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## LUMINESCENCE DURING INTERMITTENT ELECTRON BOMBARDMENT

By

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## Luminescence During Intermittent Electron Bombardment

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The dynamic luminescence characteristics of five samples of commercial phosphors excited intermittently by electron bombardment have been studied. The decay of artificial willemite follows closely a simple exponential law, except for a rapid fall during the first three milliseconds after bombardment, the prominence of this component increasing with the current density. An attempt is made to correlate the observed dependence of build-up rate on current density with the phenomenon of current-saturation under continuous bombardment. A sample of calcium

tungstate follows changes in the intensity of excitation within 100 microseconds, the resolving time of the apparatus. Two samples of ZnS·Ag and one sample of ZnS·CdS·Ag decay more rapidly the higher the intensity of excitation. The initial rate for ZnS·Ag is greater than would be predicted for a simple bimolecular reaction, and cannot plausibly be explained by non-uniformity in the initial distribution of reactants in a bimolecular reaction. The ZnS·CdS·Ag decays initially according to a simple bimolecular law.

### I. PROBLEM AND EXPERIMENTAL METHOD

The course of the luminescence of a phosphor toward a new equilibrium value, after a change in the intensity of the exciting agent, is an important datum for any theory of fluorescence. The information yielded by decay curves and build-up curves supplements that obtained by studying how the luminescence under continuous excitation varies with the chemical and physical composition of the phosphor, with its temperature, and with the nature, energy, and rate of arrival of the exciting particles. The behavior of phosphors under intermittent electron bombardment, which is the subject of this investigation, has also considerable technical interest.

Five samples of commercial phosphors, furnished by the RCA Manufacturing Company, have been studied: an artificial willemite,  $2\text{ZnO} \cdot \text{SiO}_2 \cdot \text{Mn}$ , luminescing green; two identical samples of ZnS activated with Ag, luminescing blue; a mixed sulphide, ZnS·CdS·Ag, luminescing yellow; and a calcium tungstate, presumably pure, luminescing blue. The powders are settled onto glass disks from acetone suspensions. Experiments on the luminescent and electrical properties of these same samples under continuous electron bombardment, in the tube used for the present study, have been reported.<sup>1</sup>

\* At present, RCA Manufacturing Company, Harrison, New Jersey.

† On leave of absence from Massachusetts Institute of Technology. Some of the circuits were devised by W. B. N.; the other authors are responsible for the measurements reported here.

<sup>1</sup> W. B. Nottingham, J. App. Phys. 10, 73 (1939).

The samples are mounted off the axis of the tube (Fig. 1), to prevent contamination by material evaporated from the cathode of the electron gun.<sup>2</sup> The electron beam is directed by magnets to the phosphor under study. The current in the beam is controlled by the bias on the first grid  $G_1$  and is measured by a galvanometer in series with the second anode, a layer of gold covering most of the inside of the tube. Measurements with the cage structure at the end of the tube have shown that the beam contains 99 percent of the current reaching the second anode. Two Fernico wires, completely shielded, are imbedded in each mounting disk and ground flush with the glass surface which is later coated;

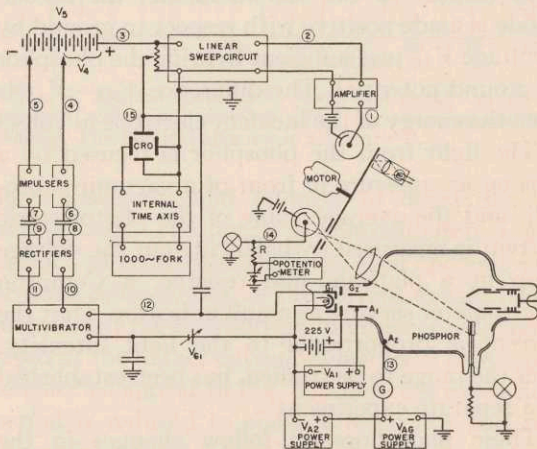


FIG. 1. Tube and circuit for studying luminescence of phosphors bombarded intermittently with electrons.

<sup>2</sup> C. H. Bachman and C. W. Carnahan, Proc. I. R. E. 26, 529 (1938).

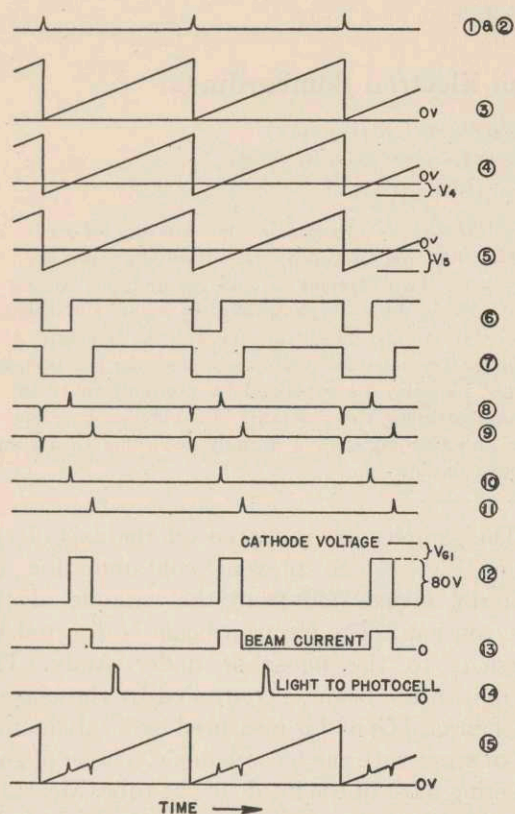


FIG. 2. Voltage waves at various points in the circuit of Fig. 1.

with these probes the potential of the phosphor with respect to ground is measured by an electrometer. For each voltage  $V_{A2}$  of the cathode with respect to the second anode, the second anode is made positive with respect to ground by a voltage  $V_{AG}$  just sufficient to bring the phosphor to ground potential. The difference  $V_{A2} - V_{AG}$  is then the energy of the incident electrons in volts.<sup>3</sup>

The light from the phosphor is focused by a lens on an aperture in front of a vacuum photo-cell, and the average value of the photoelectric current is measured by balancing out the voltage drop in a platinum-film resistor, a Compton electrometer serving as a null indicator. That the current is proportional to the light intensity, over the range to be studied, has been established in a separate experiment.

These phosphors all follow changes in the intensity of the electron beam far too rapidly to allow consecutive readings of the light during a single cycle of build-up and decay. It is required,

<sup>3</sup> W. B. Nottingham, J. App. Phys. 8, 762 (1937).

then, to turn the beam on and off periodically and to measure the average value of the light emitted during some short part of the total period. The total period, the fraction of the period during which the beam is on, and the phase difference between the turning on of the beam and the sampling of the light, should be separately variable. The block diagram (Fig. 1) shows how these requirements are met.

Immediately in front of the photo-cell aperture is a rotating Duralumin disk with a hole which admits light from the phosphor to the photo-cell during  $1/100$  of a revolution. For suppressing the electron beam periodically, a square wave of voltage from a multivibrator circuit is added to the steady grid bias on the gun. During the "on" interval this multivibrator voltage is zero, and the beam current is determined by the steady grid bias; in the "off" interval the grid voltage is carried below  $-80$  v, much farther than is necessary to stop the current completely; the change from one state to the other occurs in about one microsecond.

The remainder of the circuit is for synchronizing the multivibrator oscillations with the rotating disk, and for shifting the phases. Half a revolution from the measuring photo-cell the hole passes another stop diaphragm and lets light from a

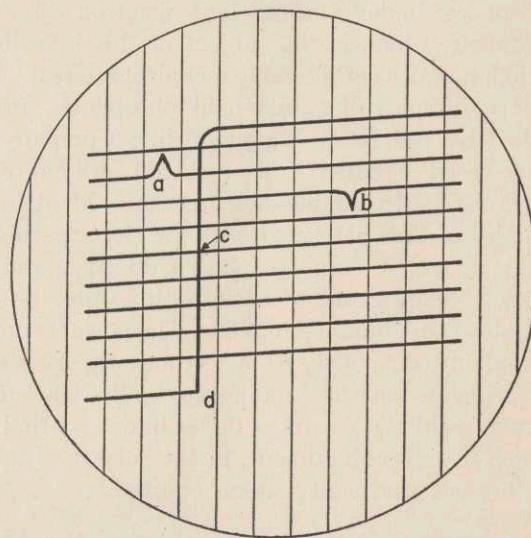


FIG. 3. Stationary monitory oscillograph pattern corresponding to the cycle of Fig. 2. (a) Beam goes on; (b) beam goes off; (c) photo-cell open; (d) end of sweep circuit cycle. By inspection, the beam persists for 0.150 cycle, and the measuring photo-cell is opened 0.160 cycle after the beam is cut off.

lamp into another photo-cell. The resultant current pulse, after amplification, synchronizes a conventional linear sweep circuit with the disk. To the sawtooth voltage output of the sweep circuit is added a variable negative bias, so that the resultant voltage is initially negative and rises through zero at a time in the cycle determined by the negative bias. This biased wave is applied to an "impulser" circuit which has a trigger action, yielding a pulse of positive voltage when its input voltage rises through zero. This pulse turns the multivibrator on and so stops the electron beam. An identical impulser, whose sawtooth input voltage differs from that of the first only in the amount of added negative bias, turns the multivibrator off, starting the beam. Rectifier tubes prevent the negative pulses which originate in the impulsers at the end of the sweep circuit cycle from reaching the multivibrator. By changing the two biases the beam can be turned on and off at any two points in the sweep circuit cycle; the measuring photo-cell is open, of course, midway in this cycle. Fig. 2 shows the voltages at several places in the circuit of Fig. 1.

The operation is monitored continuously with an RCA Type TMV-122-B cathode-ray oscillograph. All time intervals are referred directly to the period of a 1000-cycle tuning fork oscillator, which is checked occasionally by beating the 17th submultiple of its output against the 60-cycle line voltage. This fork synchronizes the horizontal time-axis of the oscillograph at some convenient submultiple of 1000 cycles. On the vertically deflecting plates is placed a fraction of the output of the sweep circuit, to which is added, through condenser coupling, the voltage on the grid of the gun. The disk speed is held at 1/10 the frequency of the horizontal time-axis. The oscillograph pattern (Fig. 3) is then stationary, and consists of ten parallel traces and a vertical return trace, with two bumps showing where the beam is turned on and off. By inspection of the pattern, the time intervals can easily be read with an error less than one percent of the total period. Usually the shape of the beam current wave is independently monitored, on a cathode-ray oscillograph (not shown) in series with the second anode.<sup>4</sup>

<sup>4</sup> Blueprints showing these circuits in detail are available on request to the authors.

The apparatus is run at speeds from ten r.p.s., limited by flicker of the monitor pattern, up to 100 r.p.s., limited by the motor rating. Tests have shown that the resolving time is actually about one percent of the period of revolution—100 microseconds for a disk speed of 100 r.p.s.

## II. RESULTS WITH ARTIFICIAL WILLEMITE

The general behavior of the willemite sample is seen in Fig. 4, where the phosphor was excited for

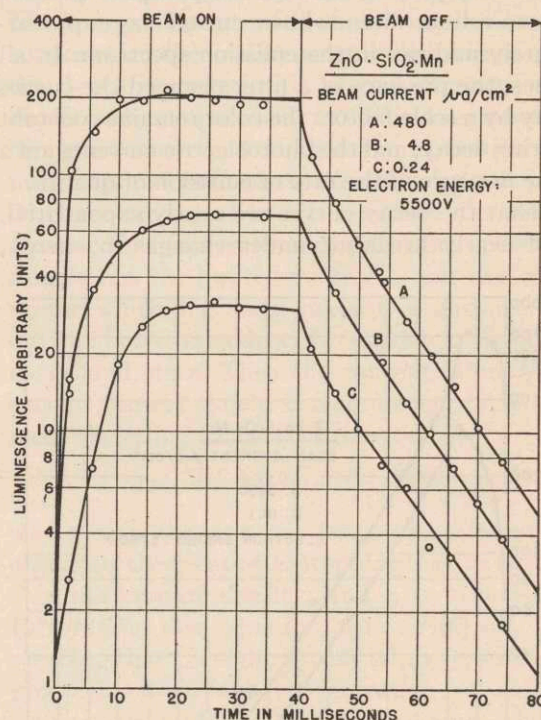


FIG. 4. Typical semi-log build-up and decay curves for artificial willemite, showing effect of changing current density. The vertical spacing is arbitrary.

40 milliseconds and allowed to decay for 40 milliseconds. The decay is approximately exponential, at a rate independent, after the first two or three milliseconds, of the current density. The rise toward the equilibrium luminescence is more rapid at the higher current densities. These same tendencies appear in Fig. 5, where the excitation period is reduced to eight milliseconds and the decay is followed for 72 milliseconds. Fig. 6 shows that the shape of the decay curve is independent of the energy of the exciting electrons. In Fig. 7, the decay during nine milliseconds, after excitation for one millisecond, is

followed in detail, and it is evident that the rapid initial decay is accentuated at the higher current density (curves A and B).<sup>5</sup> Curve C is added to show again that the course of the decay does not vary with the electron energy; curve D, a reproduction of part of curve A in Fig. 6, shows that it is independent of both the excitation period and the total decay period.

For this phosphor, and for all the others, a change in the color of the light during decay was sought by placing between the phosphor and the photo-cell a filter whose cut-off lay approximately midway in the emission spectrum. In all cases, the presence of a filter changed the curves only by a scale factor: the color remains constant during decay, and the photoelectric currents are a true measure of the rate of emission of quanta.

That the decay curves are nearly exponential, and nearly invariant under changes in energy,

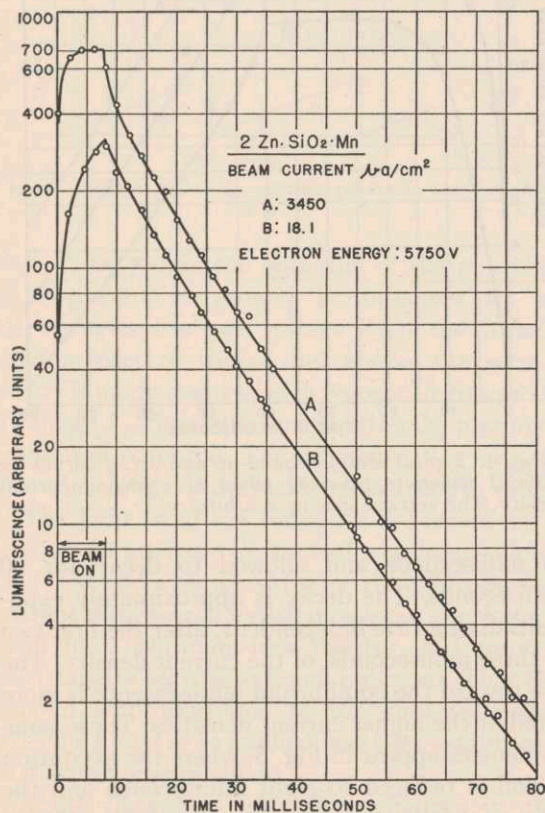


FIG. 5. Typical semi-log build-up and decay curves for artificial willemite, showing effect of changing current density. The vertical spacing is arbitrary.

<sup>5</sup> In this connection, see S. T. Martin, *J. App. Phys.* **10**, 116 (1939).

density and duration of the exciting current, suggests that at least during the first 72 milliseconds the decay process is monomolecular. The slight curvature of the semi-logarithmic plots can formally be explained by non-uniformity of the phosphor grains. Fonda,<sup>6</sup> using ultraviolet light for excitation, has found that the decay characteristics of synthetic willemite depend markedly on particle size. Büniger and Flechsig<sup>7</sup> report that single crystals of  $\text{KCl} \cdot \text{Tl}$  phosphor show an accurate simple exponential decay. If these

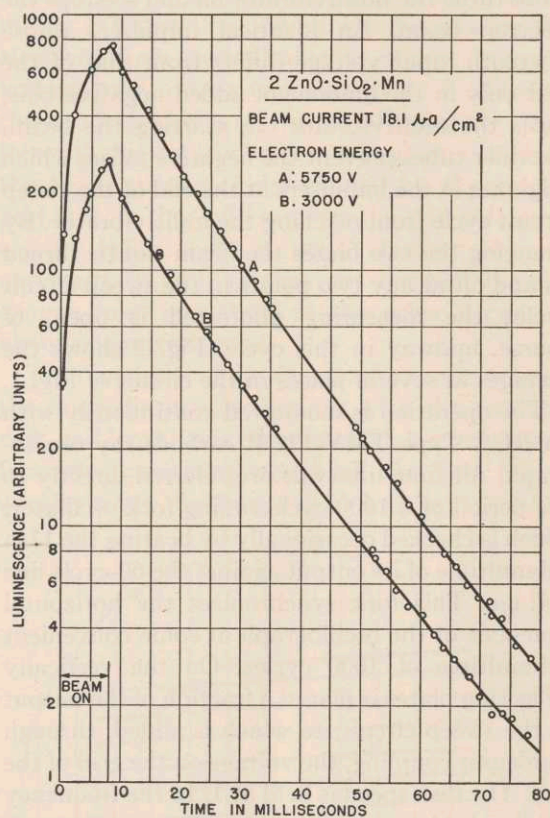


FIG. 6. Illustrating that the shape of the willemite characteristic is independent of energy of the incident electrons. The vertical spacing is arbitrary.

curves are composites of simple exponential decay curves for the individual grains, the time constants for various grains must range from about 7 to about 14 milliseconds.

The initial rapid decay, whose prominence depends on the current density, still lacks even

<sup>6</sup> G. R. Fonda, unpublished experiments in this laboratory.

<sup>7</sup> W. Büniger and W. Flechsig, *Zeits. f. Physik* **67**, 42 (1931).

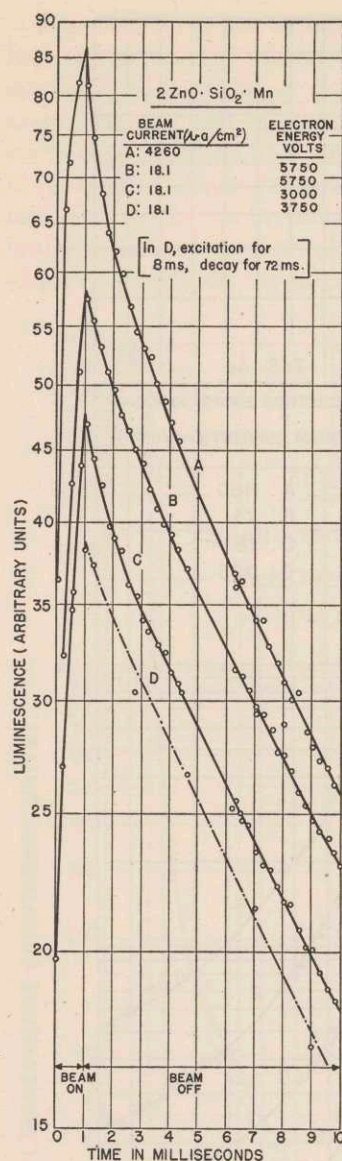


FIG. 7. Showing an initial rapid phase of the decay of willemite, prominent at high current density (curves A and B). C is added to show that the curves are independent of electron energy, D to show that they are independent of the interval of excitation and of decay. The vertical spacing is arbitrary.

formal interpretation. Heating of the phosphor during bombardment and cooling during decay cannot account for it; a rough calculation shows that the temperature rise during bombardment cannot exceed 5°C, and the day-to-day variations in room temperature, which had no effect on the decay characteristics, were greater than this.

If the decay were strictly monomolecular, and if the probability of excitation per incident electron were independent of the current density, the build-up should also follow an exponential law with the same time constant as the decay. It is known, however, that the luminescence of

willemite under continuous electron bombardment increases less rapidly than the density of the exciting current and approaches a saturation value.<sup>3</sup> This phenomenon of current-saturation should have associated with it a dependence of the build-up rate on current density, such as appears in Fig. 4. The saturation effect is practically independent of the initial energy  $E$  of the bombarding electrons—when this energy is increased the light output at every current density is multiplied by a factor proportional to  $E^2$ . It is consistent with these observations to suppose that the initial energy  $E$  determines only the depth of penetration of the electrons, this depth being proportional to  $E^2$  (in keeping with the usual theory), and that the excitation per unit length of path of the electron depends only on the concentration of excitable "centers." Assume that this concentration in the unexcited sample has the limited value  $N_0$ , and that each center which has been excited is unconcerned until it has reverted, with emission of light, to its ground state. Then the concentration  $N_1$  of excited centers should change during bombardment according to the equation

$$dN_1/dt = kI(N_0 - N_1) - \lambda N_1,$$

where  $\lambda$  is the natural decay rate (found by observing the decay after stopping the excitation),  $I$  is the current density, and  $k$  is a constant. Integrating this equation with  $N_1(0) = 0$ , and recalling that the light output is at every instant proportional to the concentration of excited centers, we find that the luminescence should build up during bombardment according to the law

$$L(t) = \mu N_1(t) = \frac{\mu k I N_0}{k I + \lambda} [1 - e^{-(kI + \lambda)t}] \quad (1)$$

and should approach an equilibrium value  $L_\infty$  given by

$$\frac{1}{L_\infty} - \frac{1}{\mu N_0} = \frac{\lambda}{\mu k N_0} \left( \frac{1}{I} \right). \quad (2)$$

Fig. 8 shows that the current-saturation effect, for this sample of willemite, follows Eq. (2) fairly closely. However, the build-up curves, such as those of Fig. 4, follow Eq. (1) only qualitatively. If a value of  $k$  is deduced from the



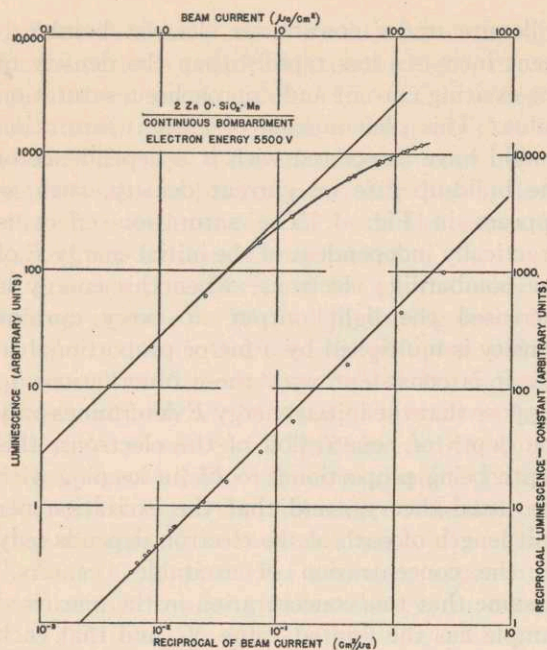


FIG. 8. (A) Current-saturation effect in artificial willemitite under continuous electron bombardment; (B) the same data, plotted to show reasonable agreement with Eq. (2).

rate of build-up at high current density, then at low current density the rise is more rapid than is to be expected.

### III. RESULTS WITH $\text{CaWO}_4$

The light from the calcium tungstate sample rises to its equilibrium value within 100 microseconds (the resolving time of the apparatus, for the diaphragm sizes used) after the electron beam is turned on, and falls by a factor of at least 2000 (too low for detection with our photo-cell) within 100 microseconds after extinction of the beam.

### IV. RESULTS WITH SULPHIDES

The two  $\text{ZnS} \cdot \text{Ag}$  samples behave alike in every respect. The rise of luminescence after the beam is turned on is too rapid to be followed with any precision. The shape of the decay curve depends strikingly on the current density (Fig. 9), the initial decay being much more rapid at higher current density. A change in energy of the incident electrons, on the other hand, makes practically no change in the shape of the curve (Fig. 10). Every ordinate is multiplied by a scale factor—the same factor by which the light output

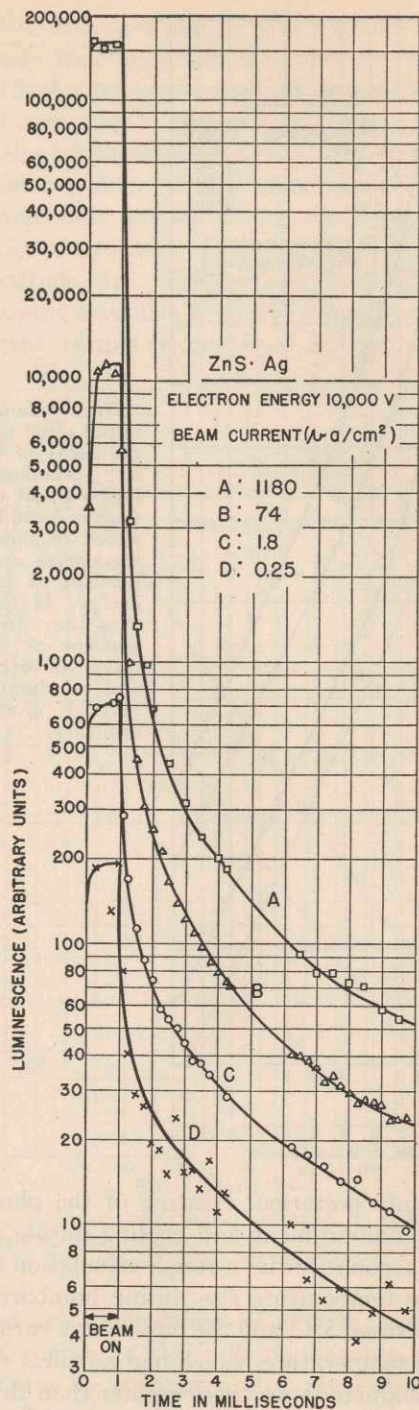


FIG. 9. Typical semi-log decay curves for  $\text{ZnS} \cdot \text{Ag}$ , showing dependence of shape on current density. The vertical spacing is arbitrary.

under continuous excitation is multiplied when the electron energy is changed.

That the decay curve depends in any marked fashion on current density seems to indicate inevitably that the decay rate is a function of the excitation per unit volume. The shape of the curve is not affected by a change in the energy  $E$  of the incident electrons; hence the excitation per unit volume is not a function of  $E$ . But the luminescence, during or after excitation, does depend strongly on the initial electron energy—

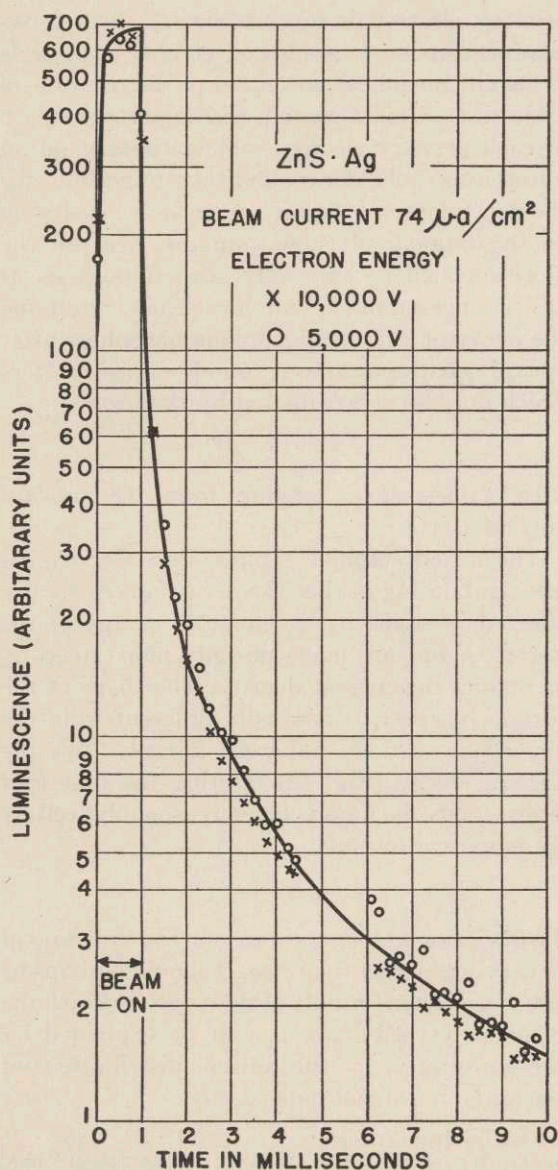


FIG. 10. Superposition to show that the decay curve for ZnS·Ag has a shape independent of the energy of the incident electrons. The two sets of ordinates differ by a scale factor of 7.5.

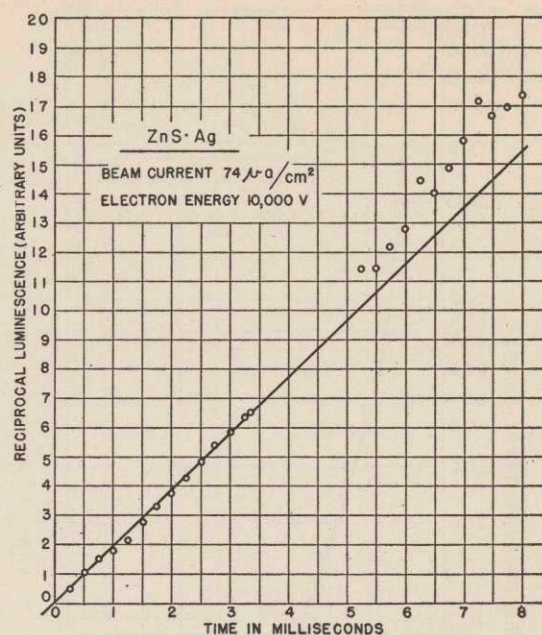


FIG. 11. Data of Fig. 9(B) plotted to show initial agreement with an empirical hyperbolic decay law.

as  $E^{2.9}$ , in the case of these samples.<sup>1</sup> It appears, then, that the excitation per unit path length of the primary electron within the phosphor is constant, while the total rate of loss of energy varies with residual energy in such a way as to give a penetration depth proportional to  $E^{2.9}$ .

The shape of the decay curves is of some interest. The simplest hypothesis for the sulphide phosphors, consistent with the fact that they are photoconducting, is that the excitation is an ionization process, and that light is emitted when an electron recombines with an ionized center.<sup>8</sup> If the electrons and ionized centers are equal in concentration and randomly distributed, the decay curve should then follow the same simple law as does the rate of a bimolecular gaseous reaction:

$$L = \frac{k}{((k/L_0)^{\frac{1}{2}} + t)^2}$$

where  $L_0$  is the initial luminescence and  $k$  is a constant of the material. Actually, all our decay curves for ZnS·Ag can be fitted, over the first five milliseconds where the photo-currents are

<sup>8</sup> This mechanism has recently been discussed by F. Seitz, *J. Chem. Phys.* **6**, 454 (1938).

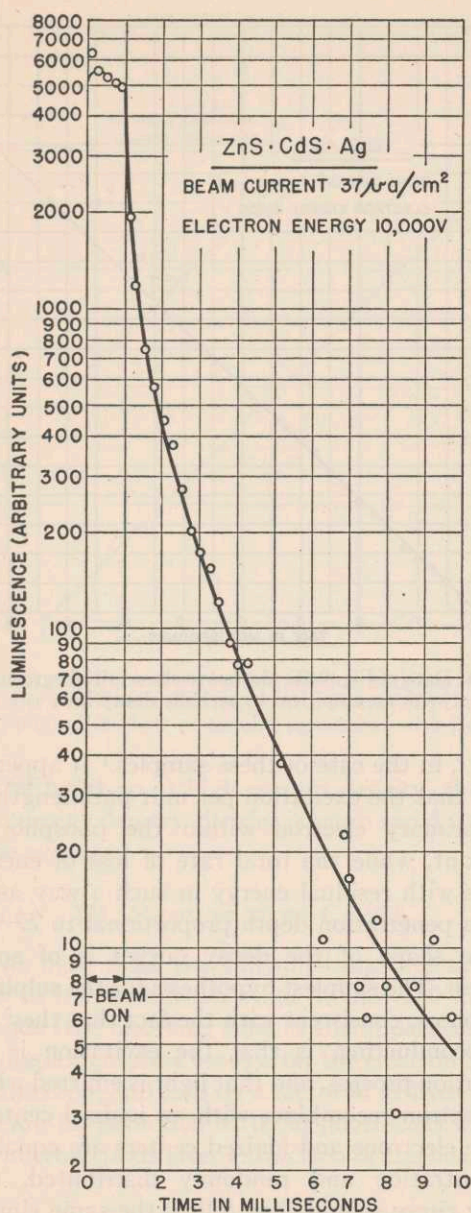


FIG. 12. Typical semi-log characteristic for mixed sulphide, ZnS·CdS·Ag.

most precisely measured,<sup>9</sup> by the empirical equation  $L=a/(b+t)$ . Fig. 11 shows the applicability of this formula. Unfortunately the curves could not be traced out far enough to tell whether the hyperbolic law, which of course

<sup>9</sup> The scattering of the observations after five milliseconds, which is somewhat greater than the experimental error, is perhaps caused by changes in the temperature of the samples. Several observers have reported that the decay of sulphide phosphors, optically excited, shows marked temperature dependence at longer times.

cannot continue to hold, eventually yields place to a simple bimolecular law; neither could the initial decay be measured at current densities low enough to give useful precision to the intercept on the time axis.

An abnormally rapid initial rate in a bimolecular reaction can formally be explained on the basis of an initial non-uniform distribution of the reacting components. In the present case, a non-uniform excitation along the path of each primary electron is improbable for the reasons advanced above. It would conceivably be possible to invent an initial non-uniform distribution of excitation within a column surrounding the path of each primary electron which would yield an initial hyperbolic decay, and then to account for the dependence of the rate on current density by an overlapping of these columns. We are the more inclined to view any such hypothesis as *ad hoc*, since a number of investigators,<sup>10</sup> studying the decay of long-lived sulphide phosphors after optical excitation, have found empirical laws which may be approximated by the form

$$L=a/(b+t)^\alpha,$$

with values of  $\alpha$  ranging from 0.8 upward beyond 2.

The mixed sulphide sample, ZnS·CdS·Ag, is like the ZnS·Ag in that the decay curves are not affected in shape by a change in energy of the electrons, but are made initially more steep by increasing the current density. The shape of the curves, however, is markedly different from the hyperbolic course followed initially by the ZnS·Ag decay (Fig. 12). During the first four milliseconds the data is fitted reasonably well by the empirical formula

$$L=a/(b+t)^2;$$

the deviation at longer times is in the direction of an exponent larger than two. It should perhaps be remarked that a formula of this type, in which the exponent exceeds two, cannot be explained by non-uniformity in the initial distribution of reactants in a bimolecular decay.

<sup>10</sup> E. Becquerel, *Comptes rendus* 51, 921 (1860); A. Guntz, *Ann. de Chimie* 6, 5 (1926); R. Coustal, *J. Chim. Phys.* 28, 345 (1931); W. L. Lewchin and W. W. Antonov-Romanovsky, *Comptes rendus (Doklady) de l'Acad. des Sciences, U. S. S. R.* 17, 95 (1937); P. J. Mulder, *J. Frank. Inst.* 225, 527 (1938); W. H. Byler, *J. Am. Chem. Soc.* 60, 632 (1938).

