

and $y=\pi-x$ may be reduced, except for a scaling factor, to an equation (with A as origin):

$$W = \frac{1}{2}(1+W_0) + \frac{1}{2}(1-W_0) \cos r,$$

W_0 being the value of W on the diagonal $y=x$. This serves a good approximation for the other direction. Along AP we have $W_0=5/6$ and $r=(l/\pi) \cos^{-1} \times (12W-11)$, where l is the length of AP . The rectangular part (ratio of sides $AN/AM=\tau$) is then divided into two regions by AP . If the rectangle is reduced to $1/\tau$ along its longer side, we have a square and can make an immediate application of Eq. (3b).¹¹ Thus the distribution function due to the rectangular part

¹¹ The following scheme is somewhat better than that illustrated in the text. By a simple test we find that the ratio $r_1/r_2=\epsilon$ in the neighborhood of A is equal to $\sqrt{5}$. This means that the contour $W \approx 1$ behaves not like a circle but rather like an ellipse. Hence we reduce the rectangle to $1/\epsilon$ along the longer side before applying Eqs. (1) and (3a). Of course, the numerical coefficients are no longer equal to those of Eq. (3b), and they should be evaluated with regards to the different values of ϑ .

may be found from

$$G(W) = \tau \{ a(\bar{r}_1 \bar{r}_1' + r_2 r_2') + b[(\bar{r}_1 \bar{\eta}_{01}' + \bar{r}_1' \bar{\eta}_{01}) + (r_2 \eta_{02}' + r_2' \eta_{02})] + c(\bar{\eta}_{01} \bar{\eta}_{01}' + \eta_{02} \eta_{02}') \},$$

where a, b, c are the numerical coefficients appearing in Eq. (3), and $\bar{r}_1=r_1/\tau$, $\tau_0=\sqrt{2}AM/l$, $\bar{\eta}_{01}=(r_0/\tau_0) - (r_1/\tau)$, $\eta_{02}=(r_0/\tau_0) - r_2$.

The approximate frequency distributions $G_A(W)$ and the exact ones $G_B(W)$ of Bower and Rosenstock are given in Table I and Fig. 2.

The extension of Eq. (1) to a three-dimensional case is straight forward. For example, as shown in Fig. 1(b), the surface of constant frequency below the first critical point (low-frequency part) is approximated by

$$r(W, \vartheta, \varphi) = r_1 + \frac{\sec \vartheta - 1}{\sec \vartheta - 1} (\rho - r_1), \quad \rho = r_2 + \frac{\sec \psi - 1}{\sec \chi - 1} (r_3 - r_2),$$

where $\chi = \tan^{-1}(\sqrt{2}/2)$, and ϑ and ψ are connected with φ by $\tan \vartheta = \sec \varphi$ and $\tan \psi = (1/\sqrt{2}) \tan \varphi$. The result of applying our method to three-dimensional cases will appear later.

Electroluminescence Excited by Short Field Pulses*

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The decay of the light emitted from several electroluminescent phosphors excited by periodically repeated voltage pulses of from 40 to 2500 microseconds duration has been determined. The slopes of the decay curves after each individual pulse excitation become steeper as the pulse duration decreases. The heights of the luminescence peaks excited at the leading and trailing edges of the pulses also depend on the pulse time. The results are interpreted as confirming previous conclusions about the influence of polarization charges. Numerical evaluation yields the correct order of magnitude for the "critical time" needed for the accumulation of polarization charges.

INTRODUCTION

EXCITATION of electroluminescence by square wave fields produces luminescence peaks at field reversals, each peak being followed by a decay of light output.^{1,2} For the green emission band of a Sylvania electroluminescent panel, it was found that this electroluminescence decay is faster than the "natural" decay obtained after steady weak ultraviolet excitation. In the blue band of this panel, however, it is slower than the corresponding natural decay. These and other

results obtained with nonsinusoidal fields were interpreted as being caused by the action of polarization charges that pile up near the surface and reduce the effective field.¹

In order to further test this assumption, phosphors were excited by voltage pulses whose duration could be made sufficiently short so that polarization charges would not accumulate. Furthermore, an attempt will be made to apply the experimental results to recent theories of polarization effects in semiconductors.³

METHOD

Repeated voltage pulses were obtained from two pulse generators and then amplified. The first generator

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¹ S. Nudelman and F. Matossi, *J. Electrochem. Soc.* **101**, 546 (1954).

² Zalm, Diemer, and Klasens, *Philips Research Repts.* **9**, 81 (1954).

³ J. R. McDonald, *Phys. Rev.* **92**, 4 (1953); R. J. Friauf, *J. Chem. Phys.* **22**, 1329 (1954).

produced wide pulses whose duration could be varied down to about 10% of the period (e.g., 500 μ sec at 200 cps), with a rise time of about 150 μ sec. The second generator provided pulses 40 to 75 μ sec wide. Pulses appreciably shorter than 40 μ sec could not be used since the finite rise time interfered. The pulse repetition rate was usually maintained at 200 cps. The potential differences applied were between 300 and 1000 volts.

The light output was observed with a photomultiplier in connection with a direct-coupled oscilloscope. Appropriate filters¹ separated the green and blue emission bands.

The phosphors were used as powdered material embedded in a plastic (parlodium) and subjected to the field in cells of the type described previously.⁴ Different kinds of electroluminescent phosphors were investigated. The results obtained are similar for all of them. Details will, therefore, be reported only for the green Sylvania phosphors, which were studied most extensively in the form of Sylvania Panelect Lamps and as phosphors made according to the method given by Homer *et al.*⁵ The results were essentially independent of the voltage and also independent of whether the pulses were applied unilaterally or by reversing the direction of the field.

RESULTS

Figure 1 shows a selection of oscillograms for the Sylvania phosphors. The difference between the curves for the blue and the green band is quite obvious. The results obtained with the wide pulses have already been reported.¹ The oscillograms for the narrow pulses readily show that the decay has become faster.

A so-called "blue" Sylvania panel with a considerably slower blue natural decay (50% of initial value in about 10 msec) than that of the green Sylvania Lamp (50%

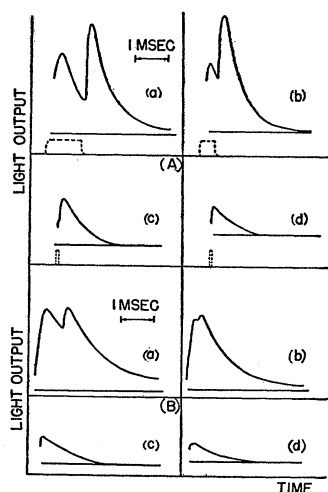


FIG. 1. Oscillograms of luminescence of a Green Sylvania Lamp excited by electric field pulses. (A) Blue luminescence: (a) 1250, (b) 500, (c) 75, (d) 40 μ sec pulse width. (B) Green luminescence: (a) 1000, (b) 500, (c) 75, (d) 40 μ sec pulse width. --- Shape of voltage pulse. The oscillograms show the luminescence intensity versus time in one period of the field. The solid horizontal line represents zero light output.

⁴ F. Matossi and S. Nudelman, *Phys. Rev.* **89**, 660 (1953).

⁵ Homer, Rulon, and Butler, *J. Electrochem. Soc.* **100**, 566 (1953). Details about the phosphors used are described in S. Nudelman's thesis, University of Maryland, 1955 (unpublished).

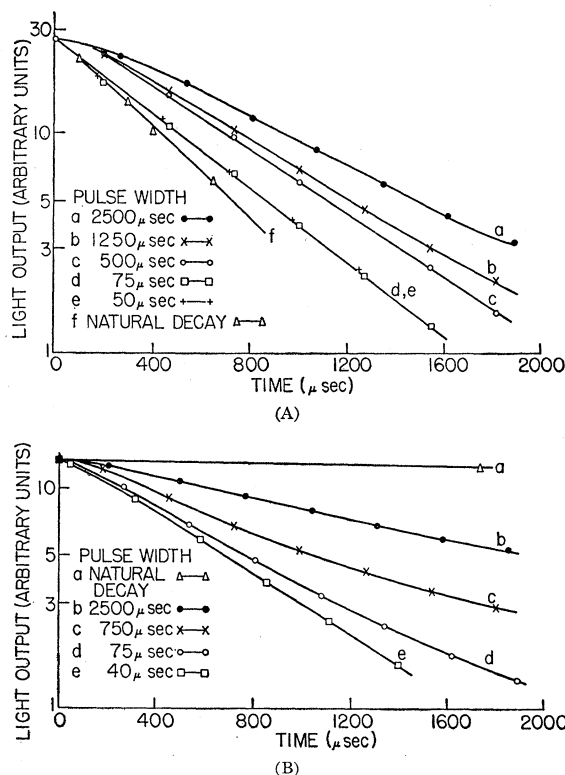


FIG. 2. Decay curves for green Sylvania phosphor. (A) Blue luminescence: (a)–(e) electroluminescence decays for different pulse widths, (f) natural decay. (B) Green luminescence: (a) natural decay, (b)–(e) electroluminescence decays. The decay curves show the decay of intensity after the second peak of Fig. 1. The origin of the time scale is the time of the maximum of the luminescence peak.

in about $\frac{1}{2}$ msec) showed, in the blue region, a pattern resembling the "green" patterns of Fig. 1.

Quantitative details are shown in Fig. 2. With decreasing pulse width, the blue decay becomes more and more rapid, and approaches the natural one shown in curve *f* of Fig. 2(A). The green decay [Fig. 2(B)] also becomes steeper with shorter excitation times and, therefore, deviates in the direction away from the natural decay. With respect to the decay curves, all phosphors behaved qualitatively alike although the natural decays varied appreciably, particularly in the green band.

DISCUSSION

The oscillograms obtained with the wide pulses can be interpreted by considering the decay times of the natural decays and the efficiency of excitation.¹ That indeed the natural decay times are controlling factors could be seen from the behavior of the blue Sylvania panel, which yielded patterns like those of Fig. 1(B) because of similar decay times.

The inspection of the oscillograms of Fig. 1 shows that the first peak, excited by the leading edge of the pulse, has practically disappeared at the very narrow

pulses. This is readily understandable since this peak needs time to grow to its normal height, as can be seen from the oscillograms for the wide pulses. The second peak, however, which corresponds to the trailing edge, should be fully developed. But in the blue band, the second increment of intensity is nevertheless smaller for narrow pulses than for the wide ones. We can understand this on the basis of the behavior of the polarization charges, which need time to pile up near the surface. If they do not have sufficient time to do so, they do not contribute fully to the effective field when the applied field is removed or reversed, and this leads to a smaller increment at the second field reversal. This begins to happen for pulse widths smaller than the "critical time"¹ of about 700 μsec , which, therefore, will be interpreted as the time necessary for piling up the polarization charges. In addition, the finite, albeit small natural decay time of the blue band may, for such small pulse widths, not be large enough for the blue centers to be refilled between field reversals in sufficient numbers. This would also tend to decrease the intensity increment at the second field reversal since a smaller number of centers is available for excitation.

The second peak of the green luminescence is expected¹ to reach the same height as the first as long as the first peak can be developed to its normal height. This is true for the frequencies around 100 cps. But there are deviations at other frequencies. At higher frequencies, the second peak is a little higher, as in Fig. 1(Bb); at lower frequencies, it is a little smaller. This detail is not yet understood.

The green decay time is controlled by the emptying of traps filled during excitation (phosphorescence decay). It can readily be assumed that field excitation will not fill as many traps as ultraviolet excitation, and that the number of traps filled will also decrease with decreasing pulse width. Therefore, the electroluminescence decay will be faster than the natural decay and will become still faster with decreasing pulse width.

The decay of the blue luminescence [Fig. 2(A)] is assumed to be intimately connected with the decay of the internal field since the blue emission band, presumably, does not involve transitions to or from the conduction band or traps. Thus the exciting field and not the filling of traps is the main controlling factor for the blue luminescence of phosphors like the green Sylvania phosphors. In the next section, this relation between electroluminescence decay and field decay shall be discussed in a semiquantitative manner.

DECAY OF THE INTERNAL FIELD

The internal field can be determined from Poisson's equation

$$\partial E/\partial x = \beta(p-n), \quad \beta = 4\pi e/\epsilon, \quad (1)$$

if the charge distribution is known. (Here ϵ is the dielectric constant and x is the space coordinate in the direc-

tion of the field.) This distribution may be obtained from the equations²

$$\begin{aligned} \partial p/\partial t &= -\mu E(\partial p/\partial x) - \mu\beta p(p-n) \\ &\quad + D\partial^2 p/\partial x^2 + \kappa(c_0^2 - pn), \\ \partial n/\partial t &= \mu E(\partial n/\partial x) + \mu\beta n(p-n) \\ &\quad + D\partial^2 n/\partial x^2 + \kappa(c_0^2 - pn), \end{aligned} \quad (2)$$

where p and n are the numbers of holes (or empty centers) and free electrons, respectively; μ is the mobility, D is the diffusion coefficient, both of which are assumed to be equal for holes and electrons, which of course is an approximation only (but other assumptions lead to similar results); E is the field; κ is a transition probability, and c_0 is the number of unexcited centers; the relation $\mu/D = e/kT$ will be assumed to be valid.

These equations adequately describe the influence of polarization charges on capacitance effects in semiconductors,³ and they could also be utilized, with the addition of a term accounting for periodic excitation by a sinusoidal field, for the interpretation of polarization effects on electroluminescence brightness waves.⁶ For the purpose of the present paper, we furthermore assume

$$\partial(p+n)/\partial x = 0, \quad (3a)$$

which is approximately true in the case of sinusoidal fields, as can be inferred from the solutions given by Friauf and McDonald.³ A more restrictive assumption is

$$\partial(p+n)\partial t = 0, \quad (3b)$$

so that $p+n = 2n_0 = \text{const}$. This is not rigorously true, but we may safely assume that a loss of electrons and holes because of recombination may be neglected near the surface and for times short with respect to the duration of the green luminescence, which is controlled by such recombinations, and which is, as is known from the observation of the green natural decay, much longer than the blue decay time.

For $x=0$ and $x=L$ (L =thickness of phosphor particle) at $t=0$, we assume $p=2n_0$, $n=0$ and $n=2n_0$, $p=0$, respectively. The situation described by the above conditions corresponds to polarization charges piled up at the surfaces by the external field. These space charges extend into the interior of the particle with a distribution determined by Eq. (2). If the external field is removed, the charge distribution changes in time according to

$$\partial(p-n)/\partial t = D\partial^2(p-n)/\partial x^2 - 2\mu\beta n_0(p-n). \quad (4)$$

Because of the assumptions (3), the considerations will be restricted to one surface ($x=0$) only. The result is

$$E = 2\beta n_0 \exp(-\rho Dt) \{1 + \cosh[(C-\rho)^{1/2}L]\} / \times (C-\rho)^{1/2} \sinh[(C-\rho)^{1/2}L], \quad (5)$$

where $C = 2\mu\beta n_0/D$, $\rho = \text{const}$.

⁶ F. Matossi, Phys. Rev. **98**, 434 (1955).

The influence of the amount of polarization charges is expressed by the dependence on n_0 . The decay of the intensity can be related to the decay of the field by taking into account the field dependence of the intensity, which can be described, with sufficient accuracy, by the empirically well established relation^{1,7}

$$I = \text{const} E^2 \exp(-b/E), \quad (6)$$

from which

$$\sigma \equiv d \ln I / dt = -\rho D(2+b/E). \quad (7)$$

In order to apply Eq. (7) to the observations, some numerical estimates are necessary. Since the observed slopes are constant over a substantial time range, it must be assumed that E is nearly constant over the same time range, or that $\rho D t$ is sufficiently small. This time range is in the order of 1 msec, which leads to the condition $\rho D \ll 10^8 \text{ sec}^{-1}$. On the other hand, ρD should not be much smaller than 100 sec^{-1} since otherwise the decay should be expected to extend to times larger than 1/100 sec. Further reasonable numerical assumptions ($n_0 \cong 10^{17} \text{ cm}^{-3}$, e.g.) give the order of magnitude of C as $C \cong 10^{13} \text{ cm}^{-2}$. Equation (5) is a useful expression for E only if $C > \rho$. This condition can be satisfied, and it may even be assumed $C \gg \rho$, if D is not too small, say $D \gg 10^{-11} \text{ cm}^2/\text{sec}$. Experimental values for D , are, however, not known.

Applying these numerical estimates, we obtain for the ratio of the slopes for two different amounts of polarization charges,

$$\sigma_1/\sigma_2 = E_2(2E_1+b)/E_1(2E_2+b), \quad (8)$$

where $E \propto n_0^{1/2}$. For very high fields ($E \gg b$), $\sigma_1/\sigma_2 = 1$; for very small fields,

$$\sigma_1/\sigma_2 = E_2/E_1 = (n_{02}/n_{01})^{1/2}. \quad (8a)$$

This ratio is larger than unity if $n_{02} > n_{01}$. Therefore, the slope increases with decreasing amount of polarization charges. It can be shown that the qualitative aspect of this result is not changed by less stringent approximations.

It is possible to utilize Eqs. (8) for a numerical evaluation, if it is assumed that the increase of polarization charges near the surface follows an exponential law like

$$n_0 = \bar{n}_0 [1 - \exp(-at)], \quad (9)$$

⁷ G. Destriau, Phil. Mag. 38, 700 (1947). Other empirical relations, except pure power laws, would not alter the general conclusions.

TABLE I. Slopes of blue decay.

Pulse width (μsec) $-\sigma(10^8 \text{ sec}^{-1})$	50	75	500	1250	2500	natural
	0.836	0.836	0.735	0.634	0.565	1.02

which is equivalent, in our approximation, to

$$E = \bar{E} [1 - \exp(-at)]^{1/2}.$$

From the observed slopes of the blue band, which are given in Table I, the time constant a can be computed.

From $\sigma_{500}/\sigma_{2500}$ and Eq. (8a), we obtain $a = 1.87 \times 10^8 \text{ sec}^{-1}$. Furthermore, σ_{1250} can be calculated as $\sigma_{1250} = 0.60$. The calculated slopes for the very narrow pulses come out much too high, indicating that the natural decay interferes and prevents the observation of the influence of the field decay.

Since, in the experiments, the applied voltage was 320 volts and b could be determined as $b \cong 500$ volts (from the field dependence of intensity), Eq. (8) should have been used instead of Eq. (8a). But then the initial value of E near the surface must be known, which is certainly larger than the average field given by the applied voltage. Under these circumstances, a becomes smaller but the order of magnitude is retained. For $\bar{E} = 2 \langle \bar{E} \rangle_{Av}$, we would obtain $a = 1.3 \times 10^8 \text{ sec}^{-1}$.

The values obtained for a have the correct order of magnitude if we identify $1/a$ with the "critical time" of 700 μsec mentioned in the previous section. The value of a varies somewhat with the selection of the slopes used for the calculation. In part, this variation is the result, of course, of the approximations in the formulas and to the limitations of the experiment, and in part to the disturbing influence of the natural decay.

The qualitative agreement with the observations (steeper slopes with decreasing amount of polarization charges) and the correct order of magnitude of the numerical evaluation may be considered as sufficient indication that the consideration of moving and diffusing polarization charges according to Eqs. (1) and (2) together with Eq. (9) gives an adequate description of the behavior of the internal field.

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