dc EL the brightness should increase more steeply with the voltage than the current. Furthermore, in ac EL, the number of centers ionized per cycle should increase more steeply with the voltage than the conductive component of the current. If the ionization were the rate-determining process, the EL emission (both dc and ac) should increase more strongly with voltage than the current. Comparison between the voltage dependencies of the EL brightness and of the currents could thus serve as a first check of this model.

We shall return to these discussions after presenting our experimental results.

II. THE EXPERIMENTAL ARRANGEMENT

A photomultiplier (IP21) in conjunction with a galvanometer and an oscilloscope served for the measurement of the EL brightness. The blue band of the emission was observed through the filter "Wratten" No. 34 and the green one through "Wratten" No. 16. The current under direct fields was measured with an electrometer amplifier. For the measurement of conductances under sinusoidal voltages, it was essential to eliminate the displacement currents. This was done by applying simultaneously with the alternating field a much smaller direct test potential.^{10,20} The direct component of the current thus generated was measured by the electrometer amplifier. From this the average (taken over the half of a cycle) of the conduction current could be determined by calculation.

In most experiments rectangular pulses were applied to the crystal. A set of "Tektronix" Series 160 pulse generators served as the source. For repetition rates above 100 cps, a conventional RC-coupled amplifier

¹³ J. Mattier, J. phys. radium **17**, 725 (1956).

¹⁴ F. Matossi and S. Nudelman, J. Electrochem. Soc. **10**, 1546 (1954); and Phys. Rev. **99**, 1100 (1955).

¹⁵ D. Hahn and F. W. Seemann, Z. Physik **149**, 486 (1957).

¹⁶ A. M. Bonch-Bruevich, Optika i Spektroskopiya **2**, 256 (1959).

¹⁷ R. Zallen, W. T. Eriksen, and H. Ahlburg, J. Electrochem. Soc. **107**, 288 (1960).

¹⁸ D. R. Frankl, G. Neumark, and A. Lempicki, Bull. Am. Phys. Soc. **3**, 45 (1958).

¹⁹ S. Narita, J. Phys. Soc. (Japan) **15**, 128 (1960).

²⁰ I. T. Steinberger, V. Bar, and Y. Berlinsky, Bull. Research Council Israel **8F**, 224 (1960).

TABLE I. Slopes of $\log B$ vs $1/\sqrt{V}$ and of $\log I$ vs $1/\sqrt{V}$ representations. [All slopes in (volt)^{1/2}.]

Crystal No.	Short description of crystal	α_I dc	α_{EL} dc	α_I ac	α_{EL} ac	Remarks
1	Growing in 10 cm H ₂ S, 1200°C, 60 hours in fused bomb. Green emission, medium persistence.	52	...	60	105	No dc EL
2	Growing in 10 cm H ₂ S, 1080°C, 72 hours in fused bomb. Blue emission, short persistence. Accidental oxidizing during cooling.	55	120	88	100	Low voltages
		95	190	140		High voltages
3	Contains 0.004% by weight of Cu. Blue and green emission, short persistence.	61	100	54	34	Green band
			143			Blue band

was used for obtaining higher voltages. For the lowest repetition rates, the output of the pulse generator was fed to the coil of a mercury-wetted contact relay ("Clare" HG 1017). Across the contacts of this relay voltages up to 500 volts could be applied. The time of switching by the relay was of the order of 10^{-8} second. Actually the parasitic capacitances increased this time up to 50 microseconds. Even this time is much shorter than most time-constants shown by the crystals.

In all experiments reported here, the crystals were equipped with nonblocking contacts. For sinusoidal excitation, colloidal graphite, silver paste or indium amalgam electrodes were used. The results were independent of the electrode material. For excitation by rectangular pulses only indium amalgam electrodes were employed. The EL light emission was studied through a low-power microscope as well. It appeared that the light originated in the crystal bulk. Under direct fields the details of the emission patterns did not change when we reversed the polarity of the voltage.

III. EXPERIMENTAL RESULTS

A. Direct and Sinusoidal Voltages

About twenty crystals, grown under various conditions, were tested for ac and for dc EL. The currents though the crystal were also measured. Figure 1 shows a typical voltage dependence of the current and of the EL brightness. It is seen that for ac the logarithm of the brightness B is linear with $(1/\sqrt{V})$, where V is the applied voltage. The dc EL and the currents, however, could be better represented by a law of the form $I = A_1 \exp(-\alpha_1/\sqrt{V}) + A_2 \exp(-\alpha_2/\sqrt{V})$, where A_1 , A_2 , α_1 , and α_2 are constants. As pointed out in the Introduction, the slopes of $\log B$ vs $(1/\sqrt{V})$ (denoted by α_{EL}) and of $\log I$ vs $(1/\sqrt{V})$ (denoted by α_I) can give information on the nature of the processes responsible for the excitation of EL. According to Zalm's assumptions,³ one could expect that $\alpha_{EL} \geq \alpha_I$ in all cases. Actually, we found this to be true for direct voltages. For ac the above inequality often does not hold. Table I serves as an illustration of this point.

It is seen that, for crystal No. 3, $\alpha_{EL} < \alpha_I$ for alternating voltages. These results seem to indicate that Zalm's assumption on tunnelling and subsequent impact

ionization does not hold. For more definite conclusions it is necessary to determine the number of centers ionized per cycle and compare this number with the current. Application of rectangular voltage pulses seemed to be a promising method for this purpose.

B. Rectangular Pulses

Figure 2 represents typical oscillograms on the current and the EL brightness of a ZnS single crystal to which a single rectangular pulse was applied. The same pattern was observed with repeated pulses, provided the repetition rate was low enough. It is seen that while the field is acting, the emission gradually reaches an equilibrium level. When the field is switched off, there appears a burst of emission which decays to zero during a time somewhat longer than the time of rise to the

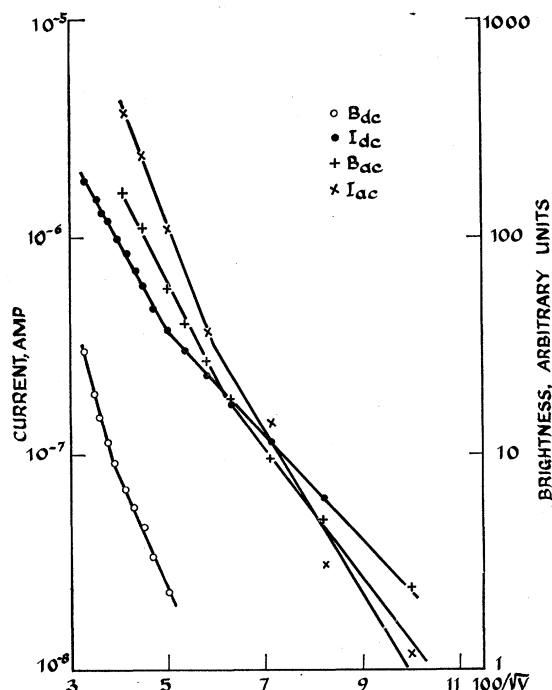


FIG. 1. EL brightness and conduction current under alternating and direct voltages. Crystal No. 2. Frequency of alternating voltage: 38 cps.

equilibrium level. The risetime of the "burst" is of the order of 0.5 millisecond. (The rise is distorted in Fig. 2 as the input impedance of the oscilloscope was normally shunted by a capacitor in order to diminish photo-multiplier noise.) This EL brightness waveform is much simpler than that reported for powder phosphors, but it is similar to that reported by Frankl¹⁸ and to some of Narita's oscillograms.¹⁹ Both these authors investigated single crystals of zinc sulfide.

In Fig. 2 the in-phase component of the current is also represented. This component has the same rise and decay times as the voltage pulse (about 50 microseconds). Another component of the current was observed during the "off" periods. This component was smaller by a factor of several hundred than the "in-phase" current; therefore it could not be represented on the scale of Fig. 2. The sense of this component is opposite to the sense of the in-phase current. It decays very slowly (time constants of the order of a second) during the "off" periods.

The time dependence of the EL brightness, as shown in Fig. 2, makes it unlikely that polarization phenomena affect the EL waveform in our case. In fact, the emission during the "on" period reaches a stationary state with no indication of decay. The current does not decay either. No decays were observed even when the field was applied for several minutes. This means that during the "on" period the effective field-strength stays con-

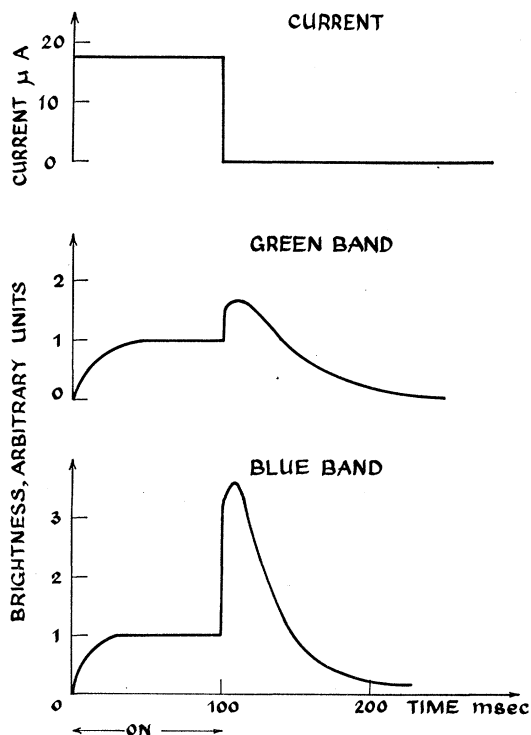


FIG. 2. Current and EL brightness versus time. Crystal No. 3 under rectangular pulse excitation. Pulse amplitude: 150 volts on crystal 0.15 mm thick.

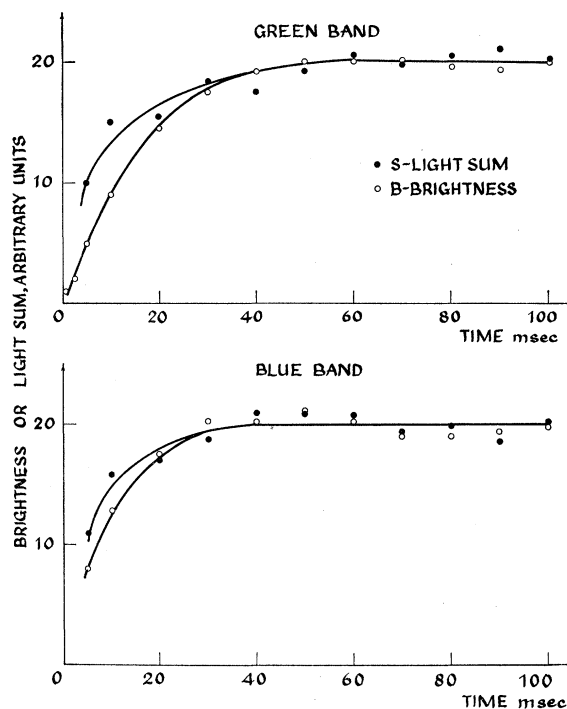


FIG. 3. Light sum S during "off" period and brightness B at the end of "on" period as a function of the length of the pulse duration. Crystal No. 3, 150 volts.

stant and there is no perceptible buildup of a polarization field. Thus in this case the burst observed during the "off" period cannot be attributed to a new excitation due to a residual polarization field.

We assumed, therefore, that during the "on" period the field sweeps out the liberated electrons from the vicinity of the centers.^{3,12,18} Only when the field is switched off can these electrons return to the region of ionized centers. In other words, the recombination of the electrons with the centers was delayed. This model has to be valid for the green and the blue bands. There exist, however, quantitative differences between the two bands, as is apparent from Fig. 2.

In some cases the oscillograms representing the brightness vs time behaved differently. Some of the samples investigated showed a behavior similar to that of powders, i.e., both the "on" and the "off" pulse decayed with time. Significantly, the resistance of these crystals was much higher. Moreover, investigation under the microscope revealed that these crystals were much less perfect than the others; in fact they looked like a conglomeration of small crystals. It seems therefore that in the case of these samples conditions were very favorable to the buildup of polarization fields. Probably some of Narita's results¹⁹ could also be similarly explained. In the following we shall deal mainly with results on "good" crystals where polarization phenomena were not discernible.

In such crystals, the area S beneath the light pulse

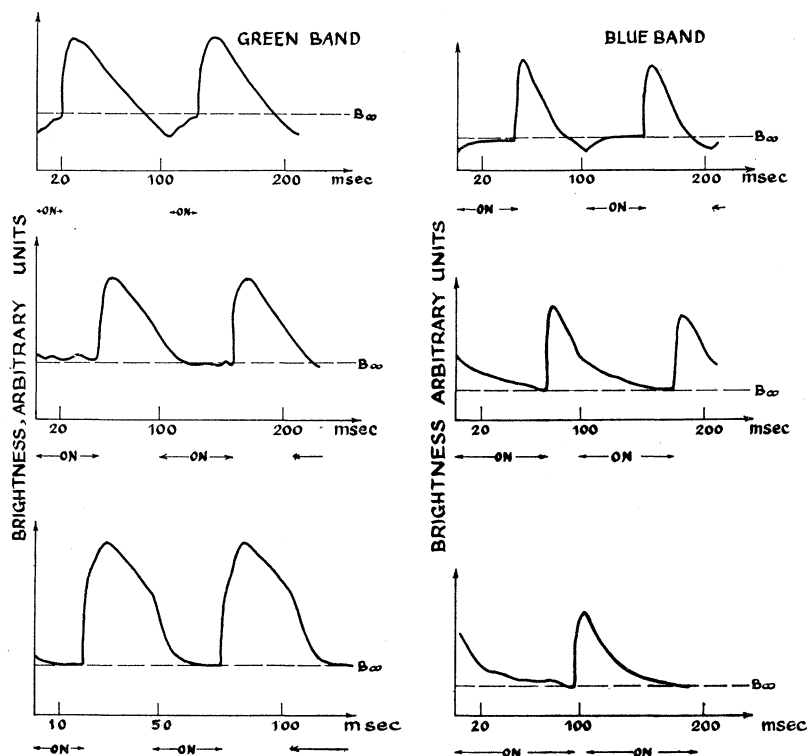


FIG. 4. EL brightness vs time, with various on and off periods. Crystal No. 3, 150 volts.

observed during the "off" period is proportional to the number of electron-center recombinations. According to our model, during the "off" period no ionization of centers occurs. The area S is therefore proportional to the number of centers m which were left ionized at the end of the "on" period. The brightness B , measured at the end of the "on" period, is also proportional to this number. (Actually B is proportional to $n \times m$, where n is the number of free carriers in the vicinity of the centers. From the constancy of the current—Fig. 2—it follows that n can be assumed to be constant during the "on" period.) The dependence of S on the length of the "on" period should therefore be the same as the dependence of the final brightness B on the length of this period. Figure 3 shows that this is actually the case. The area S tends to a saturation value S_∞ with the increase of the length of the "on" period in the same way as B tends to B_∞ . The results for both emission bands are similar. For short "on" periods, the graphs for B and for S are somewhat different.

It was indicated above that the level B_∞ is equal to the level of the dc EL at the same voltage. If the field is reapplied during the decay period this level will eventually be reached again. Figure 4 shows oscillograms representing such cases. It is apparent that if the field is reapplied after a long "off" period, the brightness increases to B_∞ . If the "off" period was short, there is a decay to the same level. The change is always monotonic.

These results give additional information on the kinetics of the recombination and light emission. When

the voltage is switched off, the electrons which had been swept out return to the luminescence centers and recombine with them. The number m of the ionized centers thus begins to decrease immediately after the end of the "on" period. Therefore at the reapplication of the field the number of ionized centers is always less than the equilibrium concentration. If the "sweeping out" at the reapplication were fast enough, the emission ought to decrease momentarily beneath the equilibrium level B_∞ . Figure 4 shows that this is not the case. From this it follows that the "sweeping out" sets in gradually on the reapplication of the field. Very probably trapping processes are involved.

In this connection it should be noted that there exists a qualitative difference between the behavior of the two emission bands. If the voltage is reapplied a short time after switching it off, the green emission decays faster to B_∞ than the normal decay rate of the brightness. Under similar conditions the blue emission decays at a slower rate than before the reapplication of the field.

Figure 5 represents the dependence of S_∞ , B_∞ , and the current I on the amplitude of the pulses applied. In all cases the repetition rate was kept low enough to allow a complete decay of the pulse in the "off" period. It is seen that the representation of the logarithms of S_∞ and of B_∞ vs $1/\sqrt{V}$ yields straight lines. I vs V can be represented as a sum of two curves of the same type. The values of A in the expression $\exp(-A/\sqrt{V})$ appear in Table II.

As indicated, S_∞ is proportional to the number of

centers which were left ionized at the end of the "on" period. According to the assumption³ about impact ionization generated by tunnelling electrons, S_∞ ought to increase with the voltage faster than the current. Table II shows that this condition is fulfilled for crystals Nos. 4 and 5. For crystal No. 3, however, S_∞ increases more slowly than the current. It does not seem probable to assume different excitation mechanisms for different crystals. The results thus indicate that one has to reject either the assumption on impact-ionization, or the assumption that the impact ionization is initiated by electrons which tunnelled into the region of ionized centers.

For the interpretation of our results it seems necessary to assume the existence of three field-dependent effects: (a) ionization of the luminescence centers; (b) sweeping out of the liberated electrons from the vicinity of the ionized centers; (c) tunnelling of electrons from the cathode side into the region of excitation. During the "on" period only the tunnelling electrons recombine with the luminescence centers.

Table II shows that for each crystal investigated there exists a voltage region where $A_{S_\infty} + A_I = A_{B_\infty}$ within the experimental error (about 5%). This result is in complete agreement with the model suggested by the first experiments described in this paper, since according to this model $S \propto m$, $I \propto n$, and $B \propto mn$. The fact that the equality $A_{S_\infty} + A_I = A_{B_\infty}$ holds, serves as a quantitative proof for the applicability of this model.

Alfrey and his co-workers²¹ reported that in single crystals of ZnS the product of the current by the ac EL is proportional to the dc EL. A similar result was observed in some of our crystals, as can be seen from Table I. In view of our results reported above (in connection with Table II) this relationship indicates that ac EL in these cases is proportional to the number of centers ionized per cycle.

As seen in Table II, the relationship $A_{S_\infty} + A_I = A_{B_\infty}$ holds only in certain ranges of the applied voltage. The experimental results are not sufficient for interpreting the deviations from this relationship in the other ranges.

IV. DISCUSSION

The experiments described in this paper show that under suitable conditions the waveforms of EL are

TABLE II. Values of A in (volt)^{1/2} for various crystals.

Crystal No.	Short description of the crystal and remarks	A_{B_∞}	A_{S_∞}	A_I current slope	
		Bright-ness slope	Light sum slope	Low voltages	High voltages
3	See Table I {Green band	132	66	70	120
4	From the same batch as Sample 2. Blue band.	115	55		
4	From the same batch as Sample 2. Blue band.	230	160	28	72
5	From the same batch as Sample 2. Blue band.	310	190	60	150

²¹ G. F. Alfrey, I. Cooke, and K. N. R. Taylor, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 2, p. 816.

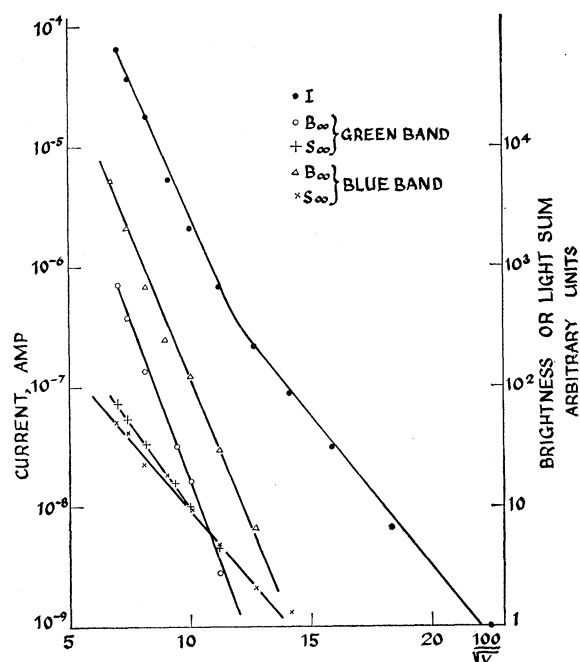


FIG. 5. Current I , brightness B_∞ , and light sum S_∞ versus pulse amplitude. Crystal No. 3.

simple enough for consistent interpretation. Elimination of the internal polarization is the most important condition. This was achieved by using good single crystals equipped with nonblocking electrodes. The other circumstances which facilitated interpretation were: (a) the use of rectangular voltage pulses; (b) the separation of the two emission bands.

The results demonstrate the existence and importance of two effects on EL, namely: (a) sweeping out of the liberated electrons from the vicinity of the centers; (b) tunnelling of electrons from the cathode side into the region of the ionized centers. In polycrystalline specimens and in powders polarization phenomena may distort or mask these processes.

According to the model proposed, the sequence of events generated by a rectangular voltage pulse is the following. On the application of the voltage pulse, luminescence centers become ionized in regions of high local fields ("barrier regions"). At the same time electrons tunnel into the barrier region from the cathode side. The current flowing to the anode consists of electrons which tunnelled into the barrier region and of electrons which were liberated from the centers. There exists a small probability for the recombination of the electrons of this flow with empty luminescence centers; this probability determines B_∞ , i.e., the dc EL. Most electrons, however, are swept away from the vicinity of the ionized centers to the anode side of the crystal. A fraction of these electrons became trapped. At the removal of the voltage these electrons return to the region of ionized centers and recombine with them. Thus a burst of emission is observed at the switching off of the field.

The nature of the barrier regions mentioned is unknown; the only assumption used here is that it is penetrable from the cathode side by electrons. The microscopic studies seem to indicate that instead of a single barrier region near the cathode, there are many such regions dispersed in the crystal.

For simplicity, we identified throughout the free carriers with electrons. Actually these experiments do not contradict the assumption that the conduction process are dependent partly on free holes. Recently more experimental evidence has been published²² which seems to indicate that for the blue center of ZnS the Klick-Lambe model holds.²³ The different dependence on time of the blue and of the green emissions can be easily explained this way. More experiments are, however, necessary in order to decide on this point.

As it was pointed out above, it is unlikely that the luminescence centers are impact-ionized by electrons which tunneled into the barrier region. Thornton's recent experiments seem to suggest that the impact ionization mechanism has to be discarded altogether. However, our experiments by themselves do not contradict the possibility of the impact ionization mechanism, provided that the accelerated electrons had been liberated from donors or traps (thermally or by the field.)

In view of these conclusions the "direct" proofs on impact ionization during EL deserve further scrutiny. The results previously reported by one of the present authors¹⁰ can be interpreted in two ways: either by assuming that electrons tunnel into the crystal without causing impact ionization, or by assuming that electrons liberated from traps cause impact ionization. As the increases of the conductance observed were very large, the first explanation seems to be more likely.

As mentioned in the Introduction, Neumark found that the thermoluminescence of an electroluminescent crystal is enhanced considerably if during the thermal glow an electric field is applied. In fact, the emission is much stronger than the sum of the thermal glow and the EL emission at the same temperature. Neumark interpreted the results by assuming that thermally liberated electrons were accelerated by the field and ionized centers by impact.

This model given by Neumark does not account for the fact that the enhancement was observed mainly in direct fields. No effect or only a very small one ap-

peared if alternating fields were applied to the crystal. Even under rectified ("half-wave") sinusoidal voltage practically no such enhancement was observed. Our model, however, can account for this difference both in the framework of Neumark's assumption on impact ionization and also according to another explanation which will be presented later.

According to our model, in direct fields the free electron concentration in the vicinity of the centers is low because of the "sweeping out" of the electrons by the field. The same is true on the region which lies between the region of the ionized centers and the cathode. With unidirectional pulses or alternating voltages this concentration should be much larger since "swept out" electrons can reach again the vicinity of ionized centers. The free electron concentration determines the number of electrons which can be accelerated and cause ionization of the centers. In direct fields the additional concentration of thermally liberated electrons will be large compared to the "normal" concentration of electrons in the vicinity of the centers; thus the number of ionized centers also increases considerably. In alternating fields the additional concentration will be comparatively small and the number of ionized centers will practically not change.

The other possible explanation of the Neumark-effect does not involve the assumption in impact ionization.

We use again the result that in a direct field the concentration of free electrons near the centers is comparatively low. This implies a low rate of electron-center recombination, i.e., a low EL brightness. The thermal release of electrons from traps during the glow raises the electron concentration considerably and thereby also the rate of recombination. In an alternating field, however, the "sweeping out" is not effective and therefore the additional electrons released are unimportant.

This alternative explanation, which does not imply impact ionization, explains without any difficulty the large enhancement ratios observed, while on the basis of Neumark's original model these large ratios are somewhat difficult to understand.

ACKNOWLEDGMENTS

The authors wish to thank Professor G. F. J. Garlick (Hull University, England) and Dr. A. Kremheller (Sylvania Laboratories, U. S. A.) for some of the crystals used in this work. Thanks are also due to Mr. G. Lerman for technical assistance.

²² H. Arbell and A. Halperin, *Phys. Rev.* **117**, 45 (1960).

²³ J. Lambe and C. C. Klick, *J. phys. radium* **17**, 663 (1956).