

field. There are reasons for believing that both cases may occur in different actual materials.

It should be pointed out that the information regarding domain behavior obtained from dispersion measurements on metals pertain only to the domains in the surface layers of the material. With this qualification, dispersion measurements may prove to be an important method for studying domain mechanisms.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor A. G. Hill for his encouragement and interest. Miss Patricia Boland has been of great assistance in the numerical work.

APPENDIX A

Relation of Intrinsic Surface Impedance to Resistive Losses and Inductance of Film

It can be shown that the resistive losses in the film considered in Section IV and the contribution of the film to the inductance of a circuit

element are related directly to the intrinsic surface impedance which is defined according to Eq. (22) by $Z = E_z/H_x$, evaluated at $y = d$.

The average rate of energy loss per unit area normal to the y direction is given by the average value of the Poynting vector

$$S = -\operatorname{Re}[(c/4\pi)E_z(d)H_x^*(d)],$$

when it is recalled that the film has two surfaces. Now $E_z = ZH_x$, so that

$$S = -(c/4\pi)H_x(d)H_x^*(d)\operatorname{Re}[Z],$$

a well-known result.

The contribution of the film to the inductance of the magnetizing circuit is given by the quotient of the magnetic flux through the film by the current in the magnetizing circuit:

$$L = \operatorname{Re}\left[\mu \int_{-d}^d H_x dy / J\right].$$

Now $J = (c/4\pi)H_x(d)$ and $\mu H_x = +j(c/\omega)(\partial E_z/\partial y)$, so that

$$\omega L = 8\pi \operatorname{Re}[jZ] = -8\pi \operatorname{Im}[Z].$$

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Decay in Brightness of Infra-Red Sensitive Phosphors*

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An equation is derived for the decay in brightness of infra-red (IR) sensitive phosphors under constant IR stimulation. The derivation is based on a second-order process, but takes into account the absorption of the stimulating IR and the emitted visible light. The theoretical curves obtained differ markedly from the simple second-order decay curve, especially when the IR absorption is greater than the visible absorption. The equation involves three arbitrary constants which depend on the quantum efficiency, the number of active centers, and the absorption coefficients of the phosphor for visible and infra-red radiation. The equation is shown to fit the decay curve of a strontium selenide phosphor for an effective decrease in brightness of 10^6 . It is shown that theories involving a distribution of electron traps, with or without interaction, lead to conclusions that do not agree with the experimental results. Some experimental evidence is offered indicating that there is no change in the trap distribution as this phosphor is exhausted. The apparent deepening of the traps as the decay process continues can be attributed to the absorption of the infra-red.

THERE have been developed recently by Urbach, Ward, Fonda, and others¹ a group

of phosphors that show a remarkable increase in brightness when irradiated with infra-red (IR) radiation. This effect can be made to occur after the normal phosphorescence has decreased to a negligible value. Although a good deal of progress has been made in the technique of making such phosphors, there is still uncertainty regarding the mechanism. An analysis of the decay of the

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¹ Proceedings of the March 1946, meeting of the Optical Society of America, J. Opt. Soc. Am. **36**, 351-353 (1946).

brightness with constant IR irradiation should throw some light on this question and it is with such data that this paper is concerned.

The phosphors that have been studied here are alkaline earth sulfides and selenides to which have been added an appropriate flux and a small amount of activator—usually a mixture of two rare earths such as cerium, samarium, or europium. They were prepared under the direction of R. Ward, and the methods of preparation will be published elsewhere.

The decay curves were measured with the arrangement shown in Fig. 1. The tungsten lamp *L* was run from a constant voltage transformer. Light from it passed through the IR filter *F* (Polaroid XR7X25) to the opal glass plate *G*. The infra-red light stimulated the sample *P* and the light emitted by the sample was collected by the spherical mirror *M* and focused on the electron multiplier tube *T*. The anode current in the multiplier tube was read directly on a galvanometer equipped with an Ayrton shunt. The sensitivity of the galvanometer as set up was 3×10^{-10} amp. per mm. The intensity of the stimulating light could be changed from 0.001 to 0.1 lumen per cm² by moving the scale *S* on which the lamp was mounted.

It was possible to extend the range of the measurements by using the following procedure. When the brightness had fallen to a rather low value, the intensity of the IR was suddenly increased by a factor *F*. This factor was determined by fitting the last few readings before, and the first few readings after the change with curves of the form $B = B_0 / (1 + at)^2$. The factor *F* is the ratio of the two brightnesses calculated from these equations for the time at which the IR intensity is changed. The arrows on Fig. 7 indicate times at which such changes in the stimulating intensity were made.

Using this artifice, it was possible to get a curve in two and one-half hours that would

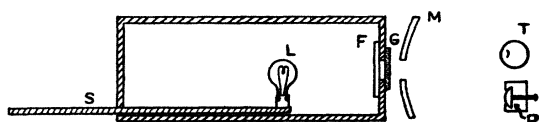


FIG. 1. Experimental arrangement for measuring decay curves.

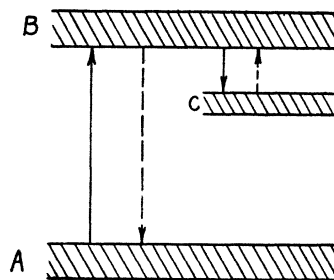


FIG. 2. Energy bands in the phosphor. The solid lines correspond to excitation and the dotted lines to stimulation by infra-red with resultant emission of visible light.

have taken something over two weeks with constant IR intensity.

The energy levels in the phosphor are taken to be as shown in Fig. 2 which is the usual schematic diagram that is used in discussing phosphorescence. *A* represents the main energy band of the matrix which under normal conditions will be filled. *B* represents the conduction band, normally empty, and *C* represents a set of impurity levels contributed by the impurity or activator atoms present in the phosphor.

During excitation electrons are raised from *A* to *B* and then fall to *C*. In a normal phosphor the agitation of the lattice due to thermal vibrations will cause the trapped electrons to go from *C* to *B*, from whence they can return to *A*, with the emission of light. In infra-red sensitive phosphors this process does not occur readily, and the normal phosphorescence is relatively weak and dies out rather quickly. However, upon irradiation with IR the process is accelerated, and an increase in the brightness is observed which is proportional to the IR intensity.

The idea that the IR actually transfers electrons from *C* to *B* is supported by some measurements on the photo-conductivity of these phosphors.² Besides the photo-conductivity observed during excitation, the excited phosphors show a pronounced primary photo-current upon irradiation with IR. This work is being continued and will be described more fully at a later date.

The situation can be described in mathematical terms as follows: Suppose there are *N* traps in *C* occupied by *n* electrons. If each trap can hold but one electron, there will be $N - n$

² S. Fine, Thesis for M.S., Polytechnic Institute of Brooklyn, 1946.

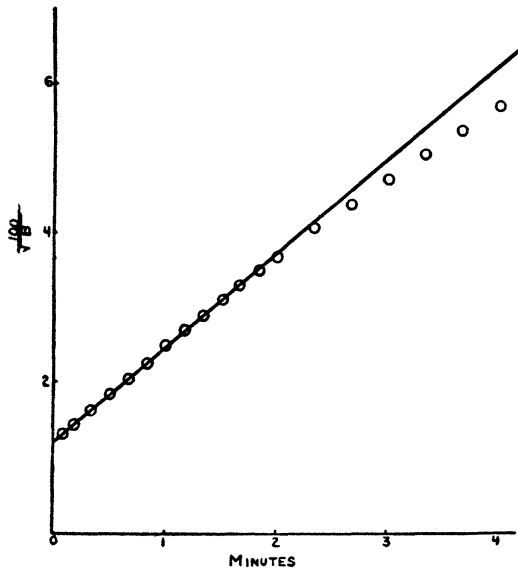


FIG. 3. Decay curve of strontium sulfide-cerium-samarium phosphor. Solid line from Eq. (5).

vacant traps. Since the electrons came from the main energy band of the matrix, there are n holes in A . The number of transitions per unit time from C to B upon irradiation with IR will be proportional to the IR intensity. Those electrons which reach B can either go to a hole in the main energy band A or return to a vacant trap in C . If the probability of going to the main energy band is proportional to the number of holes, and the probability of being retrapped is proportional to the number of vacant traps, the differential equation describing the process will be

$$\frac{dn}{dt} = -\alpha n \frac{n}{n+r(N-n)}, \quad (1)$$

where α is proportional to the IR intensity and r is the ratio of the probability that an electron in the upper band will be retrapped to the probability that it will return to the main energy band. There would probably be a somewhat higher probability that an electron should return to the trap from which it was released than to any other trap. This would not invalidate Eq. (1), since it would appear simply as a reduction of the value of α . In other words, an electron that is released from a trap and returns to the same one behaves as though it had never left.

Integration of Eq. (1) gives

$$t = -\frac{r}{\alpha} \left(\frac{N}{n} - 1 \right) + \left(\frac{1-r}{\alpha} \right) \ln \frac{N}{n} \quad (2)$$

as the relation between t and n . Unfortunately the equation cannot be solved explicitly for n in terms of t . However, Eq. (1) can be rewritten as

$$\frac{dn}{dt} = -\alpha N / \frac{N}{n} \left[1 + r \left(\frac{N}{n} - 1 \right) \right]. \quad (3)$$

The brightness B is proportional to $-dn/dt$ and therefore Eqs. (2) and (3) are a set of parametric equations for the brightness and time in terms of the parameter N/n . It is quite likely that r is not appreciably different from unity. If it is taken as such, Eq. (1) reduces to

$$dn/dt = -\alpha n^2/N. \quad (4)$$

If the phosphor is completely excited, $n=N$ at $t=0$. This gives the equation for a second-order process:

$$B = -dn/dt = \alpha N / (1 + \alpha t)^2. \quad (5)$$

If at $t=0$ the traps are not completely filled ($n=n_0$ at $t=0$), the corresponding equation is

$$B = \frac{\alpha n_0^2/N}{(1 + \alpha n_0 t/N)^2}. \quad (6)$$

From Eq. (5) or (6) one would expect that plotting the reciprocal of the square root of the brightness against time should result in a straight line. This is true for many infra-red sensitive phosphors as well as for many ordinary phosphors in the early stages of decay. A typical example is shown in Fig. 3 where the brightness of a strontium sulfide phosphor activated with cerium and samarium³ is plotted in this way. The agreement is excellent for the early stages of the decay, but the experimental points tend to lie below the straight line for larger values of the time. That is, the phosphor does not decay as rapidly as would be predicted by the simple theory outlined above. Deviation from the theory is more evident in some phosphors as indicated in Fig. 4, which shows the decay of a strontium selenide phosphor activated with samarium and

³ The infra-red sensitivity of this phosphor was discovered by F. Urbach (reference 1).

europium.⁴ There seems to be a continuous curvature in the line drawn through the experimental points, even at the very early stages of the decay process. This deviation is often explained by considering the electrons as occupying traps of different depth. The shallower traps are thought to be emptied first and the deeper ones, which would show a slower rate of decay, would be responsible for the deviations mentioned above. A second prediction of the simple theory would be that if the decay curve is plotted on log-log paper, the curve obtained should reach a constant slope of minus two. Actually this occurs very rarely, the slope usually being closer to minus one. This latter point is not so easily explained in terms of traps of different depth.

If we have a distribution of trap depths with different relative stimulabilities, and if an electron once raised to band *B* has the same probability of returning to any trap, regardless of its depth, we may replace Eq. (4) by the following set of equations:

$$\begin{aligned} \frac{dn_1}{dt} &= -\frac{\alpha_1}{N} n_1 \sum n_j, \\ \frac{dn_i}{dt} &= -\frac{\alpha_i}{N} n_i \sum n_j. \end{aligned} \tag{7}$$

The brightness of the phosphor is proportional to

$$-\frac{d}{dt} \sum n_j.$$

By a proper choice of units, we can write

$$B = f(t) = -\frac{d}{dt} \sum n_j. \tag{8}$$

Integrating,

$$\sum n_j = N - F(t). \tag{9}$$

Here *N* is the light-sum, i.e., the total amount of light stored in the phosphor, and *F(t)* is the time integral of *f(t)*, obtained by numerical integration of the observed brightness. Substituting in Eq. (7), we have

$$\frac{dn_i}{dt} = -\frac{\alpha_i n_i}{N} [N - F(t)]. \tag{10}$$

The solution of this equation is

$$n_i = n_{i0} \exp \{ -(\alpha_i/N)[Nt - \Phi(t)] \}. \tag{11}$$

In Eq. (11) *n_{i0}* is the number of electrons in the *i*th trap at *t=0* and $\Phi(t)$ is the time integral of *F(t)* obtained by a second numerical integration. Combining Eqs. (8), (10), and (11), we have for the brightness:

$$B = [N - F(t)] \sum (\alpha_i/N) n_{i0} \times \exp \{ -(\alpha_i/N)[Nt - \Phi(t)] \}. \tag{12}$$

Figure 5 shows *f(t)*, *F(t)*, and $\Phi(t)$ obtained from a particular exhaustion run, *f(t)* with the apparatus described earlier, and the latter two quantities by numerical integration.

If there are a discrete set of *m* different trap depths, Eq. (12) contains 2*m* arbitrary constants—the α_i and *n_{i0}*. If, as is more probable, there is a continuous distribution of trap depths, Eq. (12) might possibly be used to determine α and *n₀* as functions of the trap depth. There seems to be no satisfactory way of doing this. However, some interesting conclusions can be drawn from Eq. (12) regarding the behavior of the brightness at very large values of the time. It is apparent from Fig. (5) that at large values of the time we have approximately:

$$\Phi(t) = Nt - K.$$

Then Eq. (12) becomes:

$$\begin{aligned} B &= [N - F(t)] \sum (\alpha_i n_{i0}/N) \exp (-\alpha_i K/N); \\ B &= \text{constant} \times [N - F(t)]. \end{aligned}$$

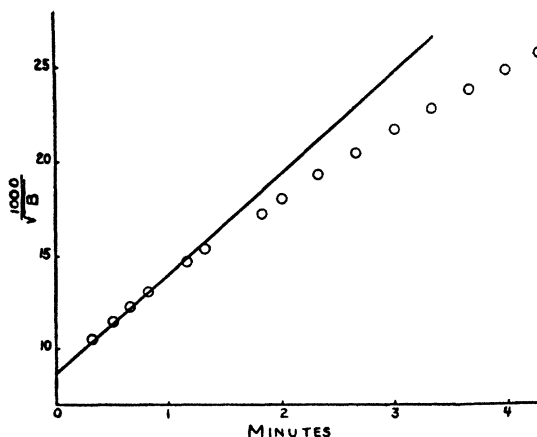


FIG. 4. Decay curve of strontium selenide-europium-samarium phosphor. Solid line from Eq. (5).

⁴ The infra-red sensitivity of this phosphor was discovered by R. Ward (reference 1).

From Eqs. (8) and (9) we have

$$\frac{d}{dt} \sum n_j = -\text{constant} \times \sum n_j. \quad (13)$$

The solution of Eq. (13) is a simple exponential equation. This means that at large values of the time, the brightness *vs.* time curve should be a straight line on semi-log paper. This is quite a remarkable result since it indicates that the interaction of a number of second-order processes can give at large values of the time, an exponential decay such as is associated with a first-order process.

In view of the complexity of Eq. (12) it is perhaps fortunate that the experimental data give no indication of conforming to it. Even when the brightness has fallen by a factor of 10^4 there is still definite curvature in the plot of brightness against time on semi-log paper as shown in Fig. 6. What does happen is that the plot of brightness against time on log-log paper is a straight line after the brightness has fallen by a factor of about 100. This is shown in Fig. 7 for the same phosphor, strontium selenide acti-

vated with samarium and europium. The slope of the straight line is, however, by no means equal to minus two as would be expected from a simple second-order process.

The shape of the decay curve for this phosphor can be explained very satisfactorily by taking into account the absorption of both the incident IR and the emitted visible light. The absorption coefficients for the IR and visible light will be denoted by μ_1 and μ_2 , respectively. The effect of infra-red absorption will be to replace α , which is proportional to the IR intensity by $\alpha \exp(-\mu_1 x)$. The effect of visible absorption will be to multiply that fraction of the brightness which originates at a depth x below the surface by $\exp(-\mu_2 x)$. Let N be the number of trapping states per unit depth, which will be independent of the depth if the phosphor is completely excited. Then, that part of the brightness due to a layer of thickness dx at a depth of x will be (cf. Eq. (5)):

$$dB(t) = \frac{\alpha N \exp[-(\mu_1 + \mu_2)x] dx}{(1 + \alpha t \exp[-\mu_1 x])^2}, \quad (14)$$

and the total brightness will be:

$$B(t) = \int_0^D \frac{\alpha N \exp[-(\mu_1 + \mu_2)x]}{(1 + \alpha t \exp[-\mu_1 x])^2} dx.$$

For the values of μ_1 and μ_2 which we have in these phosphors, the brightness will be negligible when x is greater than a few tenths of a millimeter. As a result, the thickness of the phosphor D can be replaced by infinity. Doing this and making the substitutions:

$$\begin{aligned} y &= \alpha t \exp[-\mu_1 x], \\ p &= \mu_2 / \mu_1, \end{aligned} \quad (15)$$

we have

$$B(t) = \frac{\alpha N}{\mu_1 (\alpha t)^{p+1}} \int_0^{\alpha t} \frac{y^p}{(1+y)^2} dy. \quad (16)$$

By letting αt approach zero in Eq. (16), we get:

$$B_0 = B(0) = \frac{\alpha N}{\mu_1 (p+1)}, \quad (17)$$

and rewriting Eq. (16):

$$B(t) = B_0 \frac{p+1}{(\alpha t)^{p+1}} \int_0^{\alpha t} \frac{y^p}{(1+y)^2} dy, \quad (18)$$

$$B(t) = B_0 G(p, \alpha t), \quad (19)$$

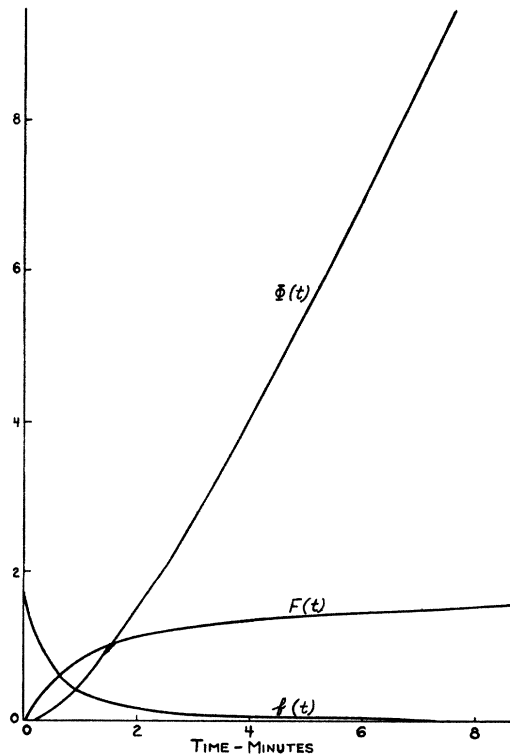


FIG. 5. Plot of the functions $f(t)$, $F(t)$, $\Phi(t)$.

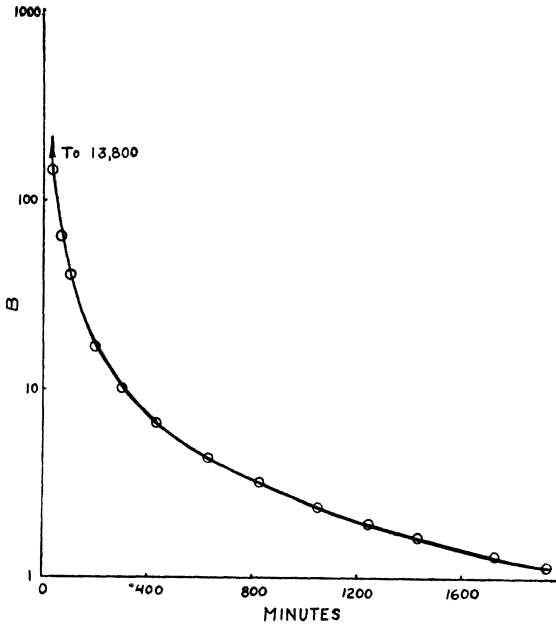


FIG. 6. Decay curve of strontium selenide phosphor. Note continuous curvature in the plot.

where the function $G(p, \alpha t)$ is defined by:

$$G(p, \alpha t) = \frac{p+1}{(\alpha t)^{p+1}} \int_0^{\alpha t} \frac{y^p}{(1+y)^2} dy. \quad (20)$$

If the phosphor is not uniformly excited, some assumption must be made as to the variation with depth of the number of filled traps per unit depth. Probably the simplest one is an exponential decrease with depth. Assuming that the surface layer is completely excited, the number of filled traps per unit depth is then:

$$n_0(x) = N \exp[-\mu_3 x].$$

The coefficient μ_3 is a function of the absorption coefficient for the exciting light and the total time of excitation. The equations corresponding to Eqs. (13) and (17) will be (cf. Eq. (6)):

$$dB = \frac{\alpha N \exp[-(\mu_1 + \mu_2 + 2\mu_3)x]}{[1 + \alpha t \exp[-(\mu_1 + \mu_3)x]]^2} dx, \quad (21)$$

$$B = B_0 \frac{q+1}{(\alpha t)^{q+1}} \int_0^{\alpha t} \frac{y^q}{(1+y)^2} dy. \quad (22)$$

Where

$$q = (\mu_2 + \mu_3) / (\mu_1 + \mu_3). \quad (23)$$

That is, Eq. (19) is valid for the case of non-

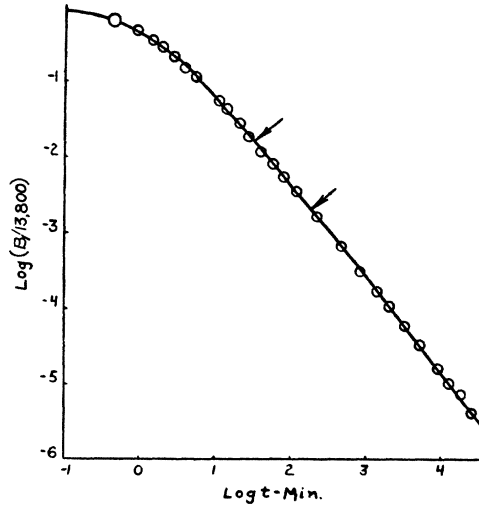


FIG. 7. Decay curve of strontium selenide phosphor. Arrows indicate times at which IR intensity was changed. Circles from experimental data, solid line from Eq. (24).

uniform excitation if the excitation decreases exponentially with the depth. The only change is to replace p by q .

An equation similar to Eq. (16) for $p=1$ was used by de Groot⁵ to explain the decay of luminescence of zinc sulfide phosphors. De Groot also points out that the theory developed here is justified only when the mean distance traveled by the electrons is small compared to the mean range of the stimulating radiation. Rough measurements on samples of different thickness indicate a value for the latter of the order of 10^{-2} cm. The former is thought⁵ to be from 10^{-4} to 10^{-5} cm.

The integral appearing in the definition of $G(p, \alpha t)$ is an incomplete beta-function.⁶ This function has been tabulated to some extent, but we have found it convenient to work with the values of p for which Eq. (20) can be integrated directly. These are integral and simple rational values of p . Table I gives $G(p, Z)$ for several values of p . The values of these functions for several values of $Z = \alpha t$ are given in Table II. Figure 8 shows the reciprocal of the square root of the function plotted against Z . The initial slope of the curve of $[G(p, Z)]^{-1/2}$ is $\alpha(p+1)/(p+2)$.

⁵ W. de Groot, *Physica* 7, 432 (1940), Eq. (9).

⁶ See for example, H. E. Soper, *The Numerical Evaluation of the Incomplete Beta Function* (Tracts for Computers, No. VII, Cambridge, 1921). We are indebted to Prof. R. M. Foster for calling this to our attention.

Figure 9 shows the functions on a logarithmic plot. It can be shown that for large values of the time, the slope of a logarithmic plot of $G(p, Z)$ against Z will be minus $(p+1)$ when $p \leq 1$, and will be minus two when $p \geq 1$. This means that if the slope of the logarithmic plot of the decay curve is to become minus two at large values of

the time (as required by the simple theory) the absorption coefficient for visible light must be equal to or greater than the absorption coefficient for IR.

TABLE I. Values of the function defined in Eq. (20) for various values of p .

p	$B/B_0 = G(p, z)$
0	$1/(1+z)$
$\frac{1}{4}$	$(5/4)z^{-5/4} \left\{ \frac{1}{4\sqrt{2}} \ln \frac{z^{\frac{1}{2}} + \sqrt{2}z^{\frac{1}{2}} + 1}{z^{\frac{1}{2}} - \sqrt{2}z^{\frac{1}{2}} + 1} + \frac{1}{2\sqrt{2}} \tan^{-1} \frac{\sqrt{2}z^{\frac{1}{2}}}{1 - z^{\frac{1}{2}} - \frac{z^{\frac{1}{2}}}{1+z}} \right\}$
$\frac{1}{3}$	$(4/3)z^{-4/3} \left\{ \frac{1}{6} \ln \frac{(1+z)^2}{1 - z^{\frac{1}{3}} + z^{\frac{2}{3}}} + \frac{1}{\sqrt{3}} \tan^{-1} \left(\frac{2z^{\frac{1}{3}} - 1}{\sqrt{3}} \right) + \frac{1}{\sqrt{3}} \tan^{-1} \frac{1}{\sqrt{3}} - \frac{z^{\frac{1}{3}}}{1+z} \right\}$
$\frac{1}{2}$	$(3/2)z^{-3/2} \{ \tan^{-1} z^{\frac{1}{2}} - z^{\frac{1}{2}}/(1+z) \}$
1	$2z^{-2} \{ \ln(1+z) - z/(1+z) \}$
2	$3z^{-3} \{ z + z/(1+z) - 2 \ln(1+z) \}$
3	$4z^{-4} \left\{ \frac{(1+z)^2 - 1}{2} - 3z - z/(1+z) + 3 \ln(1+z) \right\}$
4	$5z^{-5} \{ (z/3)(9 - 3z + z^2) + z/(1+z) - 4 \ln(1+z) \}$
∞	$1/(1+z)^2$

In order to fit Eq. (19) to a set of experimental data it is convenient to make use of a set of curves such as is given in Fig. 10. Here the negative slope of $\log B$ vs. $\log t$ for two values of αt is plotted as a function of p . The values of αt selected are those for which the brightness has fallen to one-tenth and one-hundredth of the original brightness. The original brightness can be most easily found from the experimental data by plotting the reciprocal of the square root of the brightness against time and extrapolating to zero time. When the data from which Fig. 7 was drawn are treated in this way, the original brightness is found to be 13,800. The slopes of $\log B$ vs. $\log t$ at brightnesses of 1380 and 138 are found to be -1.01 and -1.18 , respectively. From Fig. 10 we get a corresponding value for p of slightly less than 0.25. The value of α can be found by fitting the equation

$$B = 13,800G(0.25, \alpha t)$$

at several points on the decay curve. This procedure gives a value of 1.30 for α . The final form of our equation is

$$B = 13,800G(0.25, 1.30t)$$

TABLE II. Values of $B/B_0 = G(p, z)$ for various values of z . Numbers in brackets indicate negative power of ten by which the entry should be multiplied.

$z = \alpha t$	$G(0, z)$	$G(\frac{1}{4}, z)$	$G(\frac{1}{3}, z)$	$G(\frac{1}{2}, z)$	$G(1, z)$	$G(2, z)$	$G(3, z)$	$G(4, z)$	$G(\infty, z)$
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	9.09(1)	8.98(1)	8.96(1)	8.93(1)	8.80(1)	8.66(1)	8.58(1)	8.53(1)	8.27(1)
0.2	8.33(1)	8.16(1)	8.11(1)	8.04(1)	7.83(1)	7.59(1)	7.45(1)	7.36(1)	6.94(1)
0.4	7.14(1)	6.87(1)	6.78(1)	6.66(1)	6.35(1)	5.99(1)	5.79(1)	5.79(1)	5.10(1)
0.6	6.25(1)	5.91(1)	5.81(1)	5.64(1)	5.28(1)	4.86(1)	4.63(1)	4.49(1)	3.91(1)
1	5.00(1)	4.59(1)	4.48(1)	4.28(1)	3.86(1)	3.41(1)	3.18(1)	3.04(1)	2.50(1)
2	3.33(1)	2.85(1)	2.77(1)	2.57(1)	2.16(1)	1.76(1)	1.57(1)	1.47(1)	1.11(1)
4	2.00(1)	1.59(1)	1.49(1)	1.33(1)	1.01(1)	0.74(1)	0.63(1)	0.57(1)	0.40(1)
6	1.43(1)	1.07(1)	0.97(1)	0.85(1)	0.60(1)	0.41(1)	0.39(1)	0.35(1)	0.24(1)
10	0.90(1)	0.67(1)	0.63(1)	0.56(1)	0.39(1)	0.28(1)	0.25(1)	0.22(1)	0.17(1)
20	0.47(1)	0.35(1)	0.33(1)	0.29(1)	0.20(1)	0.15(1)	0.14(1)	0.13(1)	0.10(1)
40	0.24(1)	0.18(1)	0.17(1)	0.15(1)	0.11(1)	0.08(1)	0.07(1)	0.06(1)	0.05(1)
60	0.16(1)	0.12(1)	0.11(1)	0.10(1)	0.07(1)	0.05(1)	0.04(1)	0.04(1)	0.03(1)
100	0.10(1)	0.07(1)	0.07(1)	0.06(1)	0.04(1)	0.03(1)	0.02(1)	0.02(1)	0.02(1)
200	0.049(1)	0.036(1)	0.034(1)	0.030(1)	0.022(1)	0.016(1)	0.015(1)	0.014(1)	0.011(1)
400	0.024(1)	0.018(1)	0.017(1)	0.015(1)	0.011(1)	0.008(1)	0.007(1)	0.006(1)	0.005(1)
600	0.016(1)	0.012(1)	0.011(1)	0.010(1)	0.007(1)	0.005(1)	0.004(1)	0.004(1)	0.003(1)
1000	0.010(1)	0.007(1)	0.007(1)	0.006(1)	0.004(1)	0.003(1)	0.002(1)	0.002(1)	0.002(1)
2000	0.005(1)	0.004(1)	0.003(1)	0.003(1)	0.002(1)	0.001(1)	0.001(1)	0.001(1)	0.001(1)
4000	0.0025(1)	0.0018(1)	0.0017(1)	0.0015(1)	0.0011(1)	0.0008(1)	0.0007(1)	0.0006(1)	0.0005(1)
6000	0.0016(1)	0.0012(1)	0.0011(1)	0.0010(1)	0.0007(1)	0.0005(1)	0.0004(1)	0.0004(1)	0.0003(1)
10000	0.0010(1)	0.0007(1)	0.0007(1)	0.0006(1)	0.0004(1)	0.0003(1)	0.0002(1)	0.0002(1)	0.0002(1)

or

$$B = 13,800 \frac{1.25}{(1.30t)^{1.25}} \int_0^{at} \frac{y^{0.25}}{(1+y)^2} dy. \quad (24)$$

The agreement of Eq. (24) with the experimental data is indeed remarkable. The solid line in Fig. 7 is drawn from Eq. (24) and the circles are experimental points. Here the brightness has fallen by a factor of over 10^5 and yet the equation fits the data, probably within experimental error. Figures 11 and 12 show the plot of the brightness itself against time. Again the solid line is from Eq. (24) and the circles are experimental points. The agreement is certainly all that could be expected.

Another possible way of fitting an experimental curve such as that of Fig. 7 would be to use a sum of terms of the type given by Eq. (5). Physically this would mean that there were several different types of traps each with a different stimulability. The explanation given here which leads to Eqs. (19) and (20) seems to us to be much preferable for several reasons.

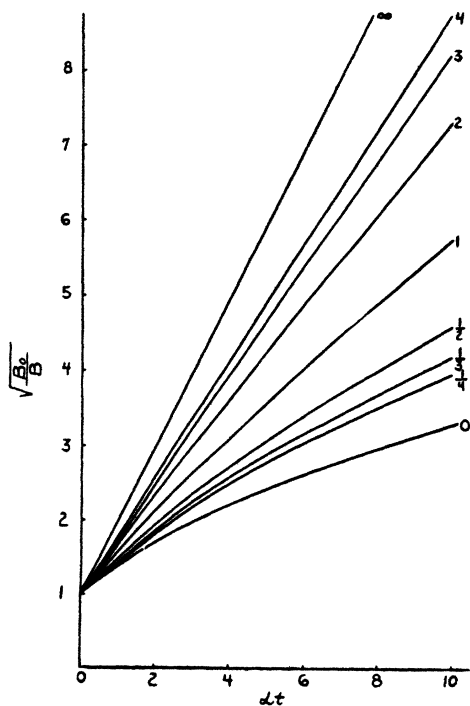


FIG. 8. Effect of IR absorption on decay curve. Numbers on the curves indicate corresponding ratios of visible and IR absorption coefficients.

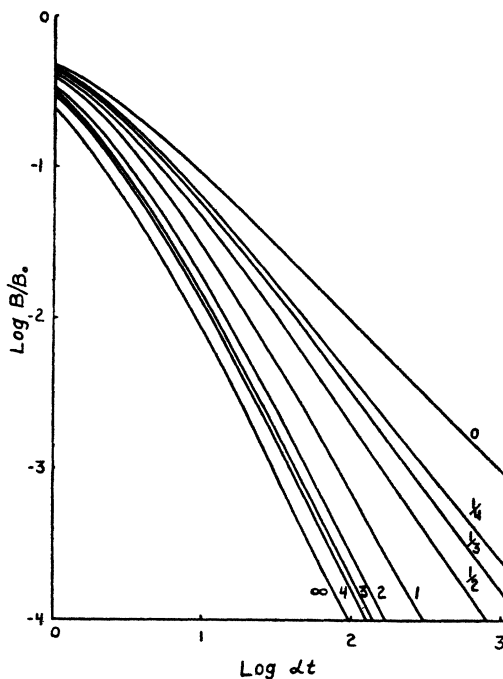


FIG. 9. Effect of IR absorption on decay curve. Numbers on the curves indicate corresponding ratios of visible and IR absorption coefficients.

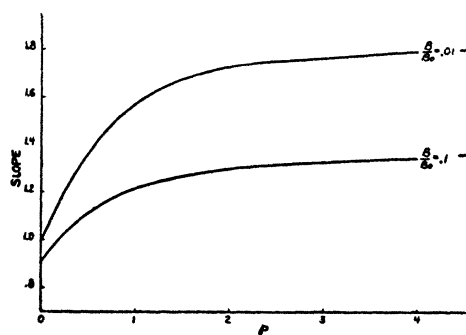


FIG. 10. Slope of decay curve on log-log paper as a function of p , the ratio of visible to IR absorption coefficients.

First, a smaller number of arbitrary constants is involved. Some work was done toward fitting the data plotted in Fig. 7 with a sum of simple second-order terms, and it was found that at least five terms involving ten arbitrary constants would be needed. Equation (24) fits the entire curve, however, with only three arbitrary constants.

Second, such a sum of simple second-order terms should eventually give a slope of minus

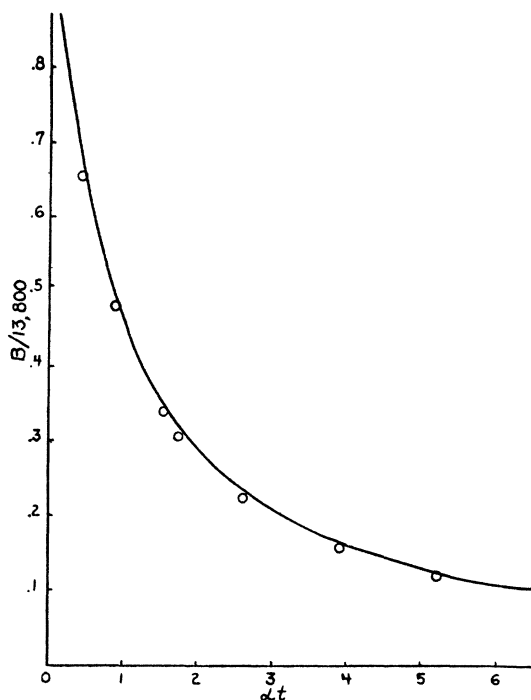


FIG. 11. Short-time decay curve of strontium selenide phosphor. Circles from experimental data, solid line from Eq. (24).

two for a logarithmic plot of the brightness.⁷ Equation (24), however, leads to a value of -1.25 for this slope which agrees quite well with the experimental data.

Third, if there were different types of traps with different relative stimulabilities, the only reasonable conclusion would seem to be that they are different because of different trap depths. If this is the case, as the phosphor becomes exhausted and the more easily stimulated traps are emptied the stimulation spectrum of the phosphor should change. This can be checked experimentally by measuring the stimulation spectra at various levels of exhaustion.

The method of measuring the stimulation spectra will be described elsewhere. Briefly it consists of using a Beckman spectrophotometer equipped with the diffuse reflectance attachment as a monochromator to supply the stimulating light. The brightness of the emitted light, corrected to equal energy for the stimulating light,

⁷ Cf. Mott and Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1940), p. 211.

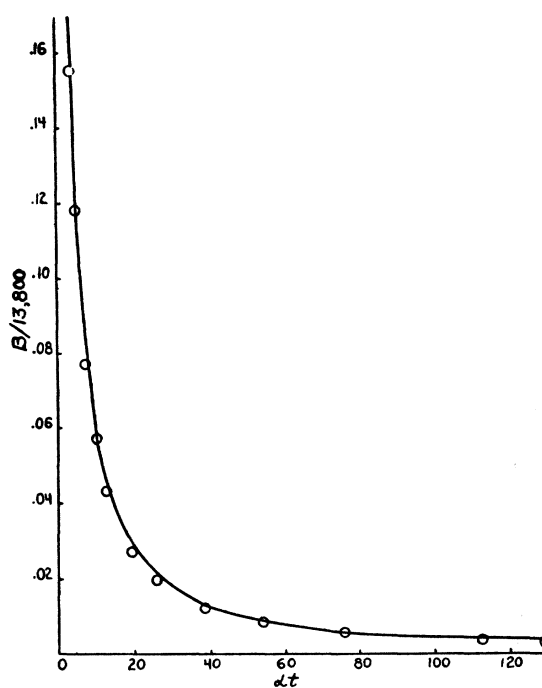


FIG. 12. Decay of strontium selenide phosphor. Circles from experimental data, solid line from Eq. (24).

plotted against the stimulating wave-length gives the stimulation spectrum.

Figure 13 shows the result of such an experiment run on a phosphor similar to the one whose decay curve is shown in Fig. 7 and fitted by Eq. (24). Here the logarithm of the corrected brightness is plotted against the stimulating wave-length for five different levels of exhaustion. It is noteworthy that there is no change of any importance in the shape of the curve even after the brightness has fallen by a factor of approximately eighty. In particular, there is no perceptible change in the wave-length at which the maximum stimulation occurs. This result would seem to rule out the possibility of having traps of different depth with different stimulabilities in this particular phosphor.

This would not necessarily be true of all such infra-red sensitive phosphors. ZnS, which has been investigated a good deal by G. R. Fonda,¹ is known to have quite different phosphorescent properties when excited at different temperatures, which would indicate that it contains trapping states of quite different stimulabilities.

We see then that an explanation of the decay

curve for the phosphor dealt with here that is based on a sum of simple second-order processes leads to conclusions which are incompatible with the experimental results. The decay curve can, however, be explained by considering a simple second-order mechanism for the phosphorescence together with the absorption of the stimulating and emitted radiations. Only three arbitrary constants are involved and each has a simple physical significance. The first, B_0 , is proportional to the concentration of active centers, the sensitivity of the apparatus used to measure bright-

ness, to α , and inversely proportional to the sum of the absorption coefficients. The second, α , is proportional to the IR intensity and the quantum efficiency of the process. The third, p , is the ratio of the absorption coefficients for visible and infra-red light.

No precise measurements of the absorption coefficients of these materials have been made and it is not possible at this time to state that the ratio of absorption coefficients as determined by the form of the decay curve is in fact equal to what would be obtained by such measurements. It is likely that the IR absorption changes somewhat during exhaustion, but there seems to be no easy way to take this into account.

There would be a variation in the light intensity with depth due to scattering also. However, the variation would also be exponential⁸ and would not alter the form of the equation derived here. It would mean that the absorption coefficients referred to here are not true absorption coefficients, but are the sum of the absorption and scattering coefficients. This would indicate that the particle size of the phosphor should affect the shape of the decay curve. Such an effect is known to exist, but no attempt has been made here to investigate it.

We wish to express our appreciation to all the members of this laboratory who have cooperated in this work, particularly for the preparation of the various phosphors studied. Dr. Roland Ward, the director of the laboratory, has given us much help and encouragement. Most of the numerical calculations were made by Mr. Harry Knutson. We are deeply indebted to Dr. Franz Urbach, now of the Eastman Kodak Company, for many stimulating discussions of possible mechanisms for the explanation of infra-red phosphorescence.

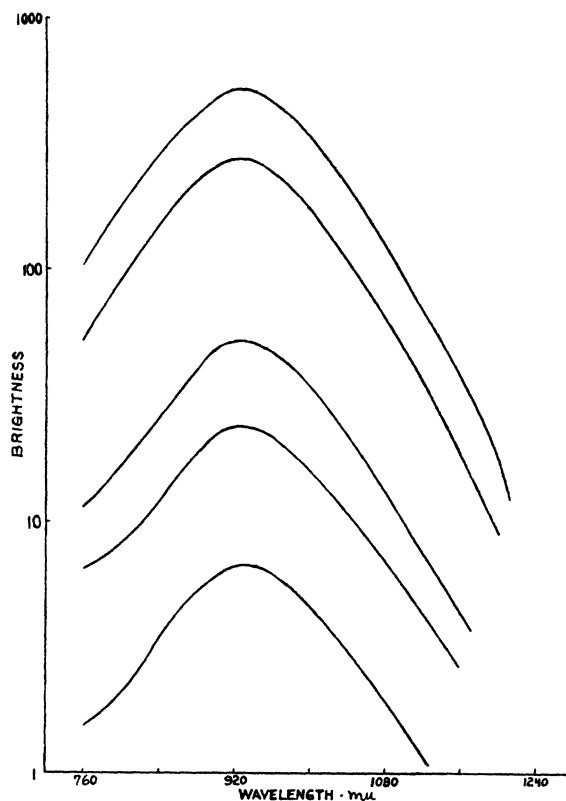


FIG. 13. Stimulation spectrum of strontium selenide phosphor at various stages of decay.

⁸ R. R. Newton, J. App. Phys. 14, 481 (1943).