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Electroluminescence of ZnS Single Crystals with Cathode Barriers

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Certain ZnS crystals show electroluminescence predominantly near the cathode. The major emission from Cu-activated crystals occurs as a burst of light when the exciting voltage is suddenly removed, as electrons flowing back toward the cathode to neutralize the barrier charge recombine with ionized luminescent centers. This burst may be quenched by a voltage in the initial direction or enhanced by a voltage in the opposite direction. There is also a small steady component of emission due either to capture of electrons that entered the crystal from the cathode or to excitation of centers to discrete levels. In Mn-activated crystals, only the latter has been observed.

These results, as well as the emission peaks obtained from copper-activated ZnS under sinusoidal voltage excitation, are explained in terms of ionization of luminescent centers in a barrier region. The "primary" peak, which predominates in powder samples and under low voltages in single crystals with metal contacts, is due to recombination of centers left over from the previous half-cycle. A capture cross section of about 10^{-12} cm^2 is deduced. The peak at about 150 to 170 phase degrees is due to recombination of ionized centers left in the neutral part of the crystal as the barrier width diminishes. A barrier space-charge density of (very roughly) 10^{16} e/cm^3 is deduced. The in-phase peak is analogous to dc electroluminescence.

INTRODUCTION

One of the most interesting aspects of the electroluminescence of ZnS is the rather complicated time dependence of the emission intensity under time-varying exciting voltage. In copper-activated ZnS powder samples suspended in a dielectric medium there is usually a "primary" peak and one or more "secondary" peaks of emission per half-cycle, these designations referring to the heights of the intensity maxima. Destriau[1] proposed that the phase displacement of the primary peak from the voltage maximum was due to a phase shift between the electric field within the phosphor grains and that applied to the entire system. While this effect may play some role in powder suspensions, it is clearly incapable of accounting for the complicated changes in the emission patterns with voltage and frequency observed even in single crystals with metallic contacts. Payne, Mager, and Jerome[2] reported that the primary peak was in phase with the power absorption, which suggests that the emission is associated with the motion of free carriers. Thornton[3] proposed a model based on field-enhanced thermal release of trapped electrons, which accounted well for voltage and frequency effects on the primary peak but failed to account satisfactorily for temperature effects.

The secondary peaks are attributed by Zalm, Diemer, and Klasens[4] and Haake[5] to trapping effects, although Destriau and Ivey[6] report that these peaks are influenced by the metal electrode of the powder cell.

In single crystals with metallic contacts, Piper and Williams[7] found that the emission under sinusoidal voltage comprises an in-phase and an out-of-phase peak in each half cycle. They proposed that the former was due to excitation by electrons entering the crystal from the cathode and the latter to excitation by electrons field emitted from deep donors, the light emission supposedly occurring immediately after excitation. Under half-wave voltage excitation, this model would place the out-of-phase emission *before* the in-phase, in contradiction to the results of Watson, Dropkin, and Halpin.[8] These workers observed that the in-phase emission was predominantly blue and the out-of-phase predominantly green, and proposed that the former was due to excitation of blue centers to discrete states with immediate emission and the latter to ionization of green centers with delayed emission. It was, however, then found that the color difference was not at all universal[9] and that the out-of-phase emission comprised two distinct peaks, one before and one at the voltage zero.[10] Only the latter was attributable to the return of displaced electrons to ionized centers. For the former, the writer proposed a model based on an *ad hoc* assumption concerning the action of the field on trapped electrons, which had to be discarded when Birman[11] showed it to be incapable of accounting for the relative voltage dependencies of the in-phase and out-of-phase peaks.

The excitation of electroluminescence in ZnS is generally believed to occur by impact on the lumi-

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[1] G. Destriau, Phil. Mag. **38**, 700 (1947).

[2] Payne, Mager, and Jerome, Illum. Eng. **45**, 688 (1950); Sylvania Technologist **4**, 2 (1951).

[3] W. A. Thornton, Phys. Rev. **102**, 38 (1956).

[4] Zalm, Diemer, and Klasens, Philips Research Repts. **9**, 81 (1954).

[5] C. H. Haake, J. Appl. Phys. **28**, 117 (1957); J. Opt. Soc. Am. **47**, 881 (1957).

[6] G. Destriau and H. F. Ivey, Proc. Inst. Radio Engrs. **43**, 1911 (1955).

[7] W. W. Piper and F. E. Williams, Phys. Rev. **81**, 151 (1952); **98**, 1809 (1955); Brit. J. Appl. Phys., Suppl. No. **4**, 39 (1955).

[8] Watson, Dropkin, and Halpin, Phys. Rev. **94**, 777 (1954); Enlarged Abstracts of the Electrochemical Society Spring Meeting, 1954 (unpublished), p. 42.

[9] D. R. Frankl, Phys. Rev. **100**, 1105 (1955); Sylvania Technologist **9**, 6 (1956).

[10] D. R. Frankl, Enlarged Abstracts of the Electrochemical Society Spring Meeting, 1956 (unpublished), p. 38; D. R. Frankl *et al.*, J. phys. radium **17**, 731 (1956).

[11] J. L. Birman, paper presented at Electrochemical Society Spring Meeting, San Francisco, May, 1956 (unpublished).

nescent centers of fast conduction electrons. Calculations by Burns[12] and Piper and Williams[7] and experiments by Neumark[13] and Cusano[14] support this viewpoint. If this is correct, the observation by Ince[15] that strong magnetic fields fail to produce perceptible quenching of electroluminescence shows that the acceleration of the electrons to impacting energies must occur in regions where the electric field strength is much greater than the average field strength applied to the crystal, that is in barrier regions.

In the present state of the art of growing ZnS single crystals, various sorts of imperfections appear to give rise to internal barriers. For example, stacking fault planes appear to be highly effective barriers for current flow parallel to the *c* axis, as evidenced by the strong anisotropy of dark-conduction, photoconduction, and electroluminescence in these crystals.[16] Even for current flow perpendicular to the *c* axis (parallel to the stacking fault planes), however, there appear in most crystals to be internal barriers. Loebner and Freund[17] and Diemer[18] have shown that in certain crystals the emission of light occurs at discrete spots, similar to the observation in powders by Waymouth and Bitter.[19] Similar crystals have been found in this laboratory. In crystals where the internal barriers are closely spaced throughout the crystal, the emission can be essentially uniform. The electroluminescent behavior of such crystals has already been described.[9,10]

Still another type of barrier that can occur is that at the contact between the ZnS and a metal or strongly *n*-type semiconductor. Such "cathode barriers" were part of a model proposed by Piper and Williams.[7] It appears that in crystals sufficiently perfect so that internal barriers are negligible, the cathode barrier plays the dominant role. A number of such crystals have been found in this laboratory, and the present paper will be denoted exclusively to them. Even though these crystals are usually less brightly electroluminescent than those with numerous internal barriers, the fact that a single barrier dominates their behavior makes them much more readily understandable.

The barrier layer at the contact between a metal and an *n*-type semiconductor may be an exhaustion layer, in which the donors are present in their normal concentration but are partially or completely ionized; a depletion layer, in which the concentration of donors is less than in the bulk; or some intermediate type. For an exhaustion layer under an applied voltage V, large compared to the "built-in" voltage drop, the width and the maximum field strength are both proportional to $V^{\frac{1}{2}}$. For a depletion layer, the width is constant and the field strength is proportional to V. At the instant when the voltage is applied, the applied field is uniformly distributed throughout the crystal including the barriers, and there is a flow of current limited only by the bulk resistance of the crystal. Owing to the presence of the cathode barrier, however, this current decays toward a smaller value, zero if the barrier is completely impenetrable. For an exhaustion layer, the theory developed by Von Hippel and co-workers[20] for photoconduction in *F*-centered alkali halides is directly applicable and the decay law of the current is, for a thin barrier,

$$\mathrm{I}=\mathrm{I}_0(\cosh t/2\tau)^{-2},$$

where (1)

$$\tau=(2N_0e\mu^2V/\epsilon'l^2)^{-\frac{1}{2}},$$

N_0e = space-charge density, μ = mobility of electrons, V = applied voltage, ϵ' = permittivity of crystal, and l = length of crystal. This equation predicts a current-decay which is initially flat and becomes essentially exponential after a few time constants. In the experiments of Von Hippel *et al.*,[20] only the exponential portion appears to have been observed. For a depletion layer, the initial decay is truly exponential with time constant $\tau=RC$, where R is the bulk resistance of the crystal and C is the capacitance of the two barrier layers (one at each end of the crystal) in series.

As shown by Von Hippel *et al.*,[20] the field strength at the cathode can readily become high enough so that field emission (tunneling) from the metal into the semiconductor occurs. The current will then decay to some final value greater than zero. In this event, the space charge of the tunneling electrons modifies the field distribution in the barrier. The transient solution has not yet been carried out, but Geller[20] has given an expression for the cathode field strength in an exhaustion layer in terms of the ratio of final to initial current. If this ratio is small, as will certainly be the case at sufficiently low voltages, the effects of the moving charges are negligible. Then, according to the Fowler-Nordheim equation for field emission from a metal, the final current density-voltage relationship for exhaustion and depletion layers, respectively, will be

$$J=CV\exp(-BV^{-\frac{1}{2}}),\quad \text{(exhaustion)} \qquad (2)$$

$$J=C'V^2\exp(-B'V^{-1}),\quad \text{(depletion)} \qquad (3)$$

where C, C', B, and B' are constants.

With either type of barrier, it is clear that the field strength near the cathode is much greater than the average applied field strength and consequently, as suggested by Piper and Williams,[7] that electrons tunneling into the crystal from the cathode have the possibility of being accelerated to energies where they may impact-excite or ionize luminescent centers and

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[12] L. Burns, J. Electrochem. Soc. **100**, 573 (1953).

[13] G. F. Neumark, Phys. Rev. **103**, 41 (1956); Sylvania Technologist **10**, 29 (1957).

[14] D. A. Cusano, Phys. Rev. **98**, 546 (1955).

[15] A. N. Ince, Proc. Phys. Soc. (London) **B67**, 870 (1954).

[16] Lempicki, Frankl, and Brophy, Phys. Rev. **107**, 1238 (1957).

[17] E. E. Loebner and H. Freund, Phys. Rev. **98**, 1545 (1955).

[18] G. Diemer, Philips Research Repts. **10**, 194 (1955).

[19] J. F. Waymouth and F. Bitter, Phys. Rev. **95**, 941 (1954).

[20] A. Von Hippel *et al.*, Phys. Rev. **91**, 568 (1953); M. Geller, Phys. Rev. **101**, 1685 (1956).

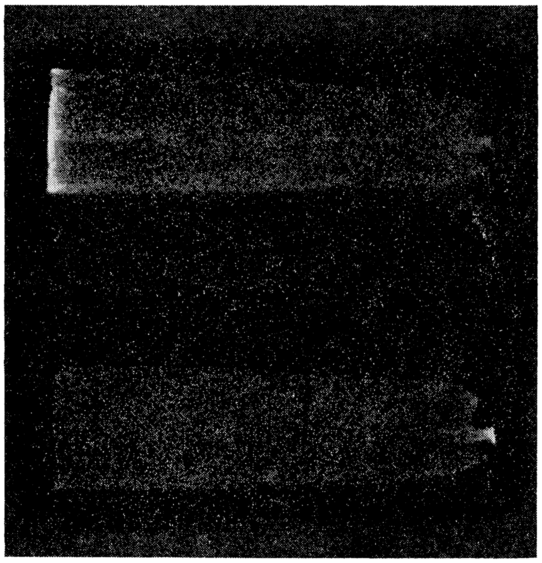

FIG. 1. Crystal No. 2. Emission under 60-cycle half-wave voltage. Top, negative at left. Bottom, negative at right. Crystal length 1.22 mm.

other levels too deep to be thermally ionized. As pointed out by Zalm,[21] this process will further contribute to the formation of the space-charge layer. The concentration of ionized centers at any distance from the cathode will build up to a steady value which is necessarily some function of the distribution of field strength in the barrier and of the probabilities of ionization and recombination.

Emission of light occurs when an ionized center recaptures an electron or when a center excited without ionization returns to the ground state. Processes of the former type, involving free carriers, may be strongly affected by the presence of the field, in contrast with processes of the latter type which should occur with the normal time constant of the center in question. In the first category, we shall consider the recapture of electrons tunneling through the barrier, which gives rise to a steady dc light emission, and recapture of electrons on removal of the applied voltage when electrons flow back into the region of ionization to neutralize the positive space charge.

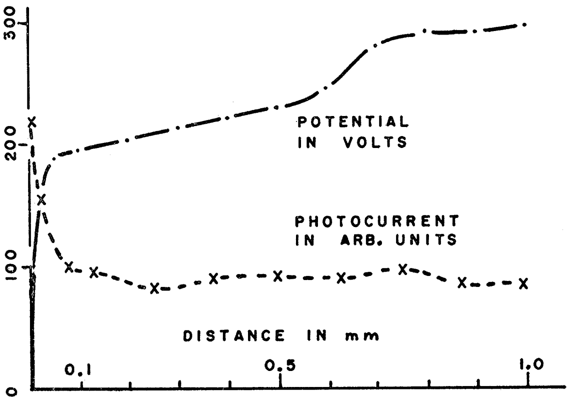

FIG. 2. Crystal No. 2. Potential and photosensitivity distributions. Distance measured from end shown at left in Fig. 1.

EXPERIMENTAL METHODS

a. Crystals.—The crystals used in this work were grown by Kremheller[22] and were selected on the basis of the existence of cathode barriers. The evidence for these will be given in a later section. Two of them (No. 1 and No. 2) were blue-fluorescent and electroluminescent as grown, presumably due to accidental contamination with copper. Crystal No. 2 broke accidentally during the course of the work; the surviving piece (left half as shown in Fig. 1) is designated No. 2′. Crystal No. 3 was a portion of an initially green-fluorescent crystal, converted to blue fluorescence and electroluminescence by heating in a bed of ZnS powder containing 0.1% of copper metal powder, by G. Neumark. Crystal No. 4 was grown by G. Neumark from ZnS powder containing 0.1% of $MnCl_2$, and showed orange fluorescence and electroluminescence. All these crystals had dimensions of the order of some tenths of a millimeter. Air-drying silver paint electrodes were used, applied to opposite faces so that the field was perpendicular to the *c* axis.

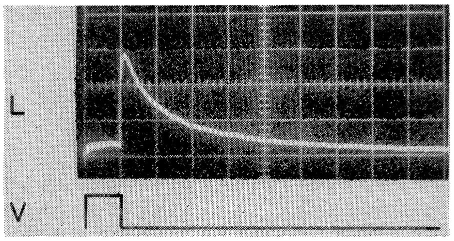

FIG. 3. Crystal No. 2. Emission under voltage pulse applied after 2 min of infrared. Abscissa scale, 0.5 msec per major div.

b. Circuits, etc.—Positive-going high-voltage (up to 10 kv) pulses having rise time of a few microseconds, length variable from a few microseconds to several hundred milliseconds and repetition rate variable from 0 to 10 kc/sec were obtained from a Beta Electric Corporation Model 2129 pulse generator. This unit consists essentially of a 4E27 tetrode driven by an Electropulse Model 1410A variable pulse generator. By choice of the polarity of the driving pulse, the output could be switched from zero to a selected positive voltage and back, or vice versa. Auxiliary circuits designed and built by Mr. J. Matarese made it possible to switch from the positive voltage to zero for a variable time, then to a negative voltage. The latter decayed exponentially to zero, but the time constant was sufficiently long that the voltage was essentially constant for the measurements described in this paper.

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[21] P. Zalm, Philips Research Repts. **11**, 353 (1956).

[22] A. Kremheller, Sylvania Technologist **8**, 11 (1955).

Light output measurements were made under these pulses and also under dc and sinusoidal ac, with a Dumont Type 6292 photomultiplier calibrated against a laboratory standard RCA Type 1P28 photomultiplier by comparison on several electroluminescent crystals.

Current measurements were made under dc using commercial meters, under 60-cycle ac using the bridge method previously described,[9] and under voltage steps up to 500-volts amplitude with a rise time of about 20 millimicroseconds, obtained from a mercury-wetted contact relay (C. P. Clare Manufacturing Company, Type HG1003). With these fast-rising steps, the spike of displacement current in the crystal and stray capacitance is initially much greater than the crystal current, and the bridge method is inapplicable since the requirements of gain, bandwidth, and rejection ratio of the differential preamplifier are too stringent. However, by using a 5000-ohm series resistance coupled via a simple cathode follower of about 5 pf (5×10^{-12} farad) input capacitance to a Tektronix Type 535 oscilloscope with Type 53B preamplifier, it was found that the spike decayed essentially completely in a few tenths of a microsecond and that the currents in some crystals could be measured thereafter. In these measurements it was necessary to use polystyrene insulation in order to avoid piezoelectric resonances in the usual crystal quartz insulators. Blank tests showed that there were no detectable leakage currents in the insulation.

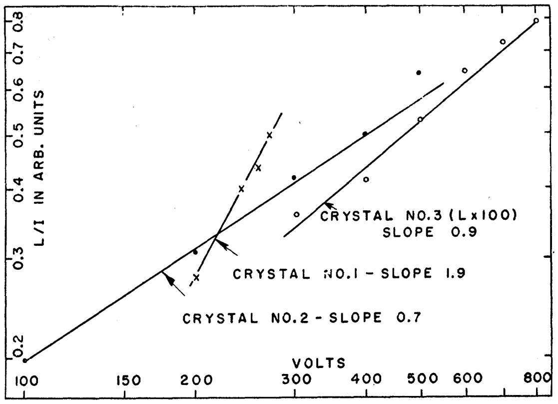

FIG. 4. Ratio of steady light output to current. Ordinate units are of the order of 4×10^{-3} photons per electron.

EXPERIMENTAL RESULTS

a. Existence of Cathode Barriers.—The existence of cathode barriers in the crystals selected can be ascertained from the distribution of light output under unipolar exciting voltage. An example is shown in Fig. 1.* Although there is some light emerging from all parts of the crystal, possibly due to scattering, the brightest region is that near the cathode under either polarity. Such a shift with polarity was absent in the uniformly-emitting crystals previously described.[9,10] Measurements of the potential distribution along the surface of the crystal and of the photocurrent under excitation by a narrow movable slit of ultraviolet light, as described by Lempicki,[23] are illustrated in Fig. 2 and give independent confirmation of the existence of the cathode barriers. It is important to emphasize that the field was applied perpendicular to the c axis, so that internal barriers due to stacking faults were inoperative.

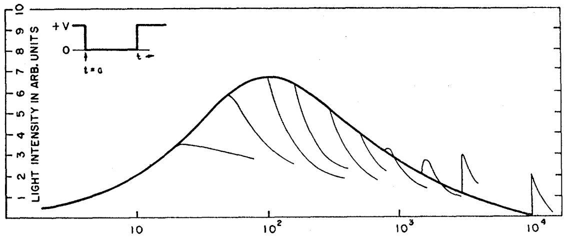

FIG. 5. Crystal No. 2. Effects of reapplication of voltage in initial direction. Heavy curve is the "normal burst" of emission on removal of voltage. Thin curves are emission intensity under voltage re-applied after various intervals from 20 μsec up.

b. Light emission.—An oscillogram of the emission from a copper-activated crystal under excitation by a single pulse of voltage applied after de-excitation of the crystal by infrared or heating is shown in Fig. 3. When the voltage is on, the emission rises in a few microseconds to a steady value that is a rapidly increasing function of the voltage. The ratio of emission intensity to current is shown as a function of voltage in Fig. 4. When the voltage is removed, there is a burst of further emission rising to a considerably higher intensity and then decaying to zero in some milliseconds. The influence of an electric field on the emission intensity during this burst is shown in Figs. 5 and 6. In Fig. 5

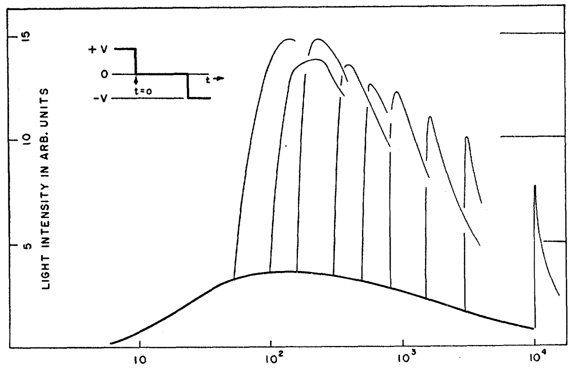

FIG. 6. Crystal No. 2. Effects of reapplication of voltage in opposite direction. Heavy curve is the "normal burst" of emission on removal of voltage. Thin curves are emission intensity under reversed voltage re-applied after various intervals from 50 μsec up.

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* *Note added in proof.*—The brightness distribution shown in Fig. 1 is somewhat exaggerated by photographic reproduction. Visually, the brightness appeared more nearly uniform, but the shift with polarity was clearly discernible.

[23] A. Lempicki, J. Opt. Soc. Am. 46, 611 (1956).

the voltage was re-applied in the *initial* direction after various intervals; this produced a pronounced quenching. In Fig. 6, the voltage was re-applied in the *opposite* direction; this produced a pronounced enhancement of the emission intensity.

In the curves of Fig. 5 for intervals greater than about 1 millisecond there is a slight increase of intensity preceding the quench. This "stimulation effect" increases with time and reaches a maximum about when the normal burst has decayed essentially to zero. It may still be seen, however, for several minutes after the normal burst. This discloses the important fact that *not all* of the ionized centers succeed in recapturing electrons during the normal burst.

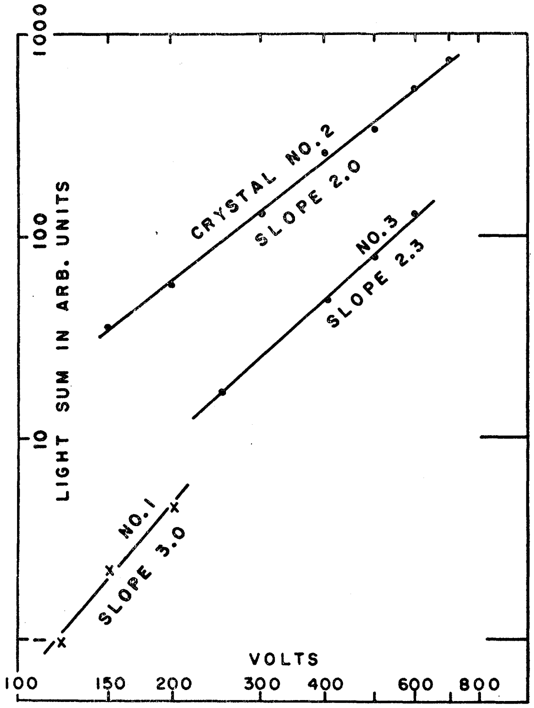

FIG. 7. Light sums on sudden reversal of voltage. Ordinate units are of the order of 10^6 photons.

In order to obtain information on the total number of ionized centers, the voltage was quickly reversed so as to promote the maximum amount of radiative recombination. The resulting light sums, measured by graphical integration of oscillograms, are shown in Fig. 7. The light sum is seen to be roughly proportional to V^n, with n ranging from 2 to 3. This result is only approximate, owing to the difficulties of measuring the long tail of the emission burst and possibly to some emission from the new cathode end of the crystal as the reversed voltage decays.

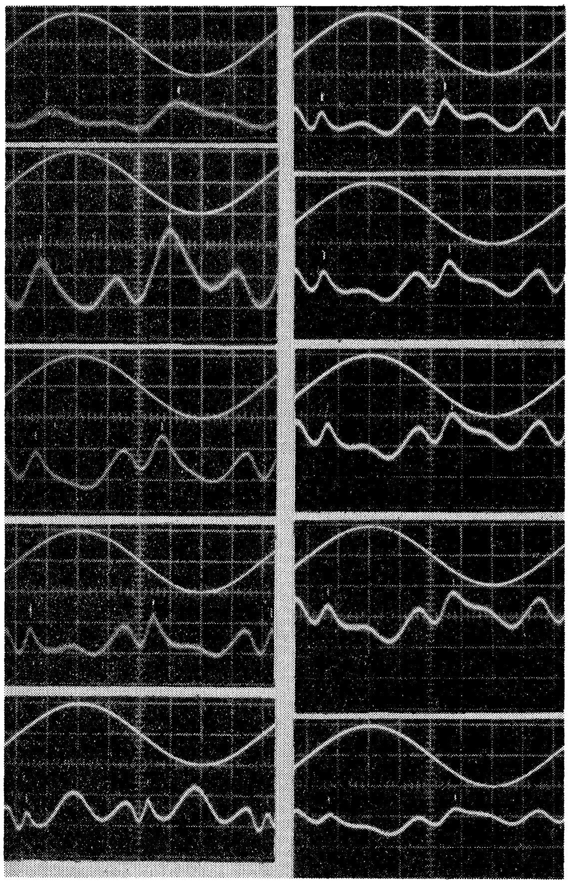

FIG. 8. Crystal No. 3. Light output under full-wave sinusoidal voltages. Left side: 60 cps; from top, 120, 180, 300, 400, 500 volts rms. Right side: 400 volts rms; from top, 180, 300, 500, 800, 1200 cps. Zero of light output at bottom grid line. "Primary" peaks indicated by marks.

Oscillograms of the emission under 60-cycle full-wave voltages are shown in the left side of Fig. 8. At low voltages, the primary peak shortly before the voltage maximum is the most prominent. With increasing voltage this peak moves toward zero phase, and the "secondary" peaks at about 150° to 170° and 90° become in turn the most prominent. The latter are best studied under half-wave voltage excitation, where the "primary" peak is much smaller. The present crystals gave results generally similar to those described earlier[9,10] for crystals with internal barriers. Observation of the emission from one end of the crystal by means of a narrow aperture showed that the primary peak occurs during the positive half-cycle and the secondary peaks during the negative half-cycle.

Oscillograms under fixed voltage and variable frequency are shown in the right side of Fig. 8. The

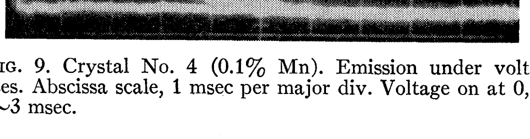

FIG. 9. Crystal No. 4 (0.1% Mn). Emission under voltage pulses. Abscissa scale, 1 msec per major div. Voltage on at 0, off at ~3 msec.

primary peak is seen to shift to the right and broaden with increasing frequency.

The behavior of manganese-activated crystals is quite different from the foregoing, as shown, for example, in the oscillogram of Fig. 9. The emission is essentially in phase with the voltage pulses, and decays at a rate comparable to that of manganese-activated ZnS phosphors excited in their characteristic absorption bands.[24] Quantitative measurements are difficult, owing to the greatly reduced sensitivity of the photomultiplier in the orange region of the spectrum. Exposure to room light (fluorescent lamps) results in a considerable increase in emission intensity under the voltage pulses, which decays over some minutes to a steady value. In many of the crystals studied, the final value was undetectably small.

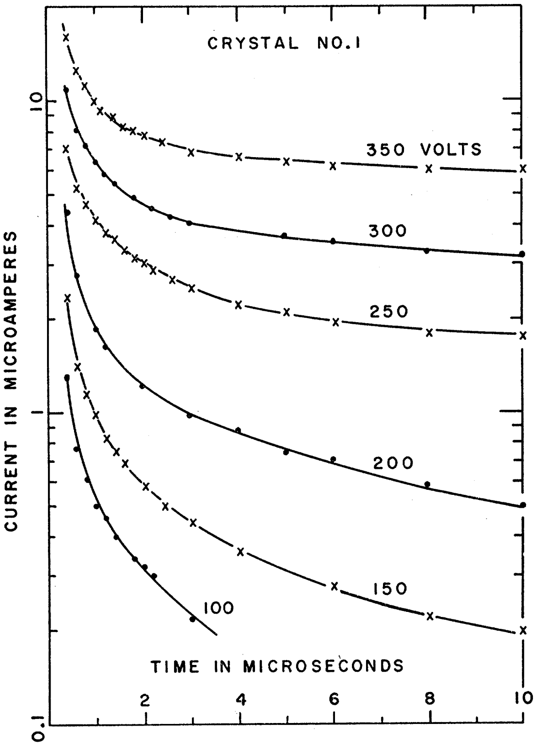

FIG. 10. Currents under voltage steps of about 20 mμsec rise time.

c. Electrical Measurements.—The transient currents under fast rising voltage steps of various amplitudes are illustrated in Fig. 10. As expected, the curves show a decay to a finite steady value that is strongly voltage-dependent. However, the absence of a well-defined exponential region makes a quantitative interpretation of the initial portions impossible. The steady currents plotted in accordance with Eqs. (2) and (3) are shown in Figs. 11 and 12, respectively. It is seen that Eq. (2) is a fair representation of the data in the lower voltage range but predicts too low a current at the higher

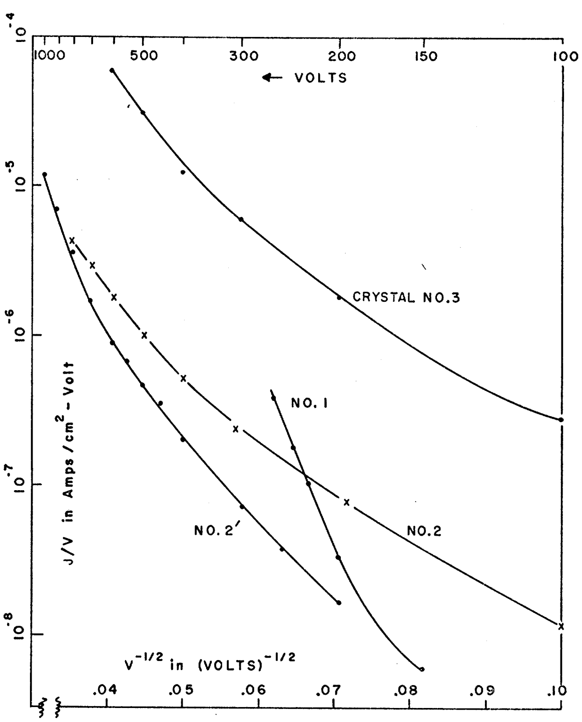

FIG. 11. Steady-state current densities, plotted in accordance with Eq. (2).

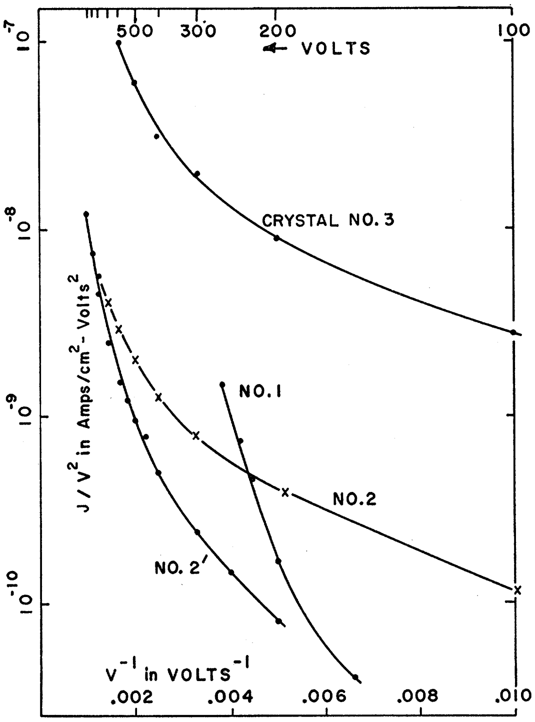

FIG. 12. Steady-state current densities, plotted in accordance with Eq. (3). Same data as in Fig. 11.

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[24] G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, London, 1949), p. 69, Fig. 33.

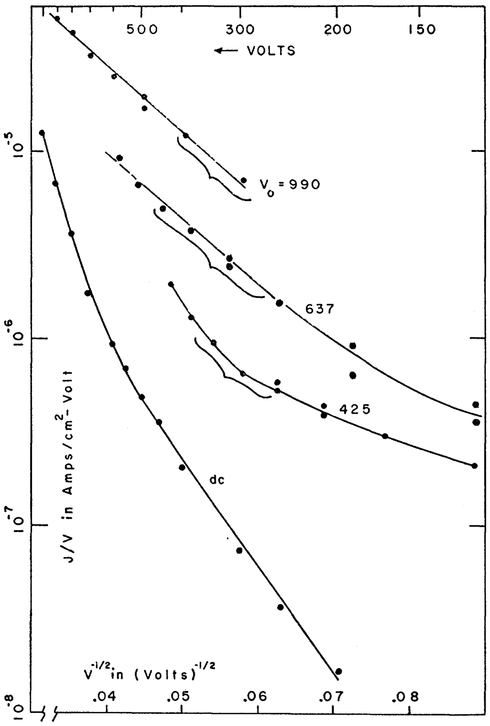

FIG. 13. Crystal No. 2′. Current-voltage curves at 60 cps, plotted in accordance with Eq. (2). Dc curve shown for comparison. Brackets indicate range of primary peak positions.

voltages. Use of Geller's[20] formula for calculation of the maximum field strength would make the discrepancy slightly worse at the highest voltages.

Sixty-cycle ac current-voltage curves, plotted in accordance with Eq. (2), are shown in Fig. 13. It is seen that the form of Eq. (2) is a moderately fair representation of the data for instantaneous voltages up to those at which the primary peaks occur, but the parameters B and C depend on V_0.

THEORY

The experiments of Figs. 3, 5, and 6 are readily interpretable in terms of ionization of the copper centers in the barrier field, as has been proposed by numerous other workers.[7,8,12,21,25] For crystals with metallic contacts, in contrast with powder phosphors suspended in a dielectric, steady currents may be drawn and steady light is emitted. However, a greater emission intensity is obtained when the barrier is allowed to collapse and a cloud of electrons flows back to the region of the ionized centers. A similar result and mechanism has been obtained by other workers.[8,19,21,25,26] The data of Figs. 5 and 6 support this mechanism by showing that the emission is readily influenced by applied fields.

We now apply this model to the emission peaks observed under sinusoidal voltage excitation. In brief, it is proposed that the events at a given end of the crystal (say for definiteness the ungrounded end) are as follows:

1. During the quarter cycle $-\pi<\phi<-\pi/2$, the barrier widens and the number of ionized centers increases due to impact by electrons entering the crystal from the cathode. Light emission occurs due to the radiative capture of some of these electrons (or possibly due to excitation of some centers to discrete levels). This emission gives rise to the "90-degree peak."
2. During the quarter cycle $-\pi/2<\phi<0$, this emission process continues as the barrier width shrinks, and there is additional emission from ionized centers which are then in the neutral part of the crystal. This gives rise to the emission peak at about 150 to 170 phase degrees.
3. During the quarter cycle $0<\phi<\pi/2$, the remaining ionized centers recombine with the increasing stream of electrons flowing through this then neutral part of the crystal. This gives rise to the "primary" emission peak.

Since the "90-degree peak" process is analogous to the steady emission under dc, we assume that at every instant it follows the same law, which is approximately, from Fig. 4 and Eq. (2)

$$L_1=DJV^n=DCV_0^{n+1}\sin^{n+1}\phi\exp[-B(V_0\sin\phi)^{-\frac{1}{2}}], \quad (4)$$

where D is a constant and $n\cong 2$ to 3.

The calculation of the "150-degree" peak will require

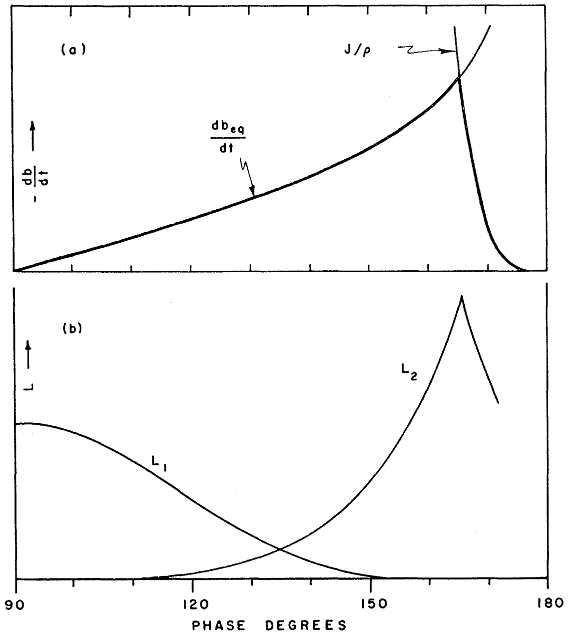

FIG. 14. Theoretical curves. (a) Rate of shrinkage of barrier, computed from Eqs. (7), (6), and (2). (b) Light output, computed from Eqs. (8), (10), and (4), taking $n=2$ in the latter.

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

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

a number of simplifying assumptions. It will serve mainly to indicate in a general way how an intensity maximum can arise. Specifically, we assume an exhaustion-type barrier with constant space-charge density, so that for any instantaneous voltage the corresponding "equilibrium barrier width" will be given by

$$b_{\mathrm{eq}}=(2\epsilon' V/N_0e)^{\frac{1}{2}}=(2\epsilon'/N_0e)^{\frac{1}{2}}(V_0\sin\phi)^{\frac{1}{2}}, \tag{5}$$

and the equilibrium rate of change under the sinusoidal voltage will be

$$db_{\mathrm{eq}}/dt=(\epsilon'/2N_0e)^{\frac{1}{2}}\omega V_0^{\frac{1}{2}}\cos\phi(\sin\phi)^{-\frac{1}{2}}. \tag{6}$$

We further assume that the actual barrier width b is essentially equal to b_{eq} when the voltage is high and there is ample tunneling current to accomplish the neutralization of space charge at the required rate. However, near the end of the half-cycle this will not be true. The actual situation will be quite complicated, as the field in the bulk of the crystal reverses direction and the final neutralization is accomplished by electrons moving in the reverse direction. We shall ignore this complication and assume simply that the actual rate of decrease of the barrier width is given by the smaller of the two expressions

$$db/dt=db_{\mathrm{eq}}/dt \quad \text{or} \quad J/N_0e. \tag{7}$$

The form of this function is shown in Fig. 14(a). The resulting component of the emission intensity, due to the recombination in those centers which are left in the neutral part of the crystal as the barrier contracts, will then be given by

$$L_2\propto c(b,V_0)db/dt, \tag{8}$$

where $c(x,V)=$ steady-state concentration of ionized centers at distance x from cathode under voltage V. To evaluate this, we further assume that c is a function of the local field strength only, i.e., that

$$c(x,V)=c[E(x,V)].$$

Then, from Fig. 6,

$$\int_0^{b_{\mathrm{eq}}(V)} c(E)dx \propto V^n, \tag{9}$$

TABLE I. Barrier space-charge density, obtained from position of "150-degree" peak. Crystal No. 2′.

V_0 (volts)	ϕ_m (deg)	N_0 (10^{15} cm^{-3})	$b_{\mathrm{eq}}(V_0)$ (10^{-4} cm)
425	160	1.3	6.4
637	166	3	4.5
850	170	9.5	3.4
990	172	10	3.5

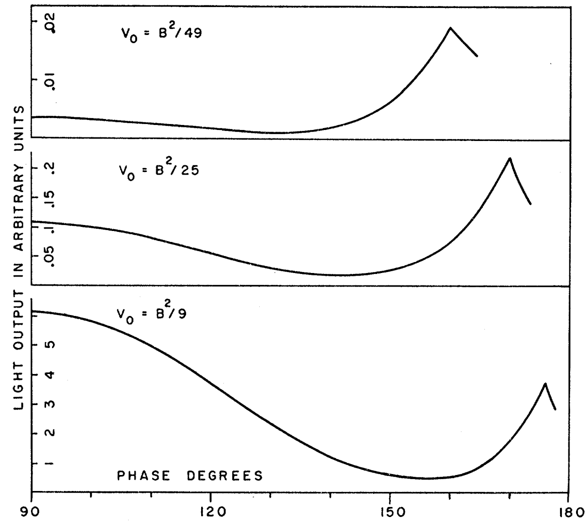

FIG. 15. Theoretical curves for "secondary" emission peaks, computed as in Fig. 14b, for several values of V_0.

a solution of which, for the exhaustion layer case $E=2V(b_{\mathrm{eq}}-x)/b_{\mathrm{eq}}^2$, is given by

$$c\propto E^{2n-1}. \tag{10}$$

The resulting emission intensity for the case $n=2$ is shown in Fig. 14(b). The total emission due to both processes is given by the sum of Eqs. (4) and (8). The computed results are given in Fig. 15.

The theory cannot be expected to predict the emission patterns in quantitative detail, but does give qualitative agreement in respect to (a) the existence of the in-phase and out-of-phase maxima, (b) the shift of the latter to the right with increasing V_0, and (c) the trend of the relative voltage dependencies of the peak heights.

If the two expressions on the right side of Eq. (7) are equated at the out-of-phase maximum, the resulting equation can be solved for the space-charge density N_0e in the barrier. Some results, which are only very approximate owing to the crudeness of the theory, are given in Table I.

For the primary peak, the instantaneous emission rate will be given, according to the process described above, by

$$L_3=-dP_c/dt=\sigma P_cJ/e, \tag{11}$$

where $P_c=$ *total number* of ionized centers remaining at time t, $\sigma=$ capture cross section of an ionized center, and $J=$ current density at time t. The use of the current density in the expression (11) for the recombination rate implies that the drift of the recombining electrons is essentially their only motion; otherwise, J would be replaced by the product of concentration and thermal velocity. This assumption will be justified by the agreement with the experimental results, and its possible significance will be discussed later. The solu-

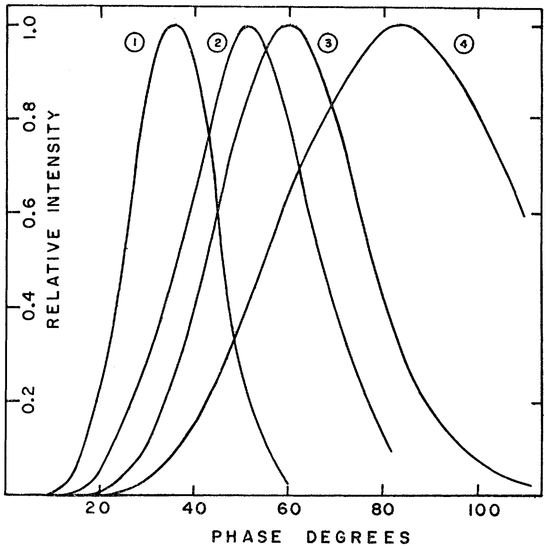

FIG. 16. Theoretical shape of "primary" peak, computed from Eqs. (12) and (2) for several sets of the parameters V_0/B^2 and $3e\omega/\sigma CB^2$, respectively, as follows: curve 1, 0.060 and 10^{-4}; curve 2, 0.040 and 10^{-4}; curve 3, 0.020 and 10^{-5}; curve 4, 0.020 and 10^{-4}.

tion of Eq. (11) is

$$L_3(\phi)=P_c^{(0)}J(\phi)\exp\left[-\frac{\sigma}{e\omega}\int_0^{\phi}J(\phi')d\phi'\right]. \qquad (12)$$

Since the current is a rapidly increasing function of the voltage, this expression is quite similar to that of Thornton,[3] except that no temperature effects are included.

Curves calculated from Eq. (12), using Eq. (2) as an analytical approximation for J, are shown in Fig. 16. The peak is seen to shift to the left and become narrower with increasing V_0 or decreasing frequency, in agreement with Fig. 8.

By differentiating Eq. (12), the maximum intensity is found to occur when

$$dJ/d\phi=(\sigma/\omega e)J^2. \qquad (13)$$

Values of σ were computed from Eq. (13), using the observed currents and peak positions. Results on crystal No. 2′ are given in Table II. The constancy of σ is probably within experimental error. Similar values were obtained on crystals No. 1 and No. 3. Thus, the agreement between theory and experiment is quite satisfactory.

DISCUSSION

It has been shown that various features of the electroluminescence of certain ZnS crystals are explainable in terms of a simple barrier model, with excitation occurring by impact of electrons tunneling into the crystal from the cathode and being accelerated in the barrier field. In particular, it is not necessary to assume a separate excitation process due to electrons from field-ionized deep donors, as in the theory of Piper and Williams.[7]

TABLE II. Capture cross sections, from Eq. (4). Crystal No. 2.

V_0 (volts)	f (cps)	$\sin\phi_m$	σ (10^{-12} cm^2)
226	60	0.91	0.8
425	60	0.62	1.3
	500	0.91	1.5
637	60	0.42	0.8
	500	0.68	0.9
850	60	0.34	0.4
	600	0.50	0.8
900	60	0.29	0.4
	600	0.41	0.8

The dc and 90-degree peak emission may result either from the excitation without ionization of some centers or from the recapture by previously ionized centers of electrons coming from the cathode. If the latter is the case, the relatively low intensity is probably due to the low concentration of electrons in the barrier region, together with a possible decrease in capture cross section for fast electrons.

The exact nature of the barrier remains, unfortunately, rather obscure. Figures 11 and 12 give some suggestion, by no means unambiguous, that it is of the exhaustion type. It seems plausible that there may be a thin depletion layer, which provides some initial ionization of deep donors and centers, and that the build-up of the ionization produces ultimately a barrier essentially of the exhaustion type. Zalm[21] has discussed this situation in some detail, although without proposing a mechanism for the initial ionization.

The theory given for the 150-degree peak entails a number of specific assumptions, and therefore does not pretend to be quantitatively exact. Its principal virtue is the demonstration that an emission peak, having reasonably correct position and relative voltage dependence, can arise due to recombination with ionized centers in excess of the number corresponding to steady-state under the decreasing voltage. This result turns out to be rather insensitive to the detailed model; for example, curves generally similar to those of Fig. 15 can be obtained with concentration distributions quite different from Eq. (10), provided only that c decreases somewhat with distance from the cathode.

The theory given for the primary peak is believed to be considerably more exact, being based only on Eq. (11) and the observed existence of some remaining ionized centers after field removal. The fact that some of the centers may remain ionized for a considerable time after removal of the excitation can be accounted for in a number of ways. Firstly, since the crystal may acquire a net positive charge in an exhaustion layer, complete neutralization will be prevented by the barrier at the opposite end. Secondly, there may well be a large density of shallow traps which greatly impede the motion of the electrons in zero field. These traps, if shallow enough, might be field-ionized under an applied voltage. Thirdly, inhomogeneities in the distribution of impurities might lead to the well known "wavy band" picture, in which the electrons would congregate in certain regions of the crystals and fail to reach other regions.

It has been remarked that the form of Eq. (11) implies that the drift motion of the recombining electrons supersedes the thermal motion. This would be surprising for the average electron even in the barrier, and appears most remarkable in the bulk of the crystal. It may, perhaps, be rationalized by the assumption that the electrons are field emitted from very shallow traps and move only a short distance, essentially in the field direction, before being retrapped. This would require that the free lifetime be, at most, comparable to the collision time of about 10^{-14} sec. Thus, for traps of geometrical cross section, a density of at least 10^{20} cm^{-3} would be required.

On the other hand, the data of Fig. 13, showing that the current depends not only on the instantaneous voltage but also on the voltage amplitude, suggest that there are field-excited conduction electrons whose lifetimes are at least comparable to the cycle period. This seems contradictory to the idea of very rapid retrapping, but may be due to excitation from deeper levels in the barrier field, the return to these being hindered by the shallow traps. These proposals are, of course, highly tentative, but, in any event, it is clear that the field must strongly perturb the distribution of electrons among whatever levels exist in these crystals.

The theory leads to a value of about 10^{-12} cm^2 for the capture cross section of an ionized center. This rather large value suggests a Coulomb attraction.

For the manganese-activated crystals, since only in-phase emission occurs, little direct inference can be drawn concerning the mechanism. However, it seems reasonable to assume, as others have done, that the same excitation mechanism as in the copper-activated crystals prevails. It is somewhat surprising that no delayed emission from accidental copper centers is observed, especially in view of the fact that green emission from these crystals can be seen under extremely strong ultraviolet (3650A) excitation and that the photomultiplier is much more sensitive to these wavelengths. It must therefore be assumed that in the present highly doped (about 10^{19} Mn/cm^3) crystals, the fast electrons make exciting collisions with manganese centers virtually as soon as they attain sufficient energy and before they can reach the ionization energy.

Although the present study has been restricted to crystals showing clearly defined cathode barriers, similar mechanisms probably apply in the case of internal barriers, since the behavior of the light emission from such crystals is quite similar. However, a quantitative understanding will probably be much more difficult to attain.

ACKNOWLEDGMENTS

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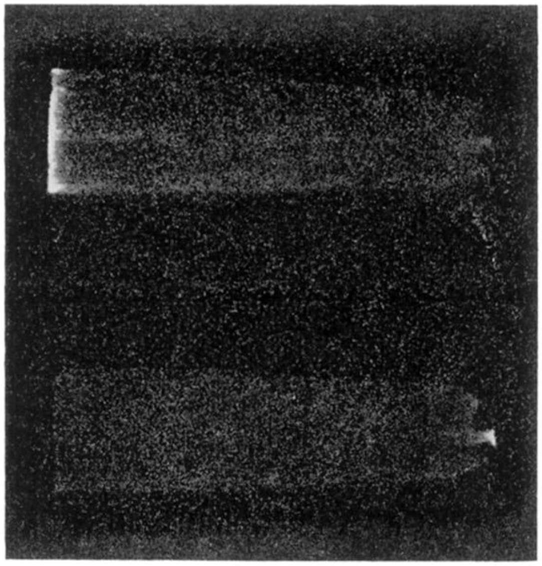

FIG. 1. Crystal No. 2. Emission under 60-cycle half-wave voltage. Top, negative at left. Bottom, negative at right. Crystal length 1.22 mm.

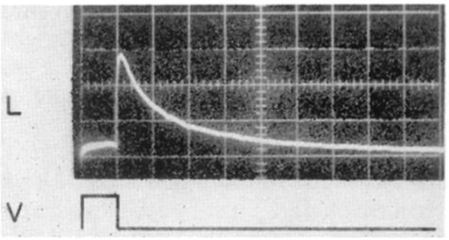

FIG. 3. Crystal No. 2. Emission under voltage pulse applied after 2 min of infrared. Abscissa scale, 0.5 msec per major div.

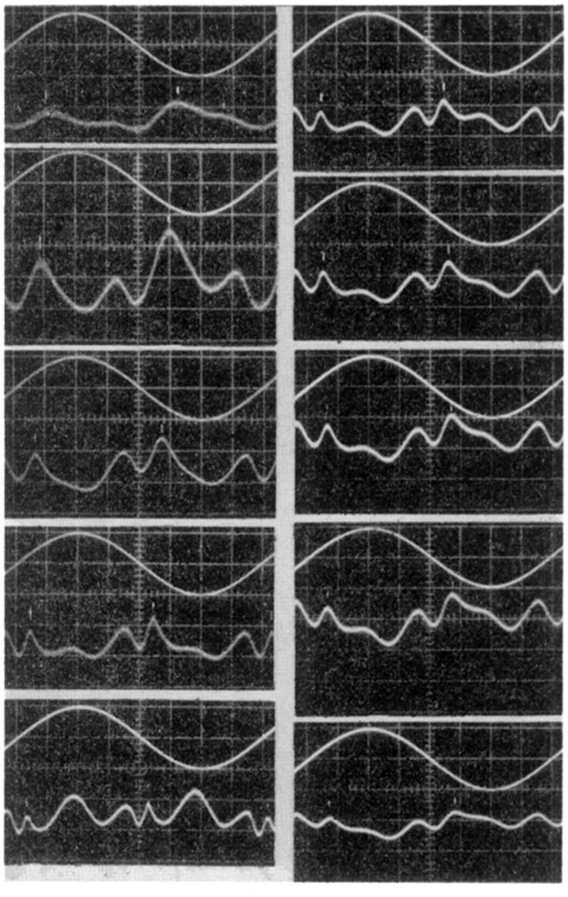

FIG. 8. Crystal No. 3. Light output under full-wave sinusoidal voltages. Left side: 60 cps; from top, 120, 180, 300, 400, 500 volts rms. Right side: 400 volts rms; from top, 180, 300, 500, 800, 1200 cps. Zero of light output at bottom grid line. "Primary" peaks indicated by marks.

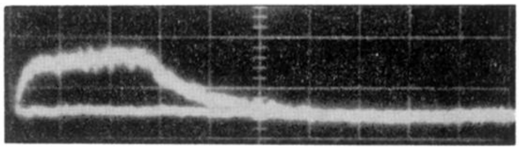

FIG. 9. Crystal No. 4 (0.1% Mn). Emission under voltage pulses. Abscissa scale, 1 msec per major div. Voltage on at 0, off at ~3 msec.