PHYSICAL REVIEW VOLUME 98, NUMBER 2 APRIL 15, 1955

Polarization Effects on the Brightness Waves of Electroluminescence

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(Received December 6, 1954)

Electroluminescence excited by sinusoidal fields yields two maxima per half-period of the field. The intensity ratio of these maxima depends on field frequency and on the superposition of ultraviolet-excited luminescence. These observations are shown to be related to the existence of polarization effects, which are treated theoretically by extending previous theories of polarization effects in semiconductors (Jaffé and others), taking into account periodic excitations of centers by the field.

INTRODUCTION

RECENTLY, several authors presented theoretical treatments of polarization effects in semiconductors.[1,2] These are based on a set of differential equations governing the kinetics of electron and hole distribution under the influence of excitation, recombination, and diffusion processes in the presence of an electric field.[3] This theory was successfully applied to the understanding of some capacitance effects. From observations of electroluminescence excited by nonsinusoidal fields, it could be inferred that polarization effects are important also in electroluminescence.[4] Similar conclusions were presented by Curie[5] in discussing the brightness waves and other features of sinusoidally excited electroluminescence.

It seems proper, therefore, to relate some pertinent results of electroluminescence experiments with the theory of the polarization effects worked out by the aforementioned authors.[1-3] This will be done for sinusoidal fields only. By introducing into the equations of this theory a term that takes into account the periodic excitation of electrons to the conduction band by the periodic electric field, it is possible to describe some characteristic properties of the brightness waves.

OBSERVATIONS

The experimental results discussed are:

(1) In many electroluminescent phosphors (polycrystalline powders embedded in a dielectric) two brightness maxima appear for every half-period of the field. One is essentially in phase with the field, the other is out of phase. The former is called a B-maximum; the latter, a C-maximum, in conformance with the designation of related peaks observed with nonsinusoidal fields.[4] The existence of the C-peaks, which always occur when the external field is diminishing, is assumed to be due to the recombination of polarization charges diffusing back into the interior from the surface where they had been held up by the field; but also the intensity and the shape of the B-peaks is influenced by the polarization charges since these affect the internal field responsible for the electroluminescence processes. This interpretation[4] for the peaks observed in nonsinusoidal fields is considered to be applicable also to the two maxima of the sinusoidal case.

(2) If an electroluminescent phosphor is excited simultaneously by ultraviolet radiation and an electric field that is strong enough to excite electroluminescence without the ultraviolet, the brightness waves show the B-peaks only. The C-peaks appear only after removal of the ultraviolet excitation; however, not at once but only after some time in the order of several minutes. Figure 1 shows the difference of a brightness wave with and without simultaneous ultraviolet excitation.

(3) The ratio of the intensities of the C-peaks to the B-peaks increases with frequency so that the C-peaks at 1000 cps become as large as the B-peaks.

The specific results mentioned under (2) and (3) were obtained[6] with a phosphor prepared in the same manner as the phosphors used in the green Sylvania electroluminescent panel.[7] Similar qualitative results were also obtained with some other phosphors.

THEORETICAL CONSIDERATIONS

The equations governing the charge distribution in semiconductors are given by[1]

$$\begin{aligned} \partial p/\partial t &= k_1 n_c - k_2 np + D_p(\partial^2 p/\partial x^2) - \mu_p[\partial(pE)/\partial x], \\ \partial n/\partial t &= k_1 n_c - k_2 np + D_n(\partial^2 n/\partial x^2) + \mu_n[\partial(nE)/\partial x], \\ \partial n_c/\partial t &= -k_1 n_c + k_2 np, \\ \partial E/\partial x &= 4\pi e(p-n)/\epsilon. \end{aligned} \tag{1}$$

These equations describe the time rate of change of the number (per unit volume) of electrons (n) and holes (p). They take into account excitation of luminescence centers ($k_1 n_c$, where n_c= number of unexcited centers); recombination ($k_2 np$); diffusion (D_p, D_n= diffusion coefficients for holes and electrons, respectively); motion under the influence of an electric field E obeying Poisson's equation (μ_p, μ_n= mobilities, ϵ= dielectric constant, e= electronic charge). Transi-

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[1] J. R. MacDonald, Phys. Rev. **92**, 4 (1953).

[2] R. J. Friauf, J. Chem. Phys. **22**, 1329 (1954).

[3] G. Jaffé, Ann. Physik **16**, 217, 249 (1933); Phys. Rev. **85**, 354 (1952).

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

[5] D. Curie, J. phys. radium **14**, 510, 672 (1953).

[6] S. Nudelman (private communication).

[7] Homer, Rulon, and Butler, J. Electrochem. Soc. **100**, 566 (1953).

tions to traps are not included. These are not important in electroluminescence, as indicated by the much faster decay with field excitation compared to that with ultraviolet excitation of the green luminescence band.[4]

The equations can be solved approximatively for sinusoidal voltages $V=\int Edx=V_1\exp(i\omega t)$ by writing for n, p, n_c, and E expressions of the form[1]

$$n(x,t)=n_0(x)+n_1(x)\exp(i\omega t) \tag{2}$$

and neglecting terms with higher powers of $\exp(i\omega t)$. Furthermore, it is assumed

$$n_0=p_0=c_0, \tag{3}$$

which implies $E_0=0$, $(n_c)_0=N-c_0$, where $N=$ total number of centers.

These assumptions restrict somewhat the applicability of the equations. This is discussed in detail by MacDonald.[1] The restrictions do not affect, however, the general features of the solutions as long as these are essentially determined by n_1, p_1, $(n_c)_1$, E_1. The changes in time will be described with sufficient approximation even if correct solutions for equilibrium may not be obtained. The assumption of bimolecular recombinations is also an approximation, which is usual in considerations of this type. It is justified in cases of continuous excitation, as is the case in electroluminescence, even if other processes should prevail.[8] Thus, increased qualitative insight is expected in applying the equations to electroluminescence effects even if it may not be possible to use the final formulas for quantitatively exact evaluation.

The general solution of (1) is then given by

$$\begin{aligned} n_1&=A^+\sinh[\rho^+(x-L/2)]+A^-\sinh[\rho^-(x-L/2)],\\ p_1&=B^+\sinh[\rho^+(x-L/2)]+B^-\sinh[\rho^-(x-L/2)],\end{aligned} \tag{4}$$

where L is the thickness of semiconductor layer; ρ^+ and ρ^- are given by the coefficients of the differential equations for p_1 and n_1, and the ratios of the constants A^+, etc., can be determined from the boundary conditions, for which the condition is accepted that charges cannot flow across the surfaces of the phosphor particles.

For the application to electroluminescence, a term which describes the effect of excitation of centers by the periodic field is added to the terms considered in Eq. (1). If k_1 is replaced by

$$k_1=k_0+k'\exp(i\omega t), \tag{5}$$

the equations for p_1 and n_1 can be written, after some elementary calculations, in the form

$$\begin{aligned} i\omega p_1=(k_0\lambda-k_2c_0)(p_1+n_1)&\\ +D_p\partial^2p_1/\partial x^2-\mu_pc_0\beta(p_1-n_1)&\\ +k'[N-c_0+k_0\lambda(c_0-N)/k_2c_0]&,\\ i\omega n_1=(k_0\lambda-k_2c_0)(p_1+n_1)&\\ +D_n\partial^2n_1/\partial x^2+\mu_nc_0\beta(p_1-n_1)&\\ +k'[N-c_0+k_0\lambda(c_0-N)/k_2c_0]&,\\ \lambda=k_2c_0/(k_0+i\omega),\quad \beta=4\pi e/\epsilon.& \end{aligned} \tag{6}$$

The last term can be simplified by assuming weak excitation so that $N\gg c_0$.

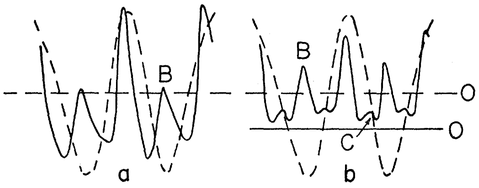

FIG. 1. Brightness waves, 60 cps. *a*: with, *b*: without ultraviolet. ——— Light output, – – – – field. The zero level of light output in *a* is far below the lower edge of the figure (superposition of ultraviolet excited steady output). The units of light output are different for *a* and *b*.

Equation (5) separates a steady excitation from a periodic one. k_0 is interpreted as describing excitation by ultraviolet radiation, and k', as the contribution of the field to excitation. Since the field is described by $E_1\exp(i\omega t)$, all the effects related to the field have the period 2π, too, and also zero average values. However, the observed electroluminescence effects are, of course, always positive and have, furthermore, the period π, since a negative field has the same effect as a positive one. This purely formal difference is a consequence of the aforementioned assumptions and is not essential to the following considerations, since only the changes produced by the field are of interest. The frequency of the effective field, which is twice the frequency of the external field, will therefore be considered as the frequency ω of the equations, notwithstanding the fact that some phosphor particles or parts of them may emit only in the one half-period and not in the other one.[9] This is due to special conditions at the surface of the particles which restrict the actions of the effective field essentially to the one half-period. This need not be considered in the mathematical formalism.

Equation (5) furthermore assumes that the excitation follows the field. This implies that E must be understood as the internal field in the phosphor particle, not as the applied field. Any phase shifts considered here are, therefore, measured relative to this internal field, which itself may be shifted with respect to the applied field. The internal field can be obtained from the last Eq. (1).

The calculations can be substantially simplified by assuming $\mu_p=\mu_n$ and $D_p=D_n$, although $\mu_p\neq\mu_n$ would probably be a more realistic description of the properties of the phosphor particles. The general rules will not be affected by this simplification, so that only the case of equal mobilities will be treated.

For $\mu_p=\mu_n=\mu$, $D_p=D_n=D$, we have

$$\begin{aligned} \partial^2(p_1-n_1)/\partial x^2&=a(p_1-n_1),\\ \partial^2(p_1+n_1)/\partial x^2&=b(p_1+n_1)+c, \end{aligned} \tag{7}$$

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[8] D. Curie, Ann. phys. **7**, 746 (1952).

[9] J. F. Waymouth, Phys. Rev. **95**, 941 (1954).

with

$$aD = 2\mu c_0\beta + i\omega, \quad bD = 2k_2c_0 - 2k_0\lambda + i\omega,$$
$$cD = 2k'N(\omega^2 + ik_0\omega)/(k_0^2 + \omega^2).$$

The solutions are

$$p_1 = p_{10} - c/2b, \quad n_1 = n_{10} - c/2b, \tag{8}$$

where p_{10} and n_{10} are the solutions of Eq. (7) for $k'=0$ or $c=0$, i.e.,

$$p_{10} = -n_{10} = A \sinh\alpha(x - L/2) \tag{9}$$

with $\alpha = 2(\mu c_0\beta/2D)^{\frac{1}{2}}(u+iv)$; $u^2,\ v^2 = \frac{1}{2}[(1+\omega^2/4\mu^2c_0^2\beta^2)^{\frac{1}{2}} \pm 1]$.

The intensity is given by

$$I = \text{const}\,pn$$
$$= \text{const}[c_0^2 + c_0(p_1+n_1)\exp(i\omega t) + p_1n_1\exp(2i\omega t)],$$

which can be written, because of Eqs. (8) and (9), as

$$I = \text{const}[c_0^2 - c_0(c/b)\exp(i\omega t) - (p_{10}^2 - c^2/4b^2)\exp(2i\omega t)]. \tag{10}$$

We write

$$-c/b = \sigma + i\tau, \quad p_{10}^2 = \xi + i\eta,$$

where

$$\sigma = (1/M)2k'N(2k_2c_0 + k_0), \quad \tau = -(1/M)2k'N\omega,$$
$$M = 4k_2^2c_0^2 + 4k_0k_2c_0 + k_0^2 + \omega^2. \tag{11}$$

ξ and η can be determined from Eq. (9). In order to eliminate the dependence on x, an average value $\langle p_{10}^2\rangle_{\text{Av}}$ may be used. The exact expressions for ξ and η are not important. It is sufficient to know that ξ and η grow with frequency.

Equation (10) can be interpreted as representing a brightness wave with two components U and V of periods 2π and π, respectively, superimposed on a constant background. It is

$$U = c_0(\sigma^2+\tau^2)^{\frac{1}{2}}\exp(i\omega t) = U_0\exp(i\omega t),$$

$$V = \left[\left(\frac{\sigma^2-\tau^2}{4} - \xi\right)^2 + \left(\frac{\sigma\tau}{2} - \eta\right)^2\right]^{\frac{1}{2}}\exp(2i\omega t)$$
$$= V_0\exp(2i\omega t). \tag{12}$$

These components have phase shifts against $\exp(i\omega t)$ or $\exp(2i\omega t)$, φ_U and φ_V, given by

$$\tan\varphi_U = -\tau/\sigma = \omega/(2k_2c_0 + k_0),$$

$$\tan\varphi_V = \left(\eta - \frac{\sigma\tau}{2}\right)\Big/\left(\frac{\sigma^2-\tau^2}{4} - \xi\right). \tag{13}$$

If ξ and η can be neglected, i.e., for very low frequencies and very weak excitation, we have

$$\varphi_V = 2\varphi_U \quad \text{and} \quad V_0 = U_0^2/c_0.$$

In this case, the superposition of the two components leads to two maxima coinciding with the maxima and minima of the U-component.

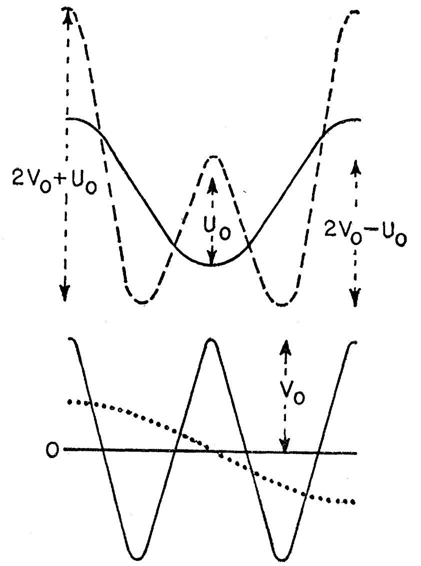

FIG. 2. Components of brightness waves. —— U and V. - - - - Superposition of U and V. ···· Applied field. The minimum of $U+V$ is not exactly at the place of the minimum of V; this is neglected in Eq. (14).

As can be seen from Fig. 2, the heights of these maxima are approximately given by $I_B = 2V_0 + U_0$, $I_C = 2V_0 - U_0$, respectively, so that the ratio of the intensities is

$$\rho = I_C/I_B = (2V_0 - U_0)/(2V_0 + U_0). \tag{14}$$

If ξ and η cannot be neglected, so that $\varphi_V \neq 2\varphi_U$, Eq. (14) should be modified, but, even as it stands, it provides a reasonable approximation also in the more general case. In Fig. 2, we have assumed $2V_0 > U_0$, which will be true for sufficiently weak excitation.

DISCUSSION

Because of the very complicated dependence of ρ on the parameters ω, c_0, k_0, k', k_2, μ of the problem, only a very general discussion can be given; but this is sufficient for the purpose of a qualitative comparison with the observations.

I_B and I_C are identified with the observed B- and C-peaks. It is easily seen that $U_0/2V_0$ becomes smaller with increasing frequency as soon as the contribution of the ξ and η terms becomes appreciable; that is, for not too low frequencies (if ω is not small compared to $\mu c_0\beta$). Therefore, the observed increase of the C-peaks with respect to the B-peaks can be expected since ρ tends to unity if $U_0/2V_0$ becomes zero. Low mobilities and weak excitation are essential for the observation of this phenomenon. Although numerical values are not available, this conclusion seems to be compatible with the general experience.

If k_0 increases, $U_0/2V_0$ increases too. This is obvious for the case of small values of ξ and η, but it will be true also for higher values because the dependence on

k_0 is contained only in σ and τ. Therefore, ρ becomes smaller, indicating that steady excitation by ultraviolet suppresses the C-peak.

Since this result has been obtained in a rather involved manner, a nonmathematical consideration may make it more plausible. Without ultraviolet, two processes superpose. One is the excitation of electrons by the field and their subsequent recombination (B-peaks). The other is movement of electrons under the influence of the field producing inhomogeneous distribution of charges. When and if these charges diffuse back, they too may recombine (C-peaks). Ultraviolet radiation increases the number of electrons excited to the conduction band, which tends to decrease the charge inhomogeneity and, therefore, decreases the chance of recombination through back diffusion. The fact that the C-peaks recover only slowly after cutting off the ultraviolet excitation may, then, be interpreted as indicating that the electrons produced by the ultraviolet radiation disappear only gradually so that the case of a pure polarization effect is attained only after some time. That these electrons disappear more slowly than would be expected from the decay of ultraviolet excited phosphorescence, may be understood by the consideration that the field has displaced the electrons from the centers so that recombination is more difficult.

The case of absence of polarization charges may be studied by considering Eq. (1) again, but for $\mu=0$, $D=0$. This condition prevents the piling up of charges. Then the equations reduce to

$$\partial p/\partial t=\partial n/\partial t=[k_0+k' \exp(i\omega t)]N-k_2p^2, \qquad (15)$$

if again weak excitation is assumed. This is an equation of Mathieu's type, which admits periodic solutions only for particular values of the parameters.[10] Although this equation may, therefore, not be useful for the stationary state, it can be used for the nonstationary state in the first instants after the application of the field, when polarization has not yet come into play. It is convenient to modify Eq. (15) slightly by writing, for $k_0=0$,

$$\partial p/\partial t=k' \cos^2\omega t-k_2p^2.$$

$\cos^2\omega t$ is an approximation for $|\cos\omega t|$. This takes into account the equivalence of positive and negative fields. A possible solution is

$$I=(\omega^2/k_2)(\zeta+\phi'/\phi)^2 \tanh^2\zeta\omega t, \qquad (16)$$

where ϕ is a periodic function with the period π and the properties $\phi(-x)=\phi(x)$, $\phi(-x)'=-\phi(x)'$ or $\phi(-x)=-\phi(x)$, $\phi(-x)'=\phi(x)'$; $\phi(x)'=d\phi(x)/dx$, $x=\omega t$. ζ is a parameter, approximatively given by $\zeta^2=k_2k'/2\omega^2$. This represents a periodic ripple with increasing amplitude superimposed on a steady rise of average intensity. This corresponds well to observations.[11]

For long times, Eq. (16) describes, of course, a periodic behavior of the brightness waves, but specific statements about phases or number of maxima cannot be made. In any case, the general theory of Mathieu's equation permits only one linearly independent periodic solution if there is one at all.

Finally, it may be pointed out that the phase shifts indicated by Eq. (13) cannot be observed directly since additional frequency-dependent phase shifts may occur that are also due to polarization effects, viz., to the phase shift of the internal field with respect to the applied field. For the problem of this paper, these phase shifts are irrelevant. It shall only be mentioned that the expression for the phase shift of the fields derived from Eqs. (1) and (9) is different from that given by Destriau and Curie[5] who take into account only the continuity of charge flow and the Poisson equation.

There are still other phase shifts observed[6] if small fields are applied to ultraviolet excited electroluminescent phosphors. An extinguishing effect is obtained, and the brightness waves are shifted in the opposite direction than in the case of high fields. This effect is due to changes in the number of available electrons, not to moving polarization charges, and is controlled by the lifetime of the electrons in the conduction band.[5]

CONCLUSION

The foregoing considerations sufficiently indicate that the processes occurring in semiconductors as inferred from capacitance effects are also responsible for electroluminescence effects. Moving polarization charges are essential for the description of the observed characteristic details of brightness waves.

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[10] E. T. Whittaker and G. N. Watson, *Modern Analysis* (University Press, Cambridge, 1927); L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946).

[11] F. Vigean, Compt. rend. **236**, 1151 (1953).