SUMMARY

Magnetization data have been obtained for two manganous salts. Analyses of these data for manganous chloride tetrahydrate and manganous bromide tetrahydrate have been carried out by (1) plotting magnetic moments against H/T and observing nonsuperposition of magnetic moment isotherms, (2) construction of Brillouin curves from the saturation magnetization and determining graphically the departures of the moments from the Brillouin moments; from these departures, we obtain molecular fields, Van Vleck antiferromagnetic exchange coefficients and exchange energy densities, (3) plotting magnetic moments against temperature for fixed fields and determining geometrically the transition temperatures corresponding to these fields; this leads to antiferromagnetic transition boundary curves which separate the regions of spontaneous antiparallel alignment from the paramagnetic regions and, (4) subjecting the Van Vleck model for simple antiferromagnetics to critical examination which consisted in plotting magnetic moment against the Van Vleck parameter, $(H_0-\gamma M)/T$; this showed that the model for simple antiferromagnetics gives a quantitative evaluation of the magnetic moment for the group of points in the H-T plane which lie outside the antiferromagnetic transition boundary.

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Interpretation of Electroluminescence Effects in an Excited Phosphor*

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The consideration of electron transitions between valence band, conduction band, and traps as presented by Randall and Wilkins' theory of luminescence growth is extended by including terms which take into account the emptying of traps by an electric field and the draining off of electrons by field-induced, nonradiative transitions. The result of the mathematical analysis corresponds to effects observed in a ZnS phosphor, embedded in a dielectric matrix, under the influence of a periodic electric field while continuously excited by ultraviolet radiation. These are a momentary illumination, an extinguishing effect, and the superposition of a ripple with twice the frequency of the field, whose amplitude decreases with increasing frequency. Some further observations are discussed qualitatively, utilizing the following assumptions: the draining effect ceases after some time; at low frequencies and for dc fields, a current effect counteracts the draining effect.

INTRODUCTION

THE influence of an electric field on luminescence can be expected to reveal fundamental properties of phosphors. However, in spite of much experimental research in this field, or rather because of the abundance of complex results, the understanding of these processes is still very limited. The present paper attempts a theoretical approach to one particular electroluminescence effect, the change of light output of a continuously excited phosphor by alternating electric fields.

The observations referred to may be briefly summarized as follows:[1] A ZnS(Cu) phosphor, embedded in a dielectric matrix and excited to equilibrium output, is subjected to a sinusoidal electric field while the excitation continues. Then a momentary illumination ("electrically stimulated luminescence" = electric stimulation) is followed by an extinguishing effect ("electric quenching"). After this, the light output recovers slowly to a new equilibrium ("intermediate recovery"). Cutting the field off may stimulate a second momentary illumination ("cut-off stimulation"), after which the original equilibrium is finally attained again ("final recovery").

The essential features of the observations are schematically illustrated in Fig. 1 and Fig. 2. The large time scale of Fig. 2 reveals the superposition, upon the "basic effect" of Fig. 1, of a periodic "ripple" whose frequency is twice the frequency of the field. The amplitude of this ripple decreases with increasing

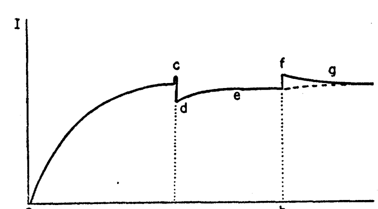

Fig. 1. Basic effect, schematical. I = luminescent output; t = time (in order of minutes); a: field on; b: field off; 0: ultraviolet on; c: electric stimulation; d: electric quenching; e: intermediate recovery; f: cut-off stimulation; g: final recovery at high (———) and at low (-----) frequencies.

* Presented at the Rochester Meeting of the American Physical Society, June, 1953 [Phys. Rev. **92**, 846 (1953)]. A preliminary account appeared in Naturwiss **40**, 239 (1953).

[1] G. Destriau and J. Mattler, J. phys. et radium **11**, 529 (1950); F. Matossi and S. Nudelman, Phys. Rev. **89**, 660 (1953). Similar results for decaying phosphors are reported by K. W. Olson, Phys. Rev. **92**, 1323 (1953).

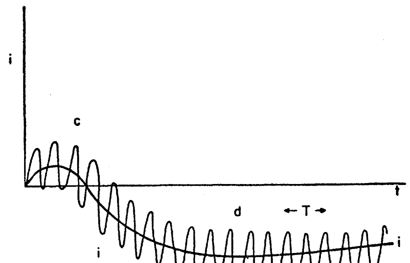

FIG. 2. Region c and d of Fig. 1 in large time scale. Ripple superimposed on basic effect, schematical. $T=2\pi/\omega$, ω = frequency of field.

frequency at high frequencies. At low frequencies (ω about 200 cps), the amplitude reaches a maximum.

The time for reaching the peak of the electric stimulation is of the order of magnitude of a few periods of the field. It decreases, therefore, with increasing frequency. The minimum is reached very slowly compared to the time for the peak, but fast compared to the time of the intermediate recovery, which is of the order of magnitude of the growth time of the phosphor.

Phase shifts between field and ripple have not yet been measured, but observations with a decaying phosphor[2] seem to indicate that phase shifts exist and that they depend on frequency.

At low frequencies, up to several hundreds of cps, some of the results may have been influenced by "polarization effects" since dc experiments showed that a dc field ceases to be effective after about 1/100 of a second. No quenching was observed in a dc field.

It may be pointed out that the qualitative features of the above described observations seem to be a quite general property of ZnS and related phosphors. (Our own experiments refer to a DuPont ZnS-phosphor No. 1300 prepared as described previously[1] and excited by a dc ultraviolet source.) Only the quantitative details vary from sample to sample. This is in particular so for the effects at field removal, while for "field on" the observations of different investigators with different substances agree very well. For phosphors of short persistence, the stimulation effects are not observed, but only quenching.[3] Phosphors of very low conductivity do not show the quenching, but only Gudden-Pohl flashes.[4] The chemical composition of most of the phosphors used is not known exactly. But the interpretation presented here is independent of any specific contents of impurities.

The observations shall be related to the band model of sulfide phosphors. Because of the empirical relationship between the intermediate recovery and the growth curve, the theory of the growth curve, as given by Randall and Wilkins[5] seemed to be a reasonable starting point of a theoretical analysis.

BASIC ASSUMPTIONS

As usual, the properties of the phosphor will be described by the distribution of electrons among the filled or valence band, the conducting band, and the traps. The electrons are excited by external radiation from emission centers in the valence band. For the purpose of this analysis, it is not necessary to consider separate impurity levels near the valence band.

The number of electrons in the conduction band may be designated by N; the number of traps, which is considered to be constant, by n; and the number of empty emission centers, by m. All these numbers refer to unit volume. Then the following equations govern the number of electrons in the conduction band and the number of empty traps $(n-m+N)$:

$$\begin{aligned} dN/dt &= \eta - A_1Nm - A_2N(n-m+N), \\ d(n-m+N)/dt &= -d(m-N)/dt \\ &= -A_2N(n-m+N). \end{aligned} \tag{1}$$

These equations are essentially identical with those of Randall and Wilkins.[5] A_1 and A_2 are two constants of the nature of transition probabilities, which, according to Randall and Wilkins, are of the same order of magnitude. η is the number of electrons transferred per unit time to the conduction band by the exciting energy. The equations take into account the spontaneous transitions from the conduction band to the valence band or to the traps, assuming a "bimolecular" type of recombination.[6] But spontaneous (thermal) transitions from the traps to the conduction band are not included. Their explicit consideration is not necessary here, since we are not interested in temperature effects. With Randall and Wilkins, we assume N to be small compared with n and m, and the total number of centers to be larger than the number of traps. Equilibrium is reached if $m=n$.

The electric field disturbs this equilibrium. It seems to be reasonable to assume the following possibilities for the action of the field:

(a) The field may empty the traps. This would add a term of the form $\epsilon|\cos\omega t|$ in both Eqs. (1). ϵ is some function of the amplitude of the field strength[7] E_0. It is further assumed to be proportional to $m-N$, the

[2] G. Destriau and J. Mattler, J. phys. et radium **13**, 205 (1952).

[3] G. Destriau, J. Appl. Phys. **25**, 66 (1954).

[4] G. Dechêne, J. phys. et radium **9**, 109 (1938).

[5] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 390 (1945).

[6] There is doubt whether the recombination is strictly of second order. But the applicability of a bimolecular approximation in the case of a phosphor during excitation seems to be assured also if other processes are assumed for the description of the decaying phosphor. See, e.g., D. Curie, Ann. phys. **7**, 746 (1952).

[7] The field is assumed to be $E=E_0\cos\omega t$. There may be a phase shift between the applied field and its effect on the traps, which is not considered here. It would not affect the essential results.

number of filled traps. It may or may not be proportional to N, depending on whether the emptying of traps is due to collisions with conduction electrons accelerated by the field or to processes independent of the conduction electrons. That collision processes may indeed be responsible for the excitation of electroluminescence effects, has recently been discussed by Curie[8] who removed one of the difficulties in understanding these processes for the low fields that apparently are effective in producing electroluminescence. But it is not necessary to specify the model in this respect since the particular form of $\epsilon=\epsilon(E_0,N)$ is immaterial. This gives the treatment the character of a phenomenological description rather than that of a specific physical interpretation. Similar considerations apply also to the other terms discussed hereafter.

Because the effect of the field is supposed not to depend on its direction, the absolute value of $\cos\omega t$ appears in the additional term. This may safely be approximated by $\cos^2\omega t$, in order to simplify the mathematical treatment. To be sure, there are directional effects observed, insofar as the cathode side of the phosphor seems to be the main seat of the phenomena.[9] However, the observations combine the light output of both surfaces of the phosphor, which alternately become cathodes.

(b) The mathematical analysis reveals that we have to introduce a term $-\beta\cos^2(\omega t+\varphi)$ in the equation for dN/dt and that this term, which describes a loss of conduction electrons, must appear also as a loss of empty centers if results agreeing with experiment shall be obtained. Therefore, the term introduced here should be formally interpreted as describing "field-induced nonradiative transitions." Although again it is not necessary to think of a particular mechanism as the cause of the effect assumed here, we may imagine that the field drains conduction electrons to the surface where they may undergo nonradiative transitions to empty surface centers. Nonradiative transitions which would possibly occur also without the field are neglected. They are considered to be in equilibrium, not contributing to the net changes of electrons by the field. Formally, they may be included in the η term.

The terms discussed above are sufficient to describe the ripple and the basic curve up to the beginning of the intermediate recovery. The other observations will be discussed in more general terms using the results of the analysis of the better understood parts of the effect as a frame of reference. This will lead to some additional information about the relative importance of the several terms during different stages of the effect. The uncertainty that will remain in the interpretation of the later parts of the basic curve does not affect the main results for the other parts of the observed effects.

[8] D. Curie, J. phys. et radium **13**, 317 (1952).

[9] W. W. Piper and F. E. Williams, Phys. Rev. **87**, 151 (1952).

MATHEMATICAL ANALYSIS

According to the foregoing section, we have the following equations:

$$dN/dt=\eta-A_1Nm-A_2N(n-m+N)+\epsilon\cos^2\omega t-\beta\cos^2(\omega t+\varphi), \quad (2)$$

$$-dm/dt+dN/dt=-A_2N(n-m+N)+\epsilon\cos^2\omega t.$$

The emitted intensity is given by

$$I=A_1Nm,$$

if, as mentioned before, we assume the recombination process as "bimolecular."

We put $N=N_0+\Delta$, $m=m_0+\delta$, $I=I_0+i$ with $I_0=A_1N_0m_0$ [except in $\epsilon=\epsilon(N_0,m_0)$ and $\beta=\beta(N_0,m_0)$], where N_0 and m_0 shall satisfy the original Eqs. (1). Δ and δ are small deviations from the values N_0 and m_0, respectively, caused by the field. We assume that equilibrium is reached before the field is applied, so that $m_0=n$. For I_0, N_0, and m_0, we write again I, N, and m, respectively, in all succeeding equations.

We omit terms quadratic in Δ and δ, and utilize the conditions $N\ll n$, $N\ll m$, $m=n$. The solution obtained for Δ, δ, and $i=A_1(N\delta+m\Delta)$ by standard and straightforward methods consists of a part $\tilde{i}$ that is periodic with frequency 2ω and a nonperiodic part $\bar{i}$. We take up first the periodic part, which after a sufficient time is the only one remaining, apart from a constant. It corresponds, of course, to the ripple. We give the result for the periodic solution only for the case $\beta=0$, which is the only important one, as the discussion will show. See the general result in the Appendix.

We write

$$\tilde{i}=A_1(p\cos 2\omega t+q\sin 2\omega t),$$

and obtain

$$\sigma^2=p^2+q^2=\epsilon^2\frac{4\omega^4A_1^2m^4+\omega^2m^2[16\omega^4+A_1^2A_2^2N^2m^2]}{[16\omega^4+4\omega^2A_1^2m^2+A_1^2(A_2-A_1)^2N^2m^2]^2}, \quad (3)$$

$$q/p=(4\omega^2-A_1A_2Nm)/2\omega A_1m.$$

σ measures the amplitude of the ripple; q/p, the phase shift against the field (or more accurately, against $\cos 2\omega t$).

For small frequencies, we have

$$\sigma_0^2=\epsilon^2A_2^2\omega^2/(A_2-A_1)^4A_1^2N^2, \quad (\text{if } A_1\neq A_2);$$

$$\sigma_0^2=\epsilon^2N^2/16\omega^2, \quad (\text{if } A_1=A_2); \quad (4a)$$

$$(q/p)_0=-A_2N/2\omega.$$

For large frequencies,

$$\sigma_\infty^2=\epsilon^2m^2/16\omega^2, \quad (q/p)_\infty=2\omega/A_1m. \quad (4b)$$

From this, we see that for very large and for very low frequencies as well, p disappears, so that there should be a phase shift of $\pm 90°$ against $\cos 2\omega t$. In between, at a certain critical frequency ω_0, the phase shift is zero. This critical frequency is given by

$$\omega_0 = \tfrac{1}{2}(A_1A_2Nm)^{\frac{1}{2}}. \quad (5)$$

The amplitude decreases with $1/\omega$ if $A_1 = A_2$. Or, if $A_1 \neq A_2$, it may show a maximum at another critical frequency ω_m, which is given by the equation

$$\omega^8 + (1/4)\omega^6 A_1^2 m^2 + (1/16)\omega^4 A_1^3 N^2 m^2 (6A_2 - 3A_1) - (1/64)\omega^2 A_1^4 N^2 m^4 (A_2^2 + 2A_1^2 - 4A_1A_2) - (1/256) A_1^4 A_2^2 N^2 m^4 (A_2 - A_1)^2 = 0. \quad (6)$$

ω_m depends on the ratio A_1/A_2. For $A_1 = 2A_2$, for instance, we have $\omega_m \cong \frac{1}{2}A_1(Nm)^{\frac{1}{2}}$.

We now turn to the unperiodic part of the solution. The constants are determined so that $\Delta = 0$ and $\delta = 0$ for $t = 0$. We have

$$\bar{\imath} = \mu_1[e^{-A_1Nt} - e^{-A_1mt}] + \mu_2[(N/m)(1 - e^{-A_1Nt}) - (1 - e^{-A_1mt})], \quad (7)$$

in which the same approximations as before are applied, and where $\mu_1 = \frac{1}{2}\epsilon(A_1/A_2)$, $\mu_2 = \beta/2$.

The first term yields an intensity curve like that shown as curve "a" in Fig. 3. Its maximum occurs at

$$t_\epsilon = (1/A_1m)\ln(m/N). \quad (8)$$

The second term is also shown, as curve "b." It gives an extinguishing effect if μ_2 is positive. The minimum of that curve is at $t_\beta = 2t_\epsilon$. It is much less pronounced than the maximum of the ϵ term.

The superposition of both terms gives a curve with either one maximum only, near t_ϵ, or one minimum only, near t_β, depending on the ratio μ_2/μ_1. The time t_m of the extreme value of $\bar{\imath}$ is given by

$$t_m = (1/A_1m)\ln\left[\frac{m}{N}\,\frac{(\mu_2/\mu_1) - 1}{(N\mu_2/m\mu_1) - 1}\right]. \quad (9)$$

If the ϵ term prevails, we obtain curves like those shown as c or c' in Fig. 3, which are similar to those obtained experimentally for times before the intermediate recovery.

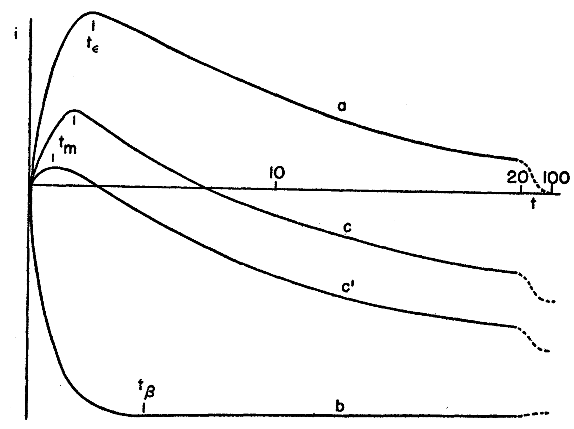

FIG. 3. Theoretical curves for basic effect. a: emptying effect in arbitrary units; b: draining-off effect; c: resultant effect $(a+\frac{1}{2}b)$; c': resultant effect $(a+\frac{3}{4}b)$; $N/m = 1/10$.

DISCUSSION

1. Effects with Field "On"

From the results of the previous section, it is obvious that the general features of the observations are adequately described qualitatively, at least with respect to electrical stimulation, quenching, and ripple. The details depend, of course, on the numerical values of the controlling parameters, about which not much is known accurately enough.[10]

Vice versa, the results, particularly the expressions for the different critical frequencies or for the time at which the peak of the basic curve occurs, might be utilized to obtain better information about these parameters. In comparing the experimental and theoretical results, however, the interference of polarization effects has to be taken into account. This particularly applies to the ripple amplitude, where the maximum of σ that is actually observed, probably has nothing to do with the maximum required by Eq. (6).

The results are derived for sinusoidal fields. One may think of discussing the effect of nonsinusoidal fields on the same basis applying Fourier analysis to the field and using for every component equations corresponding to Eq. (3). Actually, the results obtained by this method are at variance with the observations with square wave fields,[11] because the effective field is not identical with the applied field. Also in the sinusoidal case, of course, these fields will be different, but both can be supposed to be sinusoidal, and this is sufficient for the applicability of the results of the previous section.

We now want to discuss some more details of the observations in the light of the results gained above. As mentioned before, the unperiodic part of the theoretical solution agrees reasonably well with the shape of the basic curve as seen in the large time scale of Fig. 2. However, the observed minimum, as seen in Fig. 1, is obviously not described by this theory. This leads to the hypothesis that the draining-off effect is effective only over a certain time range. Formally, this interpretation can be expressed by admitting that μ_2 in Eq. (7) is time dependent.[12] It may be imagined that after a certain number of field-induced nonradiative transitions has occurred, the available empty surface centers are filled, so that no further transitions

[10] Estimates of A_1 and A_2 differ within several orders of magnitude [see, e.g., F. Stoeckmann, Naturwiss **39**, 246 (1952)] and the same can be said about the ratio A_1/A_2. We have followed the data of Randall and Wilkins with $A_2 \cong A_1$. If other data should be preferred, there would be no formal difficulty in solving the Eqs. (2). The fundamental results will not differ very much from those of our approximations. Equations (16) and (17) of the Appendix may serve as an example for this statement.

[11] S. Nudelman (unpublished).

[12] It can be considered as "slowly variable," so that β may be retained as a constant in Eq. (2).

of this kind will take place. Any nonradiative transitions that would occur from this time on are considered to be in equilibrium and are, therefore, neglected as being immaterial, just as we have neglected such transitions from the beginning. The phosphor can now be considered as a "modified" one whose continued excitation would yield a growth curve like the original one but starting from another level and reaching another equilibrium. A more detailed picture of this phase of the basic curve would be premature.[13] But it may be said that, after equilibrium is reached, only the ϵ effect would remain, so that Eq. (3) and (6) or Eq. (16) of the Appendix may safely be used for the description of the ripple.

According to the observations, t_m increases with decreasing frequency. In view of Eq. (9), this would mean that also μ_2/μ_1 decreases with decreasing frequency. The contribution of the β effect should, therefore, become less important at low frequencies. This would be in agreement with the observation that in dc fields no quenching at all could be observed. A possible mechanism for this decrease of μ_2 at low frequencies will be discussed farther below.

If the phosphor contains only few traps or none at all (phosphors of short persistence), we do not expect the ϵ effect to be present, which is in accordance with observations.[3] Of course, for any specific phosphor, even of long persistence, μ_2/μ_1 may be so large that the ϵ effect would not be manifest. On the other hand, the extinguishing effect may be weaker or even be absent if the conductivity is low, which would explain Dechêne's statement.[4]

2. Effects at Field "Off"

While so far the discussion seems to be on reasonably firm ground and has led to additional information about the presumed actions of the field, the electroluminescence effects at removing the field, i.e., the second momentary illumination followed by the final recovery, can be treated in very general terms only. The interpretation suggested is as follows.

Removing the external field restores the "modified phosphor" to its original properties, and the final recovery is the growth curve of the phosphor from the intermediate equilibrium to the original one. If there is no competing effect, the intensity will rise gradually, as it is observed at low frequencies (see the dotted curve of Fig. 1). Apparently, at such frequencies, this recovery is the only process taking place.

The momentary illumination which is observed at higher frequencies must then be due to another process. We may assume that there are, in the average, more electrons in the conduction band while the field is applied. These excess electrons may partly be due to those electrons that fail to recombine with the more or less localized holes because these electrons are moved by the field too fast across the region of a hole; partly they may be polarization charges piled up by the field near the surface; partly they may be produced by an effect considered by Krömer,[14] who showed that the tilting of the boundaries of the conduction band by the field results in an increase of the electron density. The polarization effect is probably the main contribution to the number of excess electrons. If the external field is removed, the excess electrons are released for transitions, producing a luminescent flash.[15]

But why does this effect not operate at lower frequencies, where no cut-off stimulation is observed? It is remarkable in this respect that this stimulation diminishes with decreasing frequency faster than the first stimulation and the quenching do. More light on this problem may be shed by discussing some results with dc fields described presently.

The most significant result of the application of a dc field was the production of excess illumination only, without any trace of a quenching effect. The initial excess output gradually decreased with a time constant in the order of magnitude of several hundredths of a second. No flash at removal of the field occurred. The fading off may easily be ascribed to polarization effects of some kind which need not be specified. But if we remember that the quenching effect could still be observed at 60 cps, we would expect that the dc field, although fading out, would last long enough to give at least some indication of the β effect if there was one at all at $\omega=0$.

This contradiction may be reconciled with our picture if we assume that for $\omega=0$ the loss of electrons by the draining-off effect is compensated by electrons drawn into the phosphor from the electrodes, maintaining a constant electron density or a constant current. Thus, the draining effect would be made ineffective, while the emptying effect remains. Moreover, this "current effect" would also remove all excess electrons so that cutting the field off will not have any effect.

The existence of currents is, of course, not surprising in a semiconductor. But what is important in relation to the problem discussed here is the possibility of drawing electrons off or into the phosphor particle. At low frequencies, this will be a source for compensating any electron losses or excesses at one place by contributions from other, more distant parts of the phosphor. At higher frequencies, however, the current does not have this far-reaching effect.

The current effect acts in addition to any polarization effects (effects caused by more or less localized space charges that diminish the effective field) which alone would yield only a gradual decrease of all luminescence

[13] The complexity of the processes involved during the intermediate recovery can also be seen from the discussion of the field and temperature dependence of the intermediate equilibrium by Destriau and Mattler (see reference 1).

[14] H. Krömer, Z. Physik **134**, 435 (1953).

[15] The interpretation of experiments with electroluminescent Sylvania lamps leads to the same conclusion. See F. Matossi and S. Nudelman, Helv. Phys. Acta **26**, 573 (1953) and D. Curie, J. phys. et radium **14**, 672 (1953).

phenomena because of the decreased effective field, but not a selective action on some of them. It may be easily understandable that the combination of the two effects will have different results for the quenching and for the cut-off stimulation because of the different origin which we assumed for these two phenomena (field-induced nonradiative transitions and release of excess electrons, respectively). Furthermore, we understand that the individual behavior of a specific phosphor is governed by the relative importance of the several field actions considered above. This may depend on the specific contents of impurities and the method of preparation.

Whatever the correct interpretation of the effects at "field off" may be, it will probably not invalidate the conclusions reached for the stimulating and quenching effects at the beginning of the actions of the electric field. As the essential result of these considerations, therefore, it may be stated that trap emptying and inducing nonradiative transitions are the main actions of an electric field causing the phenomena observed in some ZnS-phosphors while under the simultaneous influence of the field and excitation by radiation.

ACKNOWLEDGMENTS

I thank Mr. Sol Nudelman of this Laboratory for many discussions and for providing some as yet unpublished data.

APPENDIX

The differential equations for δ and Δ have the form

$$\begin{aligned} d\delta/dt &= a\Delta+b\delta+c+d\cos 2\omega t+f\sin 2\omega t,\\ d\Delta/dt &= a\Delta+g\delta+h+k\cos 2\omega t+f\sin 2\omega t, \end{aligned} \tag{12}$$

with

$$a=-A_1m,\quad b=-A_1N,\quad c=-\tfrac{1}{2}\beta,\quad d=-\tfrac{1}{2}\beta\cos 2\varphi,$$
$$f=\tfrac{1}{2}\beta\sin 2\varphi,\quad g=(A_2-A_1)N,\quad h=(\epsilon-\beta)/2,$$
$$k=\tfrac{1}{2}(\epsilon-\beta\cos 2\varphi).$$

The general solution can be written as

$$\begin{aligned} \delta &= A+B_1e^{\rho_1 t}+B_2e^{\rho_2 t}+C\cos 2\omega t+D\sin 2\omega t,\\ \Delta &= A'+B_1'e^{\rho_1 t}+B_2'e^{\rho_2 t}+C'\cos 2\omega t+D'\sin 2\omega t, \end{aligned} \tag{13}$$

where A to D' are constants that depend on ω and the other parameters. ρ_1 and ρ_2 are solutions of the equation

$$(\rho-a)(\rho-b)=ag.$$

In our approximation we have

$$\rho_1=-A_1m,\quad \rho_2=-A_1N, \tag{14}$$

if A_2 is not too different from A_1.

For the periodic part of the solution we have

$$\bar{\imath}=A_1(p\cos 2\omega t+q\sin 2\omega t),$$

with

$$p=NC+mC',\quad q=ND+mD',$$

and

$$\begin{aligned} C &= (1/M)[-8\omega^3f-4\omega^2(ak+bd)\\ &\qquad +2\omega fa(b-g)+a^2(b-g)(k-d)],\\ C' &= (1/M)[-8\omega^3f-4\omega^2(ak+gd)\\ &\qquad -2\omega fb(b-g)-ak(b-g)^2],\\ D &= (d/2\omega)-(1/2\omega M)[8\omega^3f(a+b)\\ &\qquad +4\omega^2(a^2k+abk+adg+b^2d)+a^2d(b-g)^2],\\ D' &= (k/2\omega)-(1/2\omega M)[8\omega^3f(a+g)\\ &\qquad +4\omega^2(a^2k+agk+adg+bdg)\\ &\qquad +2\omega fa(b-g)^2+a^2k(b-g)^2],\\ M &= 16\omega^4+4\omega^2(a^2+2ag+b^2)+a^2(b-g)^2. \end{aligned} \tag{15}$$

These formulas can be simplified some more by again taking advantage of the smallness of N.

The unperiodic part of the solution was obtained by using the conditions $A+B_1+B_2=0$ and $A'+B_1'+B_2'=0$. This introduces new integration constants, $-C$ and $-C'$, into Eq. (13). In deriving Eq. (7), the approximations must not be applied too early, but in the final result only.

Similar results are obtained also with other assumptions with respect to N. If $N\gg m-N$, for instance,[16] we have (for $A_1=A_2$)

$$p=-6\epsilon\omega^2A_1N/M',\quad q=2\epsilon(2\omega^3-A_1^2N^2\omega)/M',$$

$$M'=(4\omega^2+2A_1^2N^2)^2, \tag{16}$$

$$\bar{\imath}=(\epsilon/2)(e^{-A_1Nt}-e^{-2A_1Nt})-(\beta/2)(1-e^{-2A_1Nt}). \tag{17}$$

Equation (16) is valid for $\beta=0$ only.

[16] G. F. J. Garlick, in *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948), pp. 87 ff. In equilibrium, $N\cong m$.