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OBSERVATION AND MECHANISM OF DIRECT-CURRENT QUENCHING OF ALTERNATING-CURRENT ELECTROLUMINESCENCE IN TYPICAL ZINC SULFIDE PHOSPHORS

by Edmund J. Conway

Langley Research Center
Hampton, Va. 23365

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16. Abstract

The reduction or quenching produced by a dc voltage on light emitted during ac electroluminescence has been studied for zinc sulfide phosphor powders. The zinc sulfide was activated with copper and coactivated with either manganese, chlorine, or bromine. Quenching occurred only for cells which exhibited electrical conductivity greater than approximately 10^{-12} $(\Omega\text{-cm})^{-1}$. The fractional reduction in brightness approached zero as the ac voltage was increased, but it increased linearly with increasing dc voltage. The time dependence of quenching was approximately that of a square wave, and the magnitude of quenching was found to be independent of ac frequency from 0.2 kHz to 1 kHz. Spectrally, quenching was uniform for chlorine- and bromine-coactivated phosphors. The two-emission-band ZnS;Cu,Mn phosphor exhibited quenching for the blue emission band but enhancement for the yellow emission band. These observations are explained in terms of the deexcitation of luminescence centers followed by the space-charge-limited conduction of holes to the surface of the crystallite and nonradiative recombination of the holes with conduction electrons from the binder.

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OBSERVATION AND MECHANISM OF DIRECT-CURRENT QUENCHING OF

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ZINC SULFIDE PHOSPHORS*

By Edmund J. Conway
Langley Research Center

SUMMARY

The reduction or quenching produced by a dc voltage on light emitted during ac electroluminescence has been studied for zinc sulfide phosphor powders. The zinc sulfide was activated with copper and coactivated with either manganese, chlorine, or bromine. Quenching occurred only for cells which exhibited electrical conductivity greater than approximately 10^{-12} $(\Omega\text{-cm})^{-1}$. The fractional reduction in brightness approached zero as the ac voltage was increased, but it increased linearly with increasing dc voltage. The time dependence of quenching was approximately that of a square wave, and the magnitude of quenching was found to be independent of ac frequency from 0.2 kHz to 1 kHz. Spectrally, quenching was uniform for chlorine- and bromine-coactivated phosphors. The two-emission-band ZnS; Cu, Mn phosphor exhibited quenching for the blue emission band but enhancement for the yellow emission band. These observations are explained in terms of the deexcitation of luminescence centers followed by the space-charge-limited conduction of holes to the surface of the crystallite and nonradiative recombination of the holes with conduction electrons from the binder.

INTRODUCTION

The purpose of this report is to present the results of a study on dc voltage control of ac electroluminescence. A model is proposed to explain the major features of this control phenomenon.

The ac electroluminescence effect discovered by Destriau in the 1930's (ref. 1) consists of the periodic emission of light from a well-insulated phosphor due to excitation by an alternating electric field. Although the addition of a dc field to an ac-excited

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phosphor generally does not lead to any change in average or steady-state brightness (ref. 2), a few studies on very specialized systems (refs. 3 to 6) have disclosed a brightness decrement (quenching) or increment (enhancement).

An approximate theory proposed by Zalm (ref. 3) for the excitation of an ac electroluminescence is presented in appendix A. In this theory, an electron tunnels from an electron reservoir, such as a copper sulfide or copper inclusion, through a Mott-Schottky exhaustion barrier into the enhanced field region of the semiconductor. The high field accelerates the electron to 2 eV or more, and this energy is passed by impact to an electron in the ground state of a luminescence center. This process produces an ionized center.

The radiative recombination of ionized centers is discussed in appendix B, and a generalized equation, needed in this report, is presented. A simplified theory of one-carrier space-charge-limited current is derived in appendix C for use in the discussion of this report.

Two general types of luminescence centers in ZnS have been reported. (See ref. 3.) The first type is characterized by excitation which causes an electron to be excited into the conduction band. Copper ions or zinc vacancies in zinc sulfide are of this variety. The copper center has two levels in the lower part of the forbidden band, both of which may be occupied by electrons. (See ref. 7.) The two levels are separated in energy by approximately 1 eV. With electrons in both levels, the lowest level lies within a few tenths of an electron volt of the valence band. With one electron excited from the copper center, the lowest level is approximately 0.5 eV from the valence band.

The second type of center is characterized by lack of induced photoconductivity and by an excited electron which remains within the impurity. An example of this type is the manganese ion in zinc sulfide. Its energy levels are strongly localized in the ion, and the ground state lies approximately 6 eV below the valence band (ref. 8).

Three strongly electroluminescent zinc sulfide phosphors were studied:

ZnS;Cu,Cl
ZnS;Cu,Br
ZnS;Cu,Mn

These phosphors were chosen because they are examples of the luminescence-center types discussed previously. Copper-activated zinc sulfide, without a coactivator, exhibits only weak electroluminescence; therefore ZnS;Cu phosphors coactivated with chlorine and with bromine were studied to determine whether quenching effects were different with different halogens. Zinc sulfide doped with manganese only is also a weakly electroluminescent material. The addition of copper to ZnS;Mn makes the phosphor strongly electroluminescent, gives it two emission bands, and provides for the interaction of the two general types of centers.

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SYMBOLS

A   square root of ac voltage (measured from 0 to peak) necessary to produce e-fold increase in averaged brightness

a   absorption coefficient

B   instantaneous brightness

$\overline{B}$ time-averaged brightness

ΔB change in instantaneous brightness

$\Delta \overline{B}$ change in average brightness produced by dc voltage

C   capacitance

C_1, C_2, C_3 constants

d   average distance between free electrons

$E_i(x) = \int_x^\infty \frac{\exp(-y)}{y} dy$

e   magnitude of electronic charge

F   electric field

F_{max} maximum electric field

$f(n_e)$ functional dependence of recombination on electron concentration

H   height of exhaustion barrier

I   current

I_l light intensity

$i = \sqrt{-1}$

j   particle current

K	distance factor
$K' = \sqrt{\dfrac{Ka}{R}}$	
k	wave vector
l	thickness
M	mean value of magnitude of quenching wave
m	square root of ac voltage necessary to reduce quenching by a factor of e
m*	effective electron mass
N	charge density
n	concentration
P_1, P_2	primary, or largest, peak of brightness wave
p	probability
Q	net charge
q	quenching, or negative fractional change in instantaneous brightness
$\bar{q}$	negative fractional change in average brightness produced by dc voltage
$q'(\phi)$	idealized shape of quenching waves; negative square pulse of unit length
R	radiative recombination coefficient
r	radius
S_1, S_2	secondary peak of brightness wave
T	transmission coefficient
t	time

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V	voltage
v	drift velocity
W_F	Fermi energy
x	distance from crystal surface
x_b	width of exhaustion barrier
y	dummy variable
ϵ	permittivity of free space
κ	relative dielectric constant
μ	mobility
ν	frequency
τ	mean time between collisions
ϕ	phase angle measured in degrees from sine-wave voltage crossing of zero
ψ	potential energy
$\hbar$	Planck's constant divided by 2π

Subscripts:

ac	alternating current
dc	direct current
c	luminescence center
e	excited electron
o	extrapolated to infinite ac voltage

p	hole
pe	primary electron

DESCRIPTION OF EXPERIMENTS

The phosphors used in this study were prepared commercially by using the following procedure. To 35 grams of luminescent-grade (pure) zinc sulfide was added 0.50 mole percent of reagent grade $Cu(C_2H_3O_2)_2$ and one of the following: (a) 1.85 mole percent of NaCl, (b) 3.25 mole percent NaBr, or (c) 0.25 mole percent $Mn(C_2H_3O_2)_2$. The material was mixed and fired in a quartz crucible at approximately 1273° K for 1 hour. After being cooled and crushed, the phosphor was washed in hot distilled water, hot 1.5 percent potassium cyanide solution, and hot water and methanol.

Analysis of the powder by emission spectroscopy showed metal concentrations of 3×10^{19} to 6×10^{19} atoms/cm^3. Quantitative analysis by standard chemical techniques indicated halogen concentrations of 1×10^{19} to 3×10^{19} atoms/cm^3. In addition, X-ray analysis of the crystal structure proved the powder to be hexagonal, as expected from the firing temperature near 1273° K.

Electroluminescent cells (fig. 1) were made in a laminate or sandwich construction with one side being a transparent metal-oxide conductor on a transparent substrate. Particles of the phosphor powder smaller than 13 μm were removed by sieving in order to maximize the phosphor contact with electrode surfaces. A thin layer consisting of a mixture of phosphor powder, silicone rubber varnish, and benzene was sprayed on the conducting side of glass or plexiglass slabs. Measurements of conductivity with metals of different electronic work functions (gold, copper, aluminum) (refs. 9 and 10) and observation with an optical microscope indicate that the phosphor particles are coated and isolated by the silicone varnish. For this study, the maximum mechanical thickness of the active layer, measured with a micrometer, was 50 μm, which is less than 4 particle diameters. For these thin layers, the surface was very irregular because of particles at the surface. Samples much thicker than 50 μm exhibited smoother surfaces and greatly reduced quenching. The results for thin samples are discussed in this report.

The final layer was a vapor-deposited metal electrode, 2 by 3 cm, centered on the active layer. Initial interelectrode leakage resistance was about 1 kilohm for most of the electroluminescent cells which ultimately exhibited quenching. An electrical forming process, which consisted of applying an ac voltage of 25 volts for 1 second, led to interelectrode resistance in the range from 0.4 to 3 megohms. This change is probably due to burnout of pinhole shorts, which seemed to occur in regions between the phosphor particles where the silicone varnish could break down electrically.

Construction characteristics of 11 cells appear in table I. These data cover the range of sample construction which yields similar results. The samples differed in the phosphor, the metal used as the film electrode, cell thickness, and phosphor-to-silicone weight ratio. Since no systematic difference between chlorine- and bromine-coactivated ZnS;Cu was observed, only the results for the phosphor with chlorine are presented.

The electroluminescent cell was excited by a sine-wave voltage, while brightness, ac voltage, alternating current, and direct current were observed and photographed on a four-channel oscilloscope, as shown in figure 2. The dc bias was applied by a low-impedance, variable dc power supply. The photomultiplier had an S-20 response. For average-brightness measurements, a chart recorder was connected in parallel with the photomultiplier load resistor. Electroluminescence emission spectra were obtained by using a 30-inch Fastie-Ebert scanning monochromator between the electroluminescent cell and the photomultiplier.

All measurements were made at room temperature except one — a qualitative experiment to determine the effect of a small change from room temperature upon brightness. This cell was heated on metal film electrode surface with an electrically insulated resistance heater.

RESULTS AND DISCUSSION

The brightness data in this report are in relative units, the measured quantity being current from the photomultiplier. Brightness changes ΔB were determined from the relation $\Delta B = B_{ac+dc} - B_{ac}$. The fractional change in brightness $\Delta B/B_{ac}$ is defined as quenching (q) when negative and as enhancement when positive.

A sketch of the ac voltage and the brightness as a function of phase angle (that is, the brightness wave) is shown in figure 3. For small values of dc voltage, the brightness wave is changed in the manner shown by the curve labeled "Quenched brightness wave." The four peaks of the brightness wave have been marked as primary P_1, P_2 and secondary S_1, S_2. This designation will be used in the subsequent discussion.

Effect of Current

The relationship between direct current and voltage for three electroluminescent cells is shown in figure 4. The weight (or thickness) of the phosphor-silicone layer has been decreased to increase the current for these cells. Quenching was observed only for "thin" cells (those less than 50 μm thick and having an irregular surface). The top and bottom curves in this figure illustrate the data from typical cells. The upper one was chosen from a quenchable, thin cell group, and the lower from a nonquenchable,

thick cell group. The middle curve illustrates the current-voltage characteristics of a cell which exhibited barely discernible quenching when subjected to 20 volts ac and 50 volts dc. (This voltage combination generally led to strong quenching.) The apparent conductivity of this cell at 50 volts was approximately 10^{-12} $(\Omega\text{-cm})^{-1}$.

The cells which exhibited quenching of ac electroluminescence also emitted light under dc stimulation alone. The dependence of current and dc electroluminescence on dc voltage has been plotted in figure 5. The reverse bias corresponds to the dc polarity which led to low current and occurred when the metal film electrode was negative relative to the transparent conductor. Light was emitted for both bias directions, but the relatively high forward current tended to destroy the cell. The intensity of dc electroluminescence is approximately 1 percent of ac electroluminescence intensity at a comparable root-mean-square voltage.

Because quenching occurred only in thin cells which exhibited appreciable conductivity, a qualitative correlation exists between dc quenching of electroluminescence and current. A conductivity limit for quenching appears to be of the order of 10^{-12} $(\Omega\text{-cm})^{-1}$. At the dc voltage used for quenching, very weak dc electroluminescence was observed, with the implication that the direct current interacted with the phosphor particles. Although a more precise correlation between quenching of electroluminescence and current could not be made, the transport of charge through the dielectric to the phosphor appears to be necessary for quenching.

Dependence on ac Voltage

In figure 6, both time-averaged brightness $\overline{B}$ and magnitude of change in brightness $|\Delta\overline{B}|$ for ZnS;Cu,Mn are plotted on a logarithmic scale against $V_{ac}^{-1/2}$. These points can be fitted with straight lines in figure 6, and thus both $\overline{B}$ and $|\Delta\overline{B}|$ are of the form of equation (A24). The difference between the equations for $\overline{B}$ and $|\Delta\overline{B}|$ lies in the values of the constants $\overline{B}_0$ and A. Table I gives the values of $\overline{B}_0$ and A of equation (A24) for ac excitation alone and for ac + dc excitation.

It can be seen in figure 6 that the magnitude of average quenching $|\overline{q}|$ decreased as the ac voltage was increased for a fixed dc voltage. Since the data form a straight line in the figure, this relationship can be described by the equation

$$\overline{q} = \overline{q}_0 \exp\left(mV_{ac}^{-1/2}\right) \tag{1}$$

where $V_{ac}^{-1/2}$ is ac voltage. The parameters $\overline{q}_0$ and m are independent of ac voltage and have the following interpretations: $\overline{q}_0$ is the average quenching when extrapolated to infinite ac voltage, and m is the fractional change in quenching for an incremental change in $V_{ac}^{-1/2}$. A typical value of m is 1.2 volts$^{1/2}$.

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The fractional brightness change is plotted in figure 7 as a function of the phase angle ϕ for several ac voltages (ϕ is defined in fig. 3). The important facts about figure 7 are:

(1) Quenching changes rapidly from zero to some value M, remains approximately constant for about 100°, then returns rapidly to zero again ($q = Mq'(\phi)$ where $q'(\phi)$ is a negative square pulse of unit depth).

(2) The quenching mean value M decreases with increasing ac voltage. It should be noted that quenching is centered on one-half of the brightness wave and not on the peak voltage, as can be seen by comparing figure 7 with figure 3. Therefore, quenching is not due solely to a resistive component of electrical current.

The quenching mean values M are plotted in figure 6. These experimental values can be described by equation (1), which gives the average quenching. The data for M and $|\bar{q}|$ in figure 6 have the same slope (that is, the same value of m). Quenching represented by the M data is about twice as great as that for $|\bar{q}|$ data. This difference occurs because the M data are, in effect, averaged over one brightness wave whereas $\bar{q}$ data are averaged over the two brightness waves which occur in 1 voltage cycle.

For a range of ac voltages which led to an increase of average brightness by a factor of several hundred, the quenching decreased by a factor of less than 10. Compared with $\bar{B}$ and $\Delta\bar{B}$, $\bar{q}$ changes slowly with ac voltage.

Dependance on dc Voltage

Average brightness was found to decrease as the dc voltage was increased up to a voltage which depended upon cell construction. The incremental brightness changes were positive beyond this threshold voltage.

To separate the two modes of average-brightness behavior, fractional changes of the brightness waves were investigated as a function of dc voltage. Figure 8 (which has a change of scale at $\frac{\Delta B}{B_{ac}} = 0$) shows that enhancement of the brightness wave begins at low dc voltage. A cross plot of these data at four phase angles (fig. 9) shows that quenching changes linearly with dc voltage except near phase angles where enhancement competes strongly with quenching. Measurements of the quenching and enhancement (fig. 10) of the brightness peaks (P_2 and S_2 of fig. 3) show that quenching is a linear function of dc voltage. These measurements and those appearing in figure 9 support the following two important generalizations:

(1) Quenching increases linearly with dc voltage over the voltage range in which enhancement does not occur.

(2) Enhancement affects quenching by spreading at moderate dc voltages to the S_2 peak and at higher voltages to the P_2 peak.

Quenching cannot be performed with high dc voltages because both enhancement and dielectric breakdown occur. It appears that dc quenching is *not an efficient means for controlling emitted light power*. When the dc voltage applied to a cell was changed very rapidly (idealized as a step function), a light pulse was observed. The light pulse had about a 0.1-second decay time and was observed whether the ac field was present or absent. This phenomenon is known as the Gudden-Pohl effect. (See ref. 11, pp. 1 and 2.)

Dependence on Frequency

Average brightness was almost a linear function of frequency to 1 kHz. Experiments at a single frequency were performed at 1 kHz to avoid the great nonlinearities which occur at higher frequencies.

Average quenching $\bar{q}$ was found to be independent of frequency from 0.2 kHz to 1 kHz but decreased to 50 percent of its 1-kHz value at 8 kHz. (See fig. 11.) The decrease of the magnitude of average quenching with frequency in the high-frequency range (above 1 kHz) was observed in the same range as the nonlinear dependence of average brightness. The present study has been largely confined to observations at 1 kHz and below. Between 0.2 kHz and 1 kHz, brightness increased by a factor of 5; however, quenching was constant to within about ±6 percent. Quenching of the brightness wave peaks P_2 and S_2 as a function of frequency exhibited this same behavior.

Dependence on Wavelength

Electroluminescence spectra, normalized to unity at 460 nm for pure ac excitation, of blue-emitting ZnS;Cu,Mn phosphor are shown in figure 12. The blue emission can be ascribed to zinc vacancy centers (ref. 3) whereas the yellow emission is from the manganese impurity (ref. 12, p. 59). For pure ac excitation, the intensity of the blue (460 nm) peak measured 2.2 times that of the yellow (580 nm) peak. Application of a dc voltage decreased the intensity of blue emission and increased that of the yellow emission. Thus, one spectral peak exhibited quenching while the other showed enhancement. (See fig. 12.) Visually the ZnS;Cu,Mn luminescence changed from blue to yellow-green as the dc voltage was increased.

These effects could only be observed in cells which exhibited appreciable conductivity. Since the excitation of the manganese ion may be caused by collision of hot electrons with the ion (ref. 13, p. 129), enhancement of the yellow peak constitutes a further indication that current plays some significant role within the phosphor particles.

Electroluminescence spectra of green-emitting ZnS;Cu,Cl phosphor exhibited only a single emission band, which peaked at 500 nm and was 78 nm wide. Application of a dc voltage caused spectrally uniform quenching, that is, $\frac{\Delta B}{Bac}$ was independent of wavelength. No spectral shift was observed. More information on these results can be found in reference 14.

Phenomenological Equations

Quenching depends upon current rather than electric field strength. Evidence for this dependence is provided by the absence of quenching for cells of very low conductivity and the occurrence of dc electroluminescence in cells which exhibit quenching.

The phase distribution of quenching $q'(\phi)$ of a brightness wave is approximately a rectangular pulse of 100° duration. This distribution is centered on the brightness wave and is unsymmetric with respect to the peak voltage. The depth of the quenching pulse, that is, the degree of quenching, depends upon the ac voltage according to the function $\exp\left(mV_{ac}^{-1/2}\right)$. Furthermore, quenching is directly proportional to the dc voltage, and at low frequencies is independent of the frequency. These dependences can be expressed in the phenomenological equations

$$\Delta B(V_{ac},\nu,V_{dc},\phi) = q(V_{ac},V_{dc},\phi)B(V_{ac},\nu,\phi) \tag{2}$$

$$q(V_{ac},V_{dc},\phi) = V_{dc}q'(\phi)M \exp\left(mV_{ac}^{-1/2}\right) \tag{3}$$

Model

A complete model should explain all the previously discussed observations, especially the phase distribution of quenching $q'(\phi)$ and the linear dependence of quenching on dc voltage. Furthermore, some explanation is required for the difference between the behavior of the yellow emission band and that of the blue and green emission bands.

The life history of an electron in electroluminescence can be divided into three processes: (a) excitation, (b) electron motion and energy storage, and (c) recombination (both radiative and nonradiative). In order to perturb the magnitude of radiative recombination, the dc electric field must alter either process (a) or (c). During electron motion and energy storage (b), the electron neither gains nor loses large amounts of energy.

The reduction of luminescence brightness by a direct current which was observed in this study for electroluminescent phosphors is similar to previous observations (refs. 15 and 16) for photoluminescent phosphors. The observation of quenching for phosphors excited by different means implies that the microscopic quenching process results from a modification of the recombination process (c) rather than the excitation process (a).

Equation (B4) in appendix B relates the instantaneous brightness B to microscopic quantities. From the definition for quenching,

$$q \equiv \frac{\Delta B}{B} = \frac{\Delta R}{R} + \frac{\Delta n_c}{n_c} + \frac{\Delta f(n_e)}{f(n_e)} \tag{4}$$

According to this equation, q may be changed by altering the radiative recombination coefficient R, the number of excited luminescence centers n_c, or the number of excited electrons n_e. The coefficient R is proportional (ref. 17, p. 12) to the square of the dipole matrix element and to the cube of the energy of transition. Both the matrix element and the energy may be weak continuous functions of voltage. The phase distribution $q'(\phi)$ implies that the microscopic process is not a continuous function of the instantaneous voltage; thus quenching does not appear to be caused by a change of the radiative recombination coefficient.

Observations of Gudden-Pohl light flashes in the present work and measurements of efficiency of conversion of electrical energy to optical energy by others (e.g., ref. 18) imply that many more electrons are available to gain energy from the field than the number of ionized luminescence centers. On the basis of a specific model, Zalm has estimated the ratio of excited electrons to ionized centers to be about 10:1. (See appendix A.) If Zalm's estimate is reasonably correct, then electroluminescence must be almost independent of the number of excited electrons. Therefore, the electron-density term in equation (4) is eliminated, and the dependence of quenching on the density of excited luminescence centers is implied.

The luminescence center for green emission is thought (ref. 7) to be Cu^+ substituting for Zn^{++} in the lattice. This center has two levels in the lower part of the forbidden band. In the ground state, the center has one electron on a level very close to the valence band and another on a level approximately 1 eV above the valence band. Since the interaction of these electrons with the lattice is large, the energy of these levels changes with the charge on the center. Birman (ref. 19) has calculated that with one electron removed, the lower level rises to approximately 0.5 eV above the valence band and the upper level to 1.5 eV above the band.

Less information is available on the zinc vacancy which is generally believed to produce the center for blue emission. From optical and high-temperature defect chemistry data, Kröger (ref. 20, p. 689) has estimated the energy of the singly charged zinc vacancy level to be 0.5 eV above the valence band. Reference 19 suggests that the center for blue emission is similar to the green emission center but with levels located approximately 0.2 eV closer to the valence band. Therefore, the two levels lie approximately 0.3 and 1.3 eV above the valence band.

Ionization of the green or blue emission centers is identical to the production of a trapped hole. Replacement of the hole by a valence-band electron constitutes nonluminescent deexcitation of a single center. If such a hole is retrapped by an un-ionized center, the number of excited centers remains the same. If the hole recombines nonradiatively with an electron, the number of excited centers and the emission intensity are reduced. Quenching of electroluminescence is viewed as a three-step process: (a) excitation of the holes to the valence band, (b) transport of the holes to the surface, and (c) nonradiative deexcitation.

Several methods seem to be available to raise the hole to the valence band. Two of these methods are excitation by the impact of field-accelerated electrons and by quantum mechanical tunneling in the high-field region of the crystallite. Another method is thermal excitation of the hole from the center to the valence band.

The theory developed by Zalm (ref. 3), which expresses the dependence of impact-ionization probability on ac voltage, should apply as a first approximation to the ac-voltage dependence of hole excitation from the center. Hole excitation is more probable than electron excitation because (1) the ionized center will exert a coulomb attraction on the hot electron and thereby increase the interaction cross section and (2) the energy needed to excite a hole to the valence band is less than that needed to excite an electron to the conduction band.

The probability per unit time of direct-field ionization of a tightly bound carrier to a band has been shown (ref. 13, p. 118) to depend upon the field intensity, carrier binding energy, square well radius, and ratio of carrier effective mass to free mass. For a hole with binding energy of 1.5 eV, center radius of 3 Å, and mass ratio of unity, this development predicts an ionization probability greater than 10^5 during a voltage cycle for a field strength of 10 MV/cm. This field strength corresponds to fields generally thought to exist in the phosphor particle.

At room temperature, holes can be thermally excited to the valence band but are quickly retrapped. The probability of thermal excitation of a hole is about 10^3 sec^{-1}. (In this computation the estimated optical trap depth of 0.5 eV and the lattice interaction frequency of 3×10^{12} sec^{-1} are employed.) At a field frequency of 1 kHz or lower, most holes in the level closest to the valence band will be excited during 1 period. Since only a small fraction of the total number of trapped holes will be in this level, only a small fraction of the excited centers can be deexcited by this mechanism.

Because of the strong total (dc + ac) electric field produced in the barrier region, the trapped-hole distribution will shift toward the negative electrode. This spatial shift of holes can lead to quenching when the total number of excited luminescence centers is diminished by recombination between conduction electrons from outside the phosphor and free holes near the crystal surface.

When luminescence transitions take place entirely within an ion, no free-electron—trapped-hole pair is produced, and thus the proposed mechanism should not lead to quenching. This explanation is in agreement with observation for yellow emission of the phosphor doped with copper-manganese. The enhancement of the yellow peak at a voltage lower than that for enhancement of the blue peak is, at least in part, explainable in terms of the lack of competition between quenching and dc electroluminescence in the manganese ion.

The linear dependence of quenching upon dc voltage may arise in a number of ways. Three of these ways are: (1) If the transport of holes to the surface is the controlling factor for the quenching process, then the voltage dependence may be explained by ohmic conduction (that is, drift velocity proportional to field). (2) Quenching can be explained in terms of a one-carrier space-charge-limited hole current with drift velocity saturated by the high total electric field strength. In this case, hole current is linear with voltage (eq. (C3)). (3) If the transport of holes and the simultaneous transport of electrons through an insulating layer at the surface of the crystal are the controlling factors for the quenching process, then a depletion of holes, linear with voltage, may be explained by a two-carrier space-charge-limited current similar to that discussed by Tredgold (ref. 21, pp. 122 and 123). Available experimental evidence does not permit a choice to be made among the possible mechanisms for the linear dependence of quenching upon voltage. Further study with single crystals should resolve this problem.

CONCLUDING REMARKS

This report shows that quenching, or the reduction of electroluminescence brightness, by a dc voltage is produced by the net flow of current through the phosphor. Quenching occurred only for cells which exhibited electrical conductivity greater than approximately 10^{-12} $(\Omega\text{-cm})^{-1}$. Quenching can be understood in terms of nonradiative deexcitation of luminescence centers by the recombination of electrons at the surface of the phosphor crystallite with holes from the centers.

The fractional reduction in brightness approached zero as the ac voltage was increased, but it increased linearly with increasing dc voltage. Quenching cannot be performed with high dc voltages because both enhancement and dielectric breakdown occur. It appears that dc quenching is not an efficient means for controlling emitted light power.

The time dependence of quenching was approximately that of a square wave, and the magnitude of quenching was found to be independent of ac frequency from 0.2 kHz to 1 kHz.

Spectrally, quenching was uniform for chlorine- and bromine-coactivated phosphors. Quenching for blue emission and enhancement for yellow emission were observed for the

copper-manganese phosphor. Excitation by the impact from a rapidly moving electron has been suggested, but no quantitative correlation with theory has been made. Visually, the ZnS;Cu,Mn luminescence changed from blue to yellow-green as the dc voltage was increased. This effect may have possible use for displays, but further work is necessary to prove its usefulness.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., June 30, 1970.

APPENDIX A

ZALM'S THEORY OF IMPACT IONIZATION

Zalm (ref. 3) has proposed that a Mott-Schottky exhaustion barrier is formed by holes, liberated by excitation somewhere in the crystal, which migrate to the cathode and are trapped at donor sites. This theory of dc electroluminescence, which in principle is easily modified for ac electroluminescence, contains the proposition that electrons from the negative metal electrode tunnel through the barrier. These electrons are field accelerated and can ionize luminescence centers. The electrons thus freed are swept away by the field, but for ac voltage applied to an insulated phosphor particle, the polarized electrons are swept back toward their region of origin. This process gives rise to brightness waves which are delayed with respect to the peak voltage. Zalm's chief contribution to theory was the derivation of the dependence of time-averaged brightness on voltage. His formula agrees with experiment for 7 decades of brightness.

General Characteristics

The idealized experimental situation is a single ZnS crystal with metal electrodes on two opposite faces (fig. 13(a)). (For insulated particles, a conducting inhomogeneity, such as a surface layer of CuS or of copper, is assumed to be the reservoir for electrons needed in the electroluminescence process.) For thermodynamic equilibrium the Fermi levels of the electrodes and the ZnS crystal aline (fig. 13(b)), and a barrier of height H (in electron volts) is formed because of (1) the difference between the work function of the metal and the electron affinity of the insulator and (2) the charged-surface states on the crystal. When a voltage of the indicated polarity is applied, a Mott-Schottky exhaustion barrier is formed at the cathode by the capture of holes by donor impurities. This process leads to a barrier of high field, of thickness l (fig. 13(c)), followed by a region of very low field. Since almost all the applied voltage appears over the distance l (which Zalm estimates to be about 1000 Å), the actual field is enhanced over the average field by about the ratio of crystal thickness to exhaustion-barrier thickness. With the exhaustion barrier formed, electrons in the metal at the Fermi energy may enter the ZnS by tunneling through the barrier of width x_b. These electrons will be accelerated by the field, and some will gain sufficient energy to excite activator centers.

Potential in the Exhaustion Layer

The potential energy ψ of an electron in an exhaustion barrier satisfies Poisson's equation (in one-dimensional geometry)

$$\frac{d^2\psi}{dx^2} = \frac{4\pi Ne^2}{\epsilon} \tag{A1}$$

where ϵ is the dielectric constant and Ne a constant, positive, space-charge density. The boundary condition of equation (A1) at $x = l$ is

$$\frac{d\psi}{dx} = \psi = 0 \tag{A2}$$

Thus all the voltage appears over the barrier and there is no field outside the barrier. At $x = 0$

$$\psi = eV + H \tag{A3}$$

where V is the applied voltage. After integration and evaluation of the constants by using equations (A2) and (A3), the potential energy of an electron in the exhaustion barrier is found to be

$$\psi = \frac{2\pi Ne^2}{\epsilon} (l - x)^2 \tag{A4}$$

The dependence of the exhaustion barrier thickness l on the voltage can be found from equations (A3) and (A4) to be

$$l = \left[\frac{\epsilon(H + eV)}{2\pi Ne^2}\right]^{1/2} \tag{A5}$$

Since $\psi = eV$ for $x = x_b$ equation (A4) yields

$$x_b = l - \left(\frac{eV\epsilon}{2\pi Ne^2}\right)^{1/2} \tag{A6}$$

Transmission Coefficient for Tunneling

Through a Mott-Schottky Barrier

The standard formula for the transmission coefficient T of electrons through a barrier by tunneling is

$$T = \exp\left(-2i \int_0^{x_b} k \, dx\right) \tag{A7}$$

Here k is the (imaginary) wave vector for the electron in the barrier region, the total electron energy is the Fermi energy W_F, and the potential energy is ψ; thus

$$k = \sqrt{\frac{2m^*}{\hbar^2} (W_F - \psi)} = ik_i \tag{A8}$$

where

$$k_i = \sqrt{\frac{2m^*}{\hbar^2} \left(\psi - W_F\right)} \tag{A9}$$

$\hbar$ is Plank's constant divided by 2π, and m^* is the appropriate effective electron mass. From figure 13(c) the energy of an electron at the Fermi level of the negative electrode is eV greater than that of an electron in the positive electrode, thus

$$k_i = \sqrt{\frac{4\pi m^* N e^2}{\hbar^2 \epsilon} \left(l - x\right)^2 - \frac{2m^*}{\hbar^2} eV} \tag{A10}$$

The substitution of ik_i for k in equation (A7) and evaluation of the integral in terms of the barrier constants and eV, instead of l and x_b, lead to

$$T = \exp\left\{-\left(\frac{m^*\epsilon}{\pi\hbar^2 Ne^2}\right)^{1/2} eV\left[\sqrt{\frac{H}{eV}\left(1 + \frac{H}{eV}\right)} - \ln\left(\sqrt{1 + \frac{H}{eV}} + \sqrt{\frac{H}{eV}}\right)\right]\right\} \tag{A11}$$

The transmission coefficient is very low ($\approx 10^{-41}$) for $eV = H = 1$ electron volt, $\epsilon = 10$, and $N = 10^{18}/cm^3$. If eV is greater than about $10H$,

$$T \approx \exp\left[-\left(\frac{4m^*\epsilon}{9\pi\hbar^2 Ne^2}\right)^{1/2} \frac{H^{3/2}}{(eV)^{1/2}}\right] \tag{A12}$$

Thus for an unlimited supply of electrons, the particle current which tunnels through the barrier is

$$j \approx \exp\left(-\frac{C_1}{V^{1/2}}\right) \tag{A13}$$

Dependence of the Number of Excited Centers on Voltage

According to Zalm, the acceleration of electrons in the conduction band of a (relatively) polar material is limited by interaction with vibrations of the lattice. The probability that an electron will gain sufficient energy from the field to ionize activators is

$$p = \exp\left(-\frac{C_2}{F}\right) \tag{A14}$$

in which F is the electric field strength and C_2 is a constant. (Zalm estimated the

magnitude of C_2 to be about 2.3 MV/cm.) For real values of C_2 and F, the probability of electron acceleration to optical energies is appreciably less than unity. With Zalm's value for the constant C_2 and a field equal to 1 MV/cm, the acceleration probability is about 0.10. This probability means that in this inefficient process, only about one electron in 10 gains sufficient energy to ionize an activator.

On the basis of a classical electron gas model, the average drift velocity of an electron of mobility μ in a field F is μF. For a mean time between collisions of τ, in a distance dx an electron will make $\dfrac{dx}{\tau \mu F}$ collisions. Some fraction κ (which is assumed to be independent of energy) of these electrons collide with activator centers and ionize them. The number of these ionized electrons produced by n_e electrons being swept through a distance dx is

$$dn_e = \frac{n_e \kappa}{\tau \mu F}\, dx \, \exp\left(- \frac{C_2}{F}\right) \tag{A15}$$

The total number of secondary electrons and thus the number of ionized activators, due to n_{pe} primary electrons from the electrode, is

$$n_e - n_{pe} = n_{pe} \left\{ \exp\left[H \int_0^{F_{max}} \frac{\exp\left(- \dfrac{C_2}{F}\right)}{F}\, dF \right] - 1 \right\} \tag{A16}$$

where

$$H = \frac{\kappa \epsilon}{4\pi \mu \tau Ne}$$

and the relation between field and position comes from differentiation of equation (A4):

$$F = -\left(\frac{\partial \psi}{\partial x}\right)\frac{1}{e} \tag{A17}$$

Since the electron multiplication in the avalanche is appreciably less than unity, then

$$H \int_0^{F_{max}} \frac{\exp\left(- \dfrac{C_2}{F}\right)}{F}\, dF \ll 1 \tag{A18}$$

and

$$\frac{n_e - n_{pe}}{n_{pe}} \approx H \int_0^{F_{max}} \frac{\exp\left(-\frac{C_2}{F}\right)}{F} dF = H \int_{C_2/F_{max}}^{\infty} \frac{\exp(-y)}{y} dy \qquad (A19)$$

The final integral of equation (A19) is the exponential usually abbreviated $-E_i\left(-\frac{C_2}{F_{max}}\right)$.

The maximum field strength F_{max}, which occurs at $x = 0$, depends upon the applied voltage through equations (A17) and (A3).

$$F_{max} = \left(\frac{8\pi Ne}{\epsilon}\right)^{1/2} V^{1/2} \qquad (A20)$$

Thus equation (A19) becomes

$$\frac{n_e - n_{pe}}{n_{pe}} \approx -H E_i\left(-\frac{C_3}{V^{1/2}}\right) \qquad (A21)$$

Zalm has found that over a wide range, the plot of $\log\left[-E_i\left(-\frac{C_3}{V^{1/2}}\right)\right]$ against $\frac{C_3}{V^{1/2}}$ is a straight line. The equation for the number of ionized activators for each primary electron can therefore be written as

$$\frac{n_e - n_{pe}}{n_{pe}} \propto \exp\left(-\frac{C_3}{V^{1/2}}\right) \qquad (A22)$$

Averaged Brightness

The averaged brightness $\overline{B}$ should be proportional to the average rate at which luminescence centers are being ionized. This rate is the product of the current of primary electrons transmitted through the barrier and the efficiency of these electrons for ionizing centers. From equations (A13) and (A22),

$$\overline{B} \propto \exp\left(-\frac{C_1 + C_3}{V^{1/2}}\right) \qquad (A23)$$

or

$$\overline{B} = \overline{B}_o \exp\left(-\frac{A}{V^{1/2}}\right) \qquad (A24)$$

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APPENDIX B

RADIATIVE RECOMBINATION IN PHOTOCONDUCTING PHOSPHORS

Two types of recombination between electrons and holes have been clearly identified from the kinetics of photoconductivity in chalcogenide phosphors. One process depends upon the square of the electron (or hole) concentration (bimolecular recombination), and the other process is linearly dependent upon the electron (or hole) concentration. The theory for these effects can be presented in simplified form.

For a high-purity semiconductor at 0° K, which is irradiated by light of sufficiently short wavelength, the rate at which electrons are photoexcited into the conduction band is proportional to the absorption coefficient a and the light intensity I_l. If trapping and all indirect means of recombination are neglected, the rate at which the excited electrons and holes recombine is the product of (the average) recombination coefficient R and the probability that an electron and a hole are separated by less than a certain distance. The recombination coefficient is the probability per unit time that a radiative process will occur when the electrons and holes are in the same region of the crystal. The radiative process depends upon the detailed mechanics of the transition. A nonradiative process in competition with the radiative process will result in a lower value of R.

The separation probability can be obtained in the following simple manner: let $d = n_e^{-1/3}$ be the average distance between excited electrons. The probability of finding an electron in a sphere of radius r about some particular hole is

$$p = \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi d^3} = n_e r^3 \tag{B1}$$

The probability (per unit volume) that an electron will be within r of any hole is p times the concentration of holes, which in this case is n_e. If the recombination coefficient R is written to include the distance factor, the rate of change of the excited electrons is

$$\frac{dn_e}{dt} = KaI_l - Rn_e^2 \tag{B2}$$

For equilibrium, $\dfrac{dn_e}{dt} = 0$ and

$$n_e = K' \sqrt{I_l} \tag{B3}$$

Photoconductivity proportional to the square root of the exciting intensity has been observed experimentally.

The bimolecular recombination process should be active if the number of electrons and the number of holes (or ionized activators) are about equal. If one species (e.g., electrons in an n-type semiconductor) is sufficiently more numerous than the other (holes), then the concentration of the first (electrons) will be independent of the concentration of the second (holes). In this case, recombination will depend only upon the concentration of the second species (holes), and a monomolecular recombination process will result.

Both the bimolecular and the monomolecular processes are based on direct transitions by excited electrons. For radiative recombination in zinc sulfide, other less direct processes are possible. A common feature is the dependence on the concentration of ionized centers. Most processes fall between monomolecular and bimolecular recombination. In any case, the rate of change of ionized luminescence centers n_c may be represented, during the period of emission in one part of the crystal, by

$$\frac{dn_c}{dt} = -Rf(n_e)n_c \propto B \tag{B4}$$

where R is the appropriate recombination coefficient and n_e is the concentration of electrons in the locality of the ionized luminescence centers. The function $f(n_e)$ indicates that the detailed process of recombination is not specified.

APPENDIX C

ONE-CARRIER SPACE-CHARGE-LIMITED CURRENT

Space-charge-limited current (SCLC) has been observed in zinc sulfide type materials and is known to be the current limit in photoconductors. In the region of excitation in an electroluminescent phosphor, the positive space charge can be extremely high. A positive current in this region would be space charge limited.

A simplified theory of one-carrier SCLC yields equations which differ from the exact solutions by only a numerical factor. The derivation of the dependence of current on voltage is presented herein for later use.

Two relations form the basis for understanding space-charge-limited currents:

$$Q = en_p = CV \tag{C1}$$

and

$$I = \frac{en_p}{t_p} \tag{C2}$$

where Q is the net charge in a small region, n_p the number of positive holes, e the magnitude of the electronic charge, C the capacitance, V the voltage over the region, I the current, and t_p the transit time for holes. By using the relation $t_p = l/v_p$ where l is the thickness of the barrier region and v_p is the free-hole drift velocity, the current is given by

$$I = v_p C \frac{V}{l} \tag{C3}$$

At sufficiently low fields the drift velocity depends upon the voltage according to the formula $v_p = \mu_p \frac{V}{l}$, where μ_p is the mobility of a free hole, and therefore

$$I = \mu_p C \frac{V^2}{l^2} \tag{C4}$$

At high fields, as observed in the collision-excitation region of a phosphor, the drift velocity may become independent of voltage. In this case, equation (C3) gives the proper dependence of current on voltage.

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TABLE I.– ELECTROLUMINESCENT CELL CHARACTERISTICS

Cell	Cell construction	$\dfrac{\text{Weight phosphor}}{\text{Weight silicone}}$	Film electrode	Cell thickness, micrometers	A, $\text{volts}^{1/2}$	$\overline{B}_0$, relative units	V_{dc}, volts
1	ZnS;Cu,Mn silicone plexiglass	0.26	Au	51	56.8 60.5	2.85 5.49	0 10
2	ZnS;Cu,Mn silicone plexiglass	.26	Au	42	61.0	1.05	0
3	ZnS;Cu,Mn silicone plexiglass	.26	Au	20			
4	ZnS;Cu,Mn silicone plexiglass	.13	Au	28			
5	ZnS;Cu,Mn silicone plexiglass	.41	Au	53			
6	ZnS;Cu,Mn silicone plexiglass	.22	Al	35			
7	ZnS;Cu,Mn silicone plexiglass	.22	Cu	35			
8	ZnS;Cu,Cl silicone glass	0.37	Cu	30	50.0 51.6	45.1 54.4	0 20
9	ZnS;Cu,Cl silicone plexiglass	.18	Au	35	51.6 52.5	24.6 28.8	0 21
10	ZnS;Cu,Cl silicone plexiglass	.13	Au	42	53.2 53.5	21.9 22.0	0 20
11	ZnS;Cu,Br silicone glass	.51	Al				
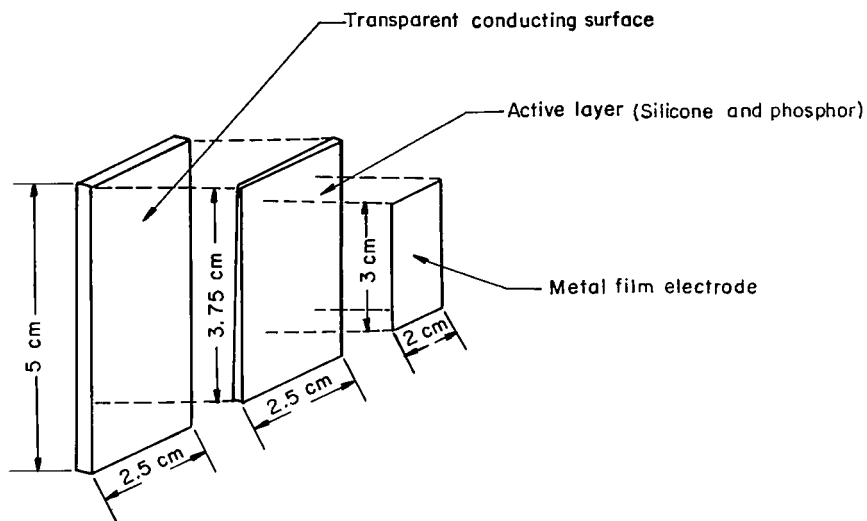
Figure 1.- Exploded view of electroluminescent cell.
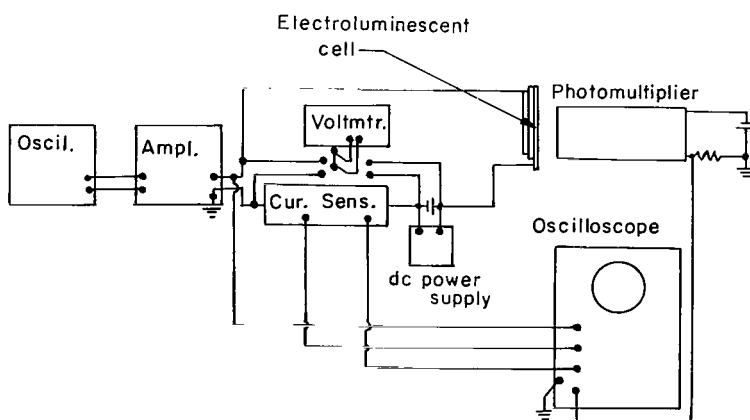
Figure 2.- Diagram of equipment for producing elec-
troluminescence and quenching and for monitoring
brightness waves.
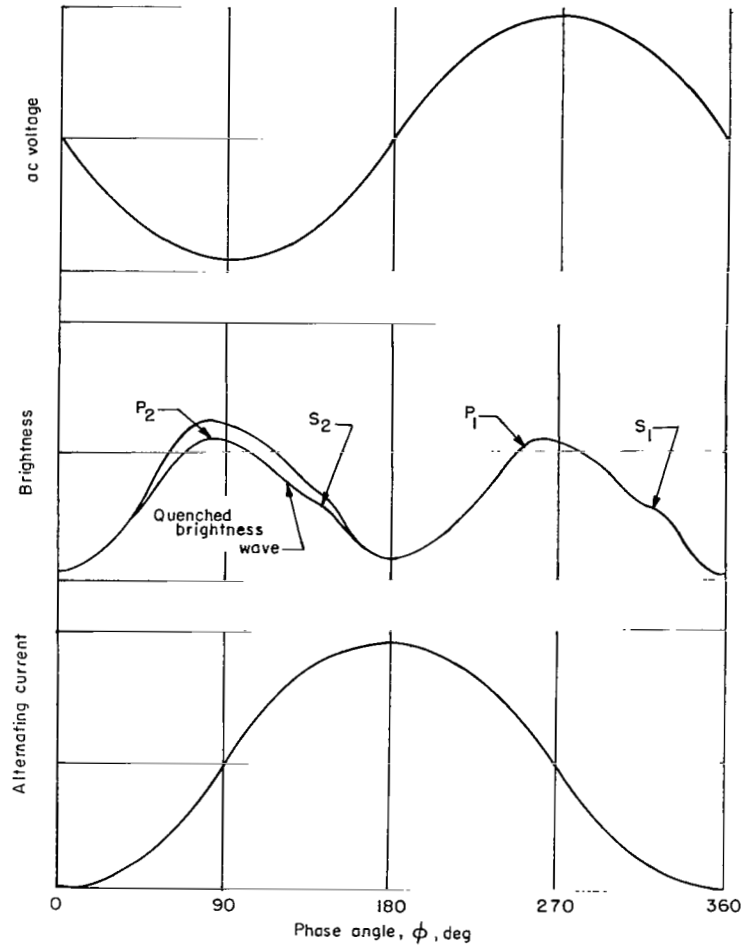
Figure 3.- Drawing of ac voltage, brightness waves, and alternating current as a function of phase angle.
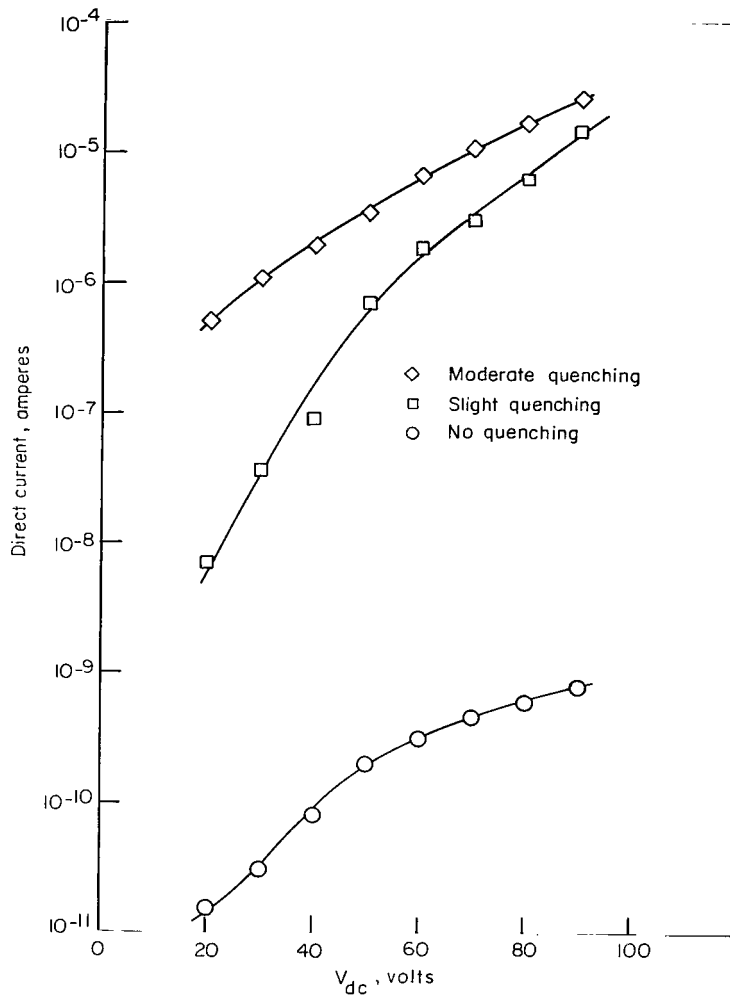
Figure 4.- Relationship between direct current and
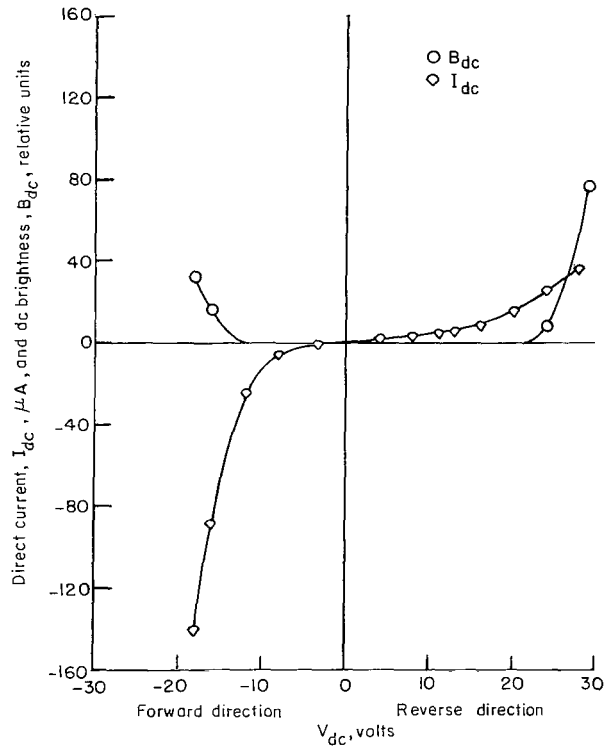voltage for three electroluminescent cells.

Figure 5.- Direct current and dc electrolumi-
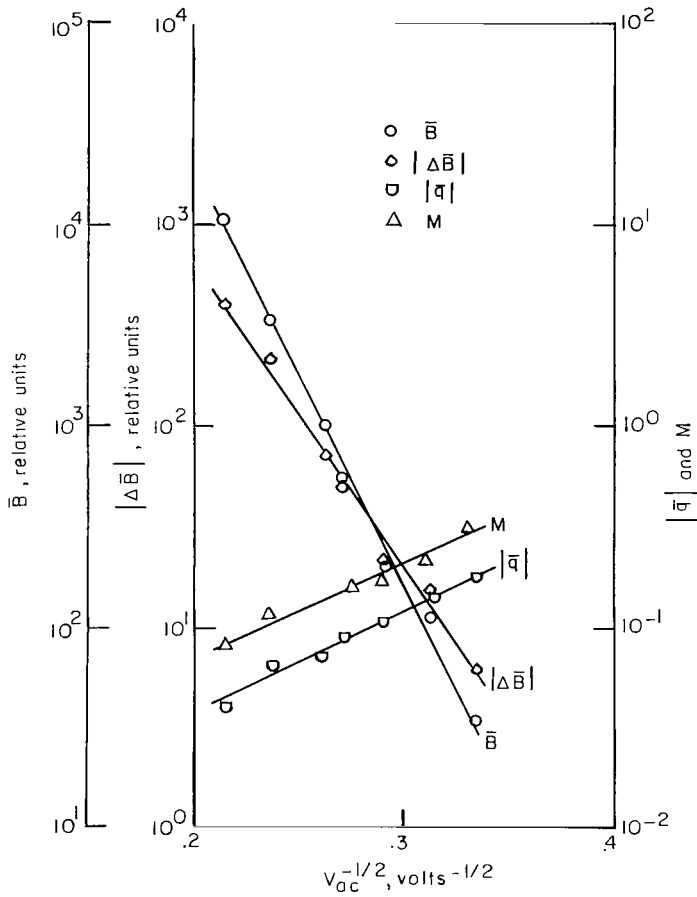nescence for cell 8 as a function of dc
voltage.

Figure 6.- Dependence on ac voltage of averaged brightness $\bar{B}$, magnitude of averaged-brightness change $|\Delta\bar{B}|$, magnitude of average quenching $|\bar{q}|$, and mean value of instantaneous quenching M. Cell 1; 1 kHz; $V_{dc} = 10$ volts.

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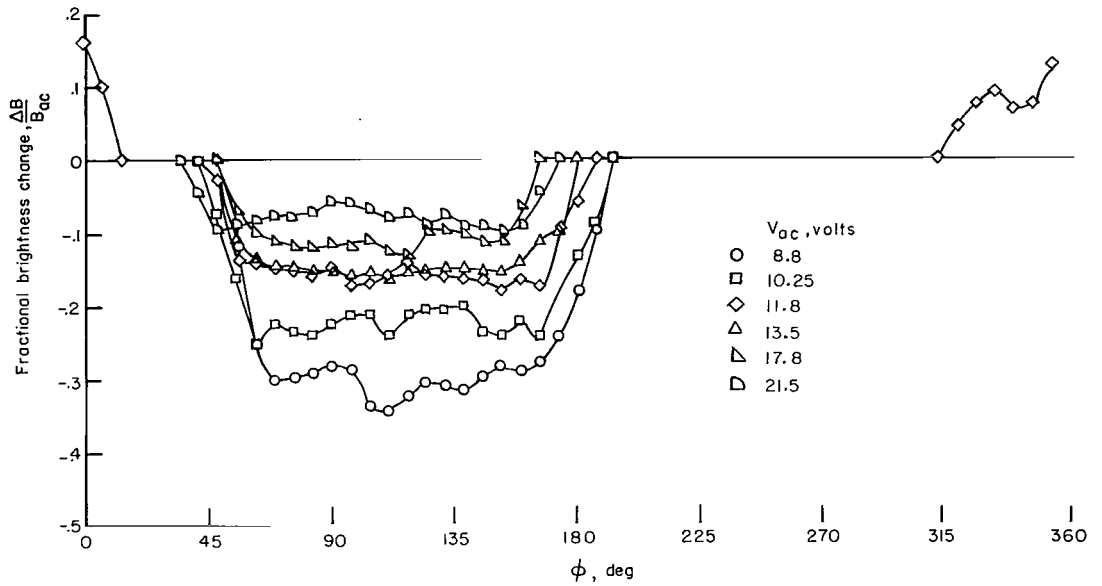
Figure 7.- Phase distribution of quenching for six ac voltages.
Cell 1; 1 kHz; V_{dc} = 10 volts.
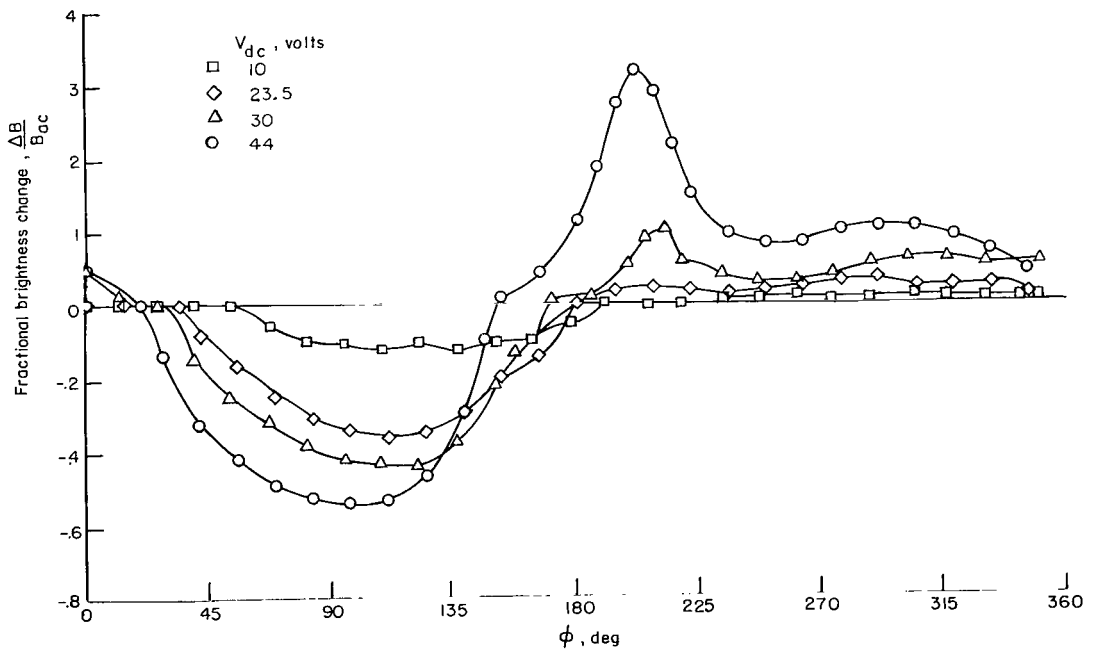
Figure 8.- Quenching and enhancement for four dc voltages. Cell 8; 1 kHz;
V_{ac} = 9.7 volts. (Note different scales for positive and negative
brightness changes.)
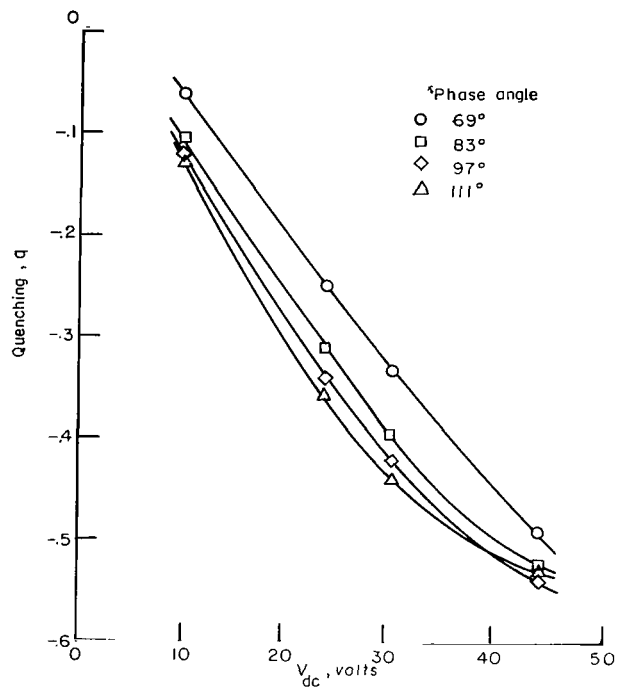
Figure 9.- Quenching at four phase angles as
a function of dc voltage. Cell 8; 1 kHz;
V_{ac} = 9.7 volts.
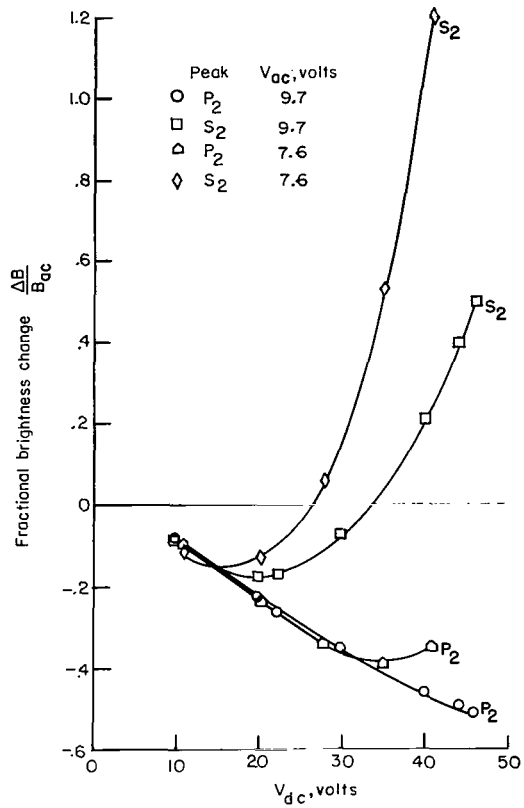
Figure 10.- Fractional changes of two
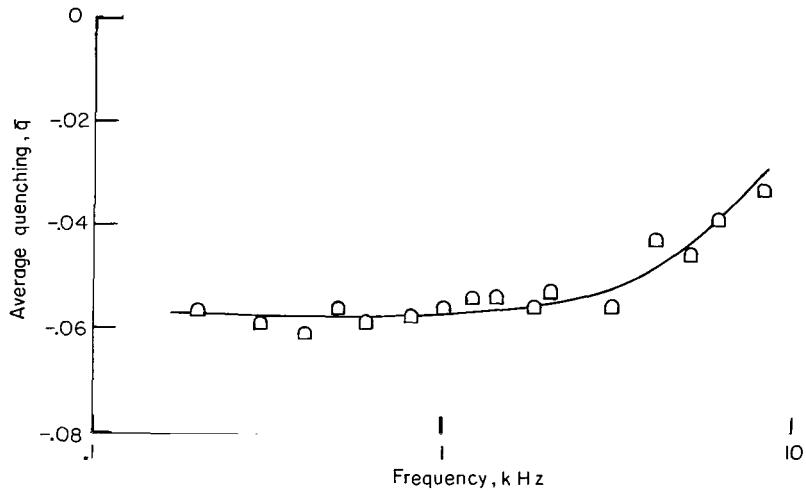brightness-wave peaks with dc voltage.
Cell 8; 1 kHz.

Figure 11.- Frequency dependence of average quenching.
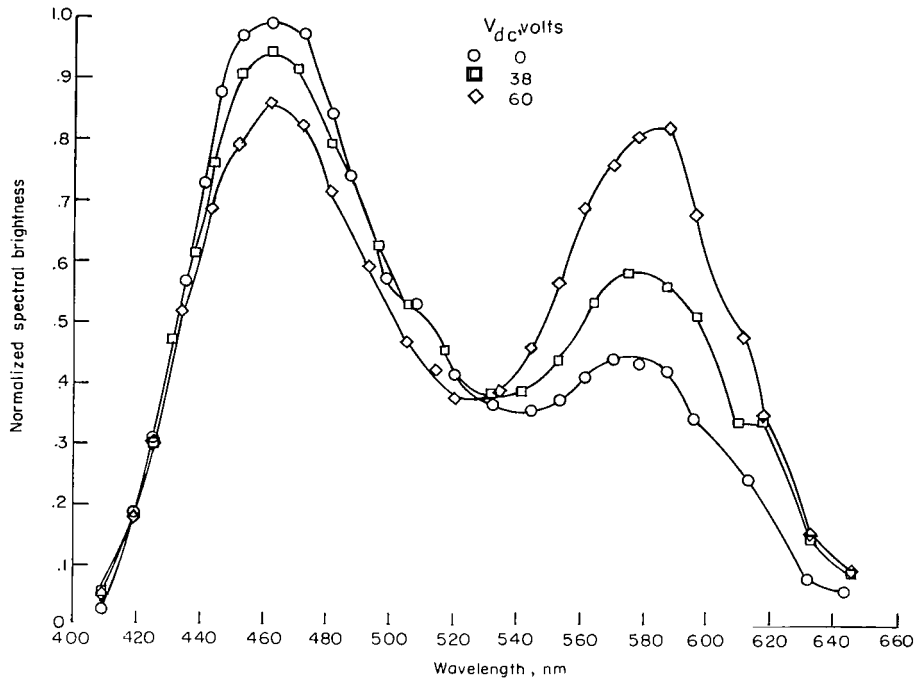Cell 9; V_{ac} = 8.1 volts; V_{dc} = 21 volts.

Figure 12.- Spectral quenching and enhancement of ZnS;Cu,Mn phosphor.
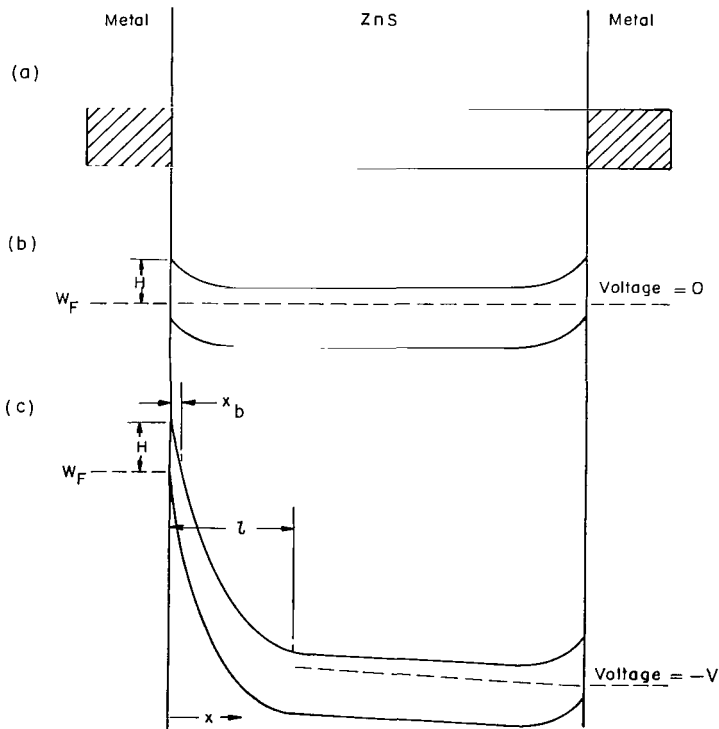Cell 5; 1 kHz; V_{ac} = 60 volts.

Figure 13.- Diagram of contact between metal electrode
and zinc sulfide and exhaustion-barrier formation.

L-5355

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