

Decay of Phosphorescence from a Distribution of Trapping Levels

W. L. MEDLIN

Field Research Laboratory, Socony Mobil Oil Company, Incorporated, Dallas, Texas

(Received March 13, 1961)

In a previous paper it was shown that the usual model for second-order decay predicted the correct form for the decay in many thermoluminescent crystals but gave the wrong behavior for the parameters involved. Specifically, it was shown that b and m in the decay expression, $I = I_0[b/(b+t)]^m$, should behave differently as functions of the decay temperature and the degree of trap filling than is observed experimentally at temperatures near or below the glow peak. In the present paper it is shown that the discrepancies can be accounted for by assuming a first-order decay from a distribution of trapping levels. Most of the results are based on a Gaussian distribution but it is shown that other distributions can produce similar results. The first-order mechanism is justified by considering the relative magnitudes of the rate constants for trap emptying, retrapping, and recombination. At temperatures well above the glow peak this assumption is no longer justified, but in this range the second-order decay predicts the observed results for b and m . The effects of retrapping and of crystal dimensions are considered. Also, the effect on the glow peak of having a distribution of levels rather than a set of discrete levels is worked out and it is shown that the peak is broadened appreciably even for relatively narrow distributions.

I. INTRODUCTION

In a previous paper¹ it was shown that the phosphorescent decay curves for a number of thermoluminescent crystals including calcite, dolomite, anhydrite, aragonite, and magnesite have the form predicted for a second-order process, namely,

$$I = I_0(b/b+t)^m, \quad (1)$$

where b and m are parameters. It was further demonstrated that the behavior of the parameters b and m with changes in temperature and the fraction of initially filled traps was not the one predicted for a second-order process except at temperatures well above the glow peak.

In this paper it is shown that the correct behavior for b and m at temperatures near the glow peak can be predicted by assuming that the trapping levels are spread over a range of energies according to a Gaussian distribution function. The results are based on the assumption that the emptying of traps is the rate-determining step in the decay process except at temperatures well above the glow peak where the second-order process predicts the correct behavior for b and m .

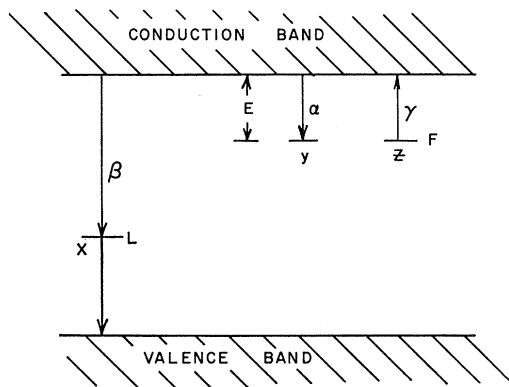


FIG. 1. Energy level scheme for second-order decay.

¹ W. L. Medlin, Phys. Rev. 122, 837 (1961).

II. THEORY

Figure 1 illustrates the transitions involved in phosphorescent decay of the type to be considered here. The constants γ , α , and β refer to the rates of emptying filled traps, filling empty traps, and recombination with empty luminescent centers, respectively. It is reasonable to expect α and β to be roughly independent of temperature over the range of a glow peak but γ is a strong function of temperature, namely,

$$\gamma = \nu e^{-E/kT}, \quad (2)$$

where ν is a frequency factor, E is the activation energy associated with the trap, and kT is the Boltzmann factor. At temperatures near or below the glow peak, γ is much less than unity for most trapping levels whereas α and β should be much larger since they are proportional to the probability that an electron will combine with positively charged centers in the crystal. Therefore, at temperatures near the glow peak, the emptying of traps should occur at a much slower rate than either the rate of retrapping or recombination and should thus be the rate-determining step for the complete decay process.

Obviously, the decay mechanism is more complicated than this in the crystals being considered here since the preceding process results in an exponential decay rate rather than the relation given by Eq. (1). The problem to be worked out here is whether the postulation of a distribution of trapping levels will result in a decay of the form of Eq. (1) and will predict the correct behavior for the constants b and m .

The postulation of a distribution of trapping levels is not new^{2,3} and there is good evidence that such distributions exist in calcite, dolomite, etc. For example, it is found that partial emptying of the traps associated with a particular glow peak (by warming the crystals

² J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 390 (1945).

³ T. Kikuchi, J. Phys. Soc. Japan 13, 526 (1958).

to temperatures near a glow peak for a brief period) results in shifting the glow peak to higher temperatures whereas the peak temperature should remain constant for a set of discrete traps. It has also been shown by Saddy⁴ and Curie⁵ that the decay curves for phosphors such as ZnS can be duplicated by a sum of exponential decay rates based on a Gaussian distribution of trapping levels.

The smearing out of discrete trapping levels into a band of levels would presumably be the result of local distortions in the crystal field due to dislocations, vacancies, impurities, etc. Since both the local distortions and the trapping centers should be randomly distributed throughout the crystal, a logical form for the distribution would be

$$N_E = N_0 \exp[-\delta(E-E_0)^2]. \quad (3)$$

At temperatures well below the glow peak, Eq. (3) expresses the distribution of filled traps after any excitation time since the rate of emptying is negligible and it can be assumed that the rate of filling is independent of trap depth, E . However, at temperatures near the glow peak where the rate of emptying becomes appreciable, the shallower traps of the distribution are emptied at a faster rate than the deep ones as given by Eq. (2). Therefore, it is clear that the value of E corresponding to the maximum number of filled traps shifts toward greater values as the excitation proceeds and the rate of shift is a function of temperature.

The method of measuring decay curves requires that the sample be excited at the same temperature for which the decay rate is measured. Therefore, it is necessary to investigate the form of the distribution of filled traps as a function of excitation time and temperature near the glow peak. Assuming that the proba-

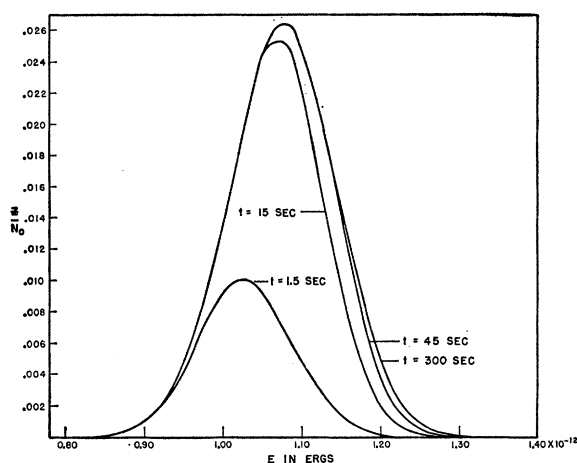


FIG. 2. Distribution of filled traps as a function of time for $\xi=0.01 \text{ sec}^{-1}$, $\delta=10^{26} \text{ ergs}^{-2}$, $\nu=10^7 \text{ sec}^{-1}$, $E_0=1.00 \times 10^{-12} \text{ ergs}$ and $T=440^\circ\text{K}$.

⁴ M. J. Saddy, Compt. rend. 228, 2022 (1949).

⁵ M. D. Curie, Compt. rend. 229, 193 (1949).

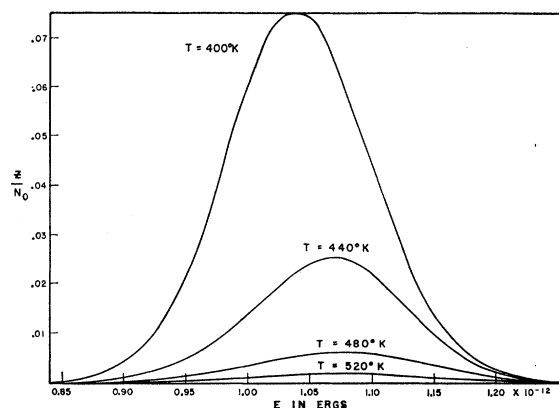


FIG. 3. Distribution of filled traps as a function of temperature for $\xi=0.01 \text{ sec}^{-1}$, $\delta=10^{26} \text{ ergs}^{-2}$, $\nu=10^7 \text{ sec}^{-1}$, $E_0=1.00 \times 10^{-12} \text{ ergs}$, and $t=15 \text{ sec}$.

bility, ξ , of filling traps is independent of T and E , the rate of filling is given by

$$dz/dt = -z\gamma + (N_E - z)\xi, \quad (4)$$

where z is the number of filled traps and γ is related to the temperature through Eq. (2). Integrating Eq. (4) and substituting the initial condition: $z=0$ when $t=0$, gives

$$z = \frac{\xi N_0 \exp[-\delta(E-E_0)^2]}{\gamma + \xi} \{1 - \exp[-(\gamma + \xi)t]\}. \quad (5)$$

The behavior of Eq. (5) is illustrated in Figs. 2 and 3 which show z/N_0 as a function of E for various values of t and T , respectively. These results show that $z(E)$ is Gaussian in form to a good degree of approximation or,

$$z(E) \approx S \exp[-\sigma(E-E_m)^2], \quad (6)$$

where S , σ , and E_m are all functions of t and γ (and hence T). At low temperatures where $\gamma \ll \xi$, it is found that $S \approx 1 - e^{-\xi t}$, $\sigma \approx \delta$, and $E_m \approx E_0$, which means that all of the traps are filled uniformly as expected. At high temperatures where $\gamma \gg \xi$, Eq. (5) reduces to a Gaussian function multiplied by $\exp(E/kT)$, which means that E_m increases to a limiting value with increasing t . For intermediate values of γ , E_m behaves in the same way but reaches a limiting value more slowly. The magnitude of ξ also determines the rate at which E_m reaches a limit, i.e., for smaller ξ longer times are required. It follows from this that the magnitude of ν , the temperature independent part of γ , has the opposite effect: For smaller ν shorter times are required for E_m to reach a limiting value. The magnitude of the limiting value of E_m is determined by the distribution parameter, δ , as well as the temperature. For broader distributions (smaller δ) and for higher temperatures the limiting value is larger.

The distribution parameter, σ , is also a function of

the excitation time and temperature. The value of σ can be computed from the relation,

$$\sigma = 0.693 / (E_{\frac{1}{2}} - E_m)^2,$$

where $E_{\frac{1}{2}}$ is the value of E for which z has half its maximum value. At a given temperature, σ increases with excitation time, passes through a maximum, and then decreases to a limiting value. The rate at which it reaches a limit still depends on the temperature and the relative magnitudes of ν and ξ as in the case of E_m . In general, σ approaches a limit in approximately the same time as E_m , the difference being that it passes through a maximum first. The occurrence of this maximum is in accordance with the trap emptying and re-trapping mechanisms involved. During the early part of the excitation, the deeper traps in the distribution are filled at a much faster rate than the shallower ones because the probability of emptying the shallow traps is greater. The distribution of filled traps is thus becoming narrower during this time and σ is increasing. But as the deeper levels become filled the rate of filling them decreases and finally becomes smaller than the rate of filling the shallower traps. During this period, the distribution is becoming broader and σ is decreasing. Eventually, equilibrium conditions are approached and σ takes on a limiting value.

Since it has been determined that the distribution of filled traps can be approximated by a Gaussian function for any excitation time, it is now necessary to determine the rate at which this distribution is emptied when the exciting source is removed. Neglecting re-trapping, the rate of emptying traps is

$$dz/dt = - \int_0^\infty \gamma z(E) \exp[-\gamma(t-t_0)] dE, \quad (7)$$

where t_0 is the time at which the exciting source is removed and the decay begins. Substituting Eqs. (2) and (6) gives

$$-dz/dt = \int_0^\infty \nu S e^{-E/kT} \exp[-\sigma(E-E_m)^2] \times \exp[-\nu e^{-E/kT}(t-t_0)] dE. \quad (8)$$

As long as the rate of emptying traps is the rate determining step, Eq. (8) expresses the decay rate. Since the distributions represented by Eq. (8) are very narrow ($\sigma \sim 100 \text{ ev}^{-2}$), the integrand cuts off very quickly on either side of E_m and it is a very good approximation for all but very shallow traps to extend the integration to $-\infty$, so that

$$I \approx \int_{-\infty}^\infty \nu S e^{-E/kT} \exp[-\sigma(E-E_m)^2] \times \exp[-\nu e^{-E/kT}(t-t_0)] dE. \quad (9)$$

The integral in Eq. (9) has the same form as the expression for the aftereffect current in a charged con-

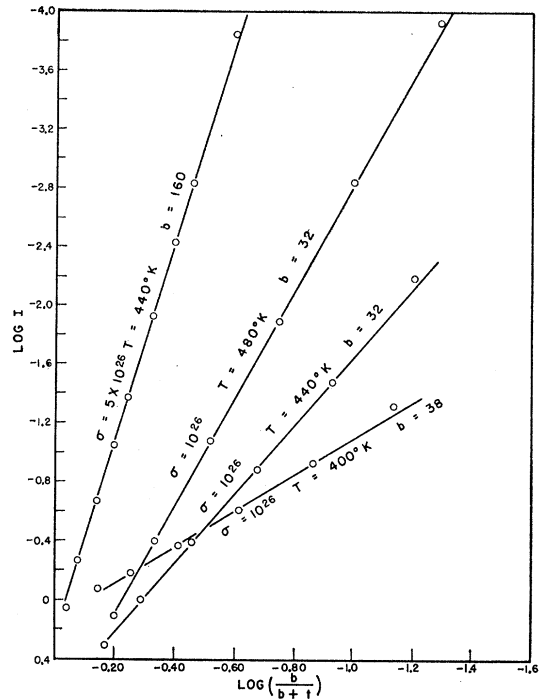


FIG. 4. Theoretical decay curves based on Eqs. (9) and (10) for $E_0 = 1.20 \times 10^{-12}$ ergs and $\nu = 1.40 \times 10^7 \text{ sec}^{-1}$.

denser.⁶ A set of numerical values for this function has been computed by Wagner⁷ and a family of curves has also been published by Jahnke and Emde.⁸ It is clear from inspection that these curves can be fitted to Eq. (1) over a range of values of $\gamma_m(t-t_0)$ which decreases with increasing values of $\delta(kT)^2$. However the results compiled by Jahnke and Emde are not complete enough to determine the functional relations between the parameters b and m in Eq. (1) and the parameters σ , E_m , ν , and T in Eq. (9). In order to determine these relations a set of supplementary values has been computed from Eq. (8). These results show that Eq. (1) can be fitted over a considerable range of values of σ , E_m , ν , and T when

$$b = \sigma E_m^6 / \nu (kTE_c)^2, \quad (10)$$

where E_c is a constant having the value of 0.01 ev. The corresponding value of m can be determined graphically. A table of results for b and m has been compiled on the basis of Eq. (10) and these results are presented in Table I. Some representative curves taken from these results are shown in Fig. 4, and Fig. 5 shows some typical experimental decay curves for comparison.

The results of Table I are not adequate to provide an expression for m in terms of E_m , σ , and T (m is independent of ν in agreement with dimensional con-

⁶ K. W. Wagner, *Ann. Phys.* **40**, 833 (1913).

⁷ K. W. Wagner, *Electrotech. Z.* **34**, 1279 (1913).

⁸ E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), p. 38.

TABLE I. Graphically determined values of b and m .

σ (erg ⁻²)	E_0 (erg)	ν (sec ⁻¹)	T (deg K)	b (sec)	m
10 ²⁵	1.200×10 ⁻¹²	1.40 ×10 ⁷	400	3.8	1.04
10 ²⁵	1.200×10 ⁻¹²	1.40 ×10 ⁷	440	3.1	1.15
10 ²⁵	1.200×10 ⁻¹²	1.40 ×10 ⁷	480	2.6	1.28
10 ²⁶	1.200×10 ⁻¹²	1.40 ×10 ⁷	400	38	1.18
10 ²⁶	1.200×10 ⁻¹²	1.40 ×10 ⁷	440	32	2.33
10 ²⁶	1.200×10 ⁻¹²	1.40 ×10 ⁷	480	26	3.60
10 ²⁷	1.200×10 ⁻¹²	1.40 ×10 ⁷	400	380	2.70
10 ²⁷	1.200×10 ⁻¹²	1.40 ×10 ⁷	440	320	12.3
10 ²⁷	1.200×10 ⁻¹²	1.40 ×10 ⁷	480	260	25.2
10 ²⁶	1.200×10 ⁻¹²	0.700×10 ⁷	400	76	1.19
10 ²⁶	1.200×10 ⁻¹²	0.700×10 ⁷	480	52	3.62
10 ²⁶	1.200×10 ⁻¹²	2.80 ×10 ⁷	400	19	1.22
10 ²⁶	1.200×10 ⁻¹²	2.80 ×10 ⁷	480	13	3.63
10 ²⁶	1.000×10 ⁻¹²	1.40 ×10 ⁷	400	13	2.65
10 ²⁶	1.000×10 ⁻¹²	1.40 ×10 ⁷	440	8.7	5.28
10 ²⁶	1.400×10 ⁻¹²	1.40 ×10 ⁷	400	96	...
10 ²⁶	1.400×10 ⁻¹²	1.40 ×10 ⁷	440	81	0.768
10 ²⁶	1.400×10 ⁻¹²	1.40 ×10 ⁷	480	66	1.90

siderations), but the following relations have been determined:

$$\begin{aligned}
 m &\approx -C_1 E_m + C_2, & C_1 &= f(\sigma); & C_2 &= f(T), \\
 m &\approx C_3 + C_4 \sigma, & C_3 &= f(E_m); & C_4 &= f(E_m, T), \\
 m &\approx C_5 T, & C_5 &= f(\sigma, E_m),
 \end{aligned}
 \tag{11}$$

where $C_1, C_2, C_3, C_4,$ and C_5 are all positive. Thus, m is

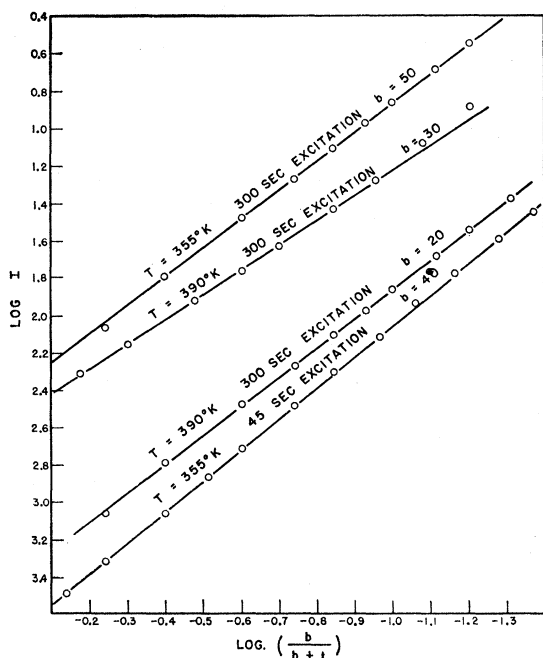


FIG. 5. Experimental decay curves for an anhydrite sample containing 680 ppm Mn⁺⁺.

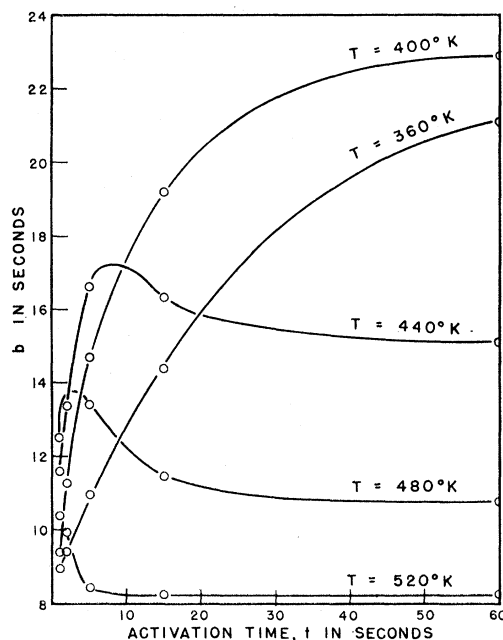


FIG. 6. Decay parameter, b , as a function of t computed from Eqs. (5) and (10) for $\delta=5 \times 10^{25}$ ergs⁻², $\xi=0.01$ sec⁻¹, and $E_0=1.00 \times 10^{-12}$ ergs.

approximately a linear function of each parameter over the range of values considered in Table I.

The results predicted for the parameters b and m of Eq. (1) can now be summarized and compared with the experimental results. At a given temperature, b varies with excitation time as the product σE_m^6 . Because of the complicated behavior of σ with t , the predicted behavior of b is not obvious. Some computed values of b have been plotted in Fig. 6. The results show that in general, b increases with excitation time to a more or less constant value at temperatures below or near the glow peak and then decreases slightly with excitation time at temperatures well above the glow peak. These results are in good qualitative agreement with the experimental data reported earlier¹ for calcite, dolomite, anhydrite, aragonite, and magnesite. It should be pointed out that the magnitude of the increase in b with excitation time is controlled mainly by the influence of E_m which depends on the relative values of ν and ξ and the value of the distribution parameter, δ .

The behavior of b as a function of temperature (at a constant excitation time) is even more difficult to predict because it involves the factor, $1/T^2$. Some computed results are plotted in Fig. 7 which shows that b should increase with temperature to a maximum value and then fall off more rapidly than $1/T^2$. These results are also in qualitative agreement with the experimental data¹ except at temperatures well above the glow peak. It is to be expected that the results are influenced in this range by the second-order process which becomes important at high temperatures.

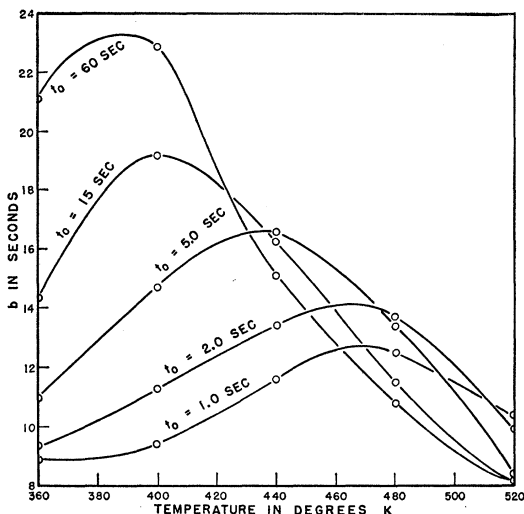


Fig. 7. Decay parameter, b , as a function of T computed from Eqs. (5) and (10) for $\delta = 5 \times 10^{25}$ ergs $^{-2}$, $\xi = 0.01$ sec $^{-1}$, and $E_0 = 1.00 \times 10^{-12}$ ergs.

The relations given for m in Eq. (11) are not precise enough to predict its behavior except as a function of temperature for long excitation times. Under these conditions σ and E_m remain approximately constant and m should increase roughly as a linear function of temperature. This behavior is observed in most cases in the experimental data. However, it is difficult to explain the result, observed in all samples,¹ that m increases to a limiting value and then falls off with increasing temperature.

It is interesting to note that in most cases the experimental curves decay faster than Eq. (1) at very short and very long times. The faster decay at short times is evidently the result of the rapid emptying of traps in shallower distributions. However, the behavior at longer times is in accordance with the curves of Fig. 4. Therefore, Eq. (8) actually fits the experimental decay for longer times than indicated by the curves of Fig. 5. This means that Eq. (1) should be interpreted merely as a convenient approximation to Eq. (8) which can be used to describe the experimental decay curves in terms of the parameters b and m . The few cases for which the decay at long times is slower than Eq. (1) can probably be explained by interference from the emptying of deep trap distributions.

The results discussed above provide good evidence that the electron traps in many thermoluminescent crystals are distributed over a range of energies. In view of this, the question arises as to what effect a distribution of traps has on the glow curve. The well-known expression derived by Randall and Wilkins² for the form of a glow peak due to a heating rate, ρ ,

$$I = N E \nu e^{-E/kT} \exp \left[- \int_0^T \frac{\nu}{\rho} e^{-E/kT} dT \right], \quad (12)$$

is based on a discrete trapping level, E . For a Gaussian distribution of filled levels, the equation for the glow peak is given by

$$I = \int_0^\infty S \nu \exp[-\sigma(E-E_m)^2] e^{-E/kT} \times \exp \left[- \int_0^T \frac{\nu}{\rho} e^{-E/kT} dT \right] dE. \quad (13)$$

Calculations for I as a function of T have been made for a set of representative values of E_m , ν , and ρ and the results are shown in Fig. 8 for four values of σ . These have been compared with the glow peak for a discrete level by introducing a suitable normalization factor. The normalizing criterion is that the total number of traps, N , be constant. For the Gaussian distribution this gives

$$N = \frac{1}{E_m} \int_0^\infty S \exp[-\sigma(E-E_m)^2] dE, \quad (14)$$

since NE_m is the total energy of all of the electrons which have an average energy, E_m . Equation (14) can be integrated by letting $x = E - E_m$ and recognizing that for all but very shallow traps,

$$\int_{-E_m}^0 \exp(-\sigma x^2) dx \approx \frac{1}{2} \int_0^\infty \exp[-\sigma(E-E_m)^2] dE.$$

The result is

$$\int_0^\infty \exp[-\sigma(E-E_m)^2] dE \approx 2 \int_0^\infty \exp(-\sigma x^2) dx = (\pi/\sigma)^{1/2}.$$

Thus, the normalizing relation for the curves of Fig. 8 is

$$N \approx (S/E_m)(\pi/\sigma)^{1/2}.$$

As would be expected, the sharpness of the glow peaks in Fig. 8 increases with σ . It is somewhat surprising, however, that the magnitude of σ should be so critical in this respect. It is clear that the values of E_m , ν , and ρ change only the temperature of the glow peak and have little effect on its shape except for very shallow traps. Therefore, Fig. 8 indicates that σ must be at least of the order 10^{26} ergs $^{-2}$ to provide a reasonably sharp glow peak. It is interesting that a σ no smaller than 10^{25} ergs $^{-2}$, which still corresponds to a very narrow distribution of traps, can account for a glow peak as broad as the one shown in Fig. 8. Some of the crystals considered here such as calcite, dolomite, and magnesite have glow curves consisting of more or less continuous levels of emission over a long range of temperature.³ The results of Fig. 8 show that these can be explained by a relatively narrow distribution of traps.

Another point which deserves some comment is the method of determining the activation energy associated with a trap. The most satisfactory means of doing this for a discrete level is to measure the exponential slope

TABLE II. Slope of exponential plot of glow curve for various values of σ .

σ in ergs ⁻²	Slope of exponential plot for $E_m/k=0.870$ deg
5×10^{25}	0.725
10^{26}	0.812
5×10^{26}	0.855
10^{27}	0.862

of the initial increase in intensity over a range of temperatures well below the glow peak. In this range,

$$\int_0^T \frac{\nu}{\rho} e^{-E/kT} dT \ll 1,$$

and Eq. (12) reduces to

$$I \approx N_E \nu e^{-E/kT},$$

from which a value of E can be determined graphically.

When N_E is replaced by the Gaussian distribution of Eq. (6), the early rise of the glow peak is given by

$$I = \int_0^\infty N_0 \nu \exp[-\sigma(E - E_m)^2] e^{-E/kT} dE. \quad (15)$$

Equation (15) is nonintegrable in closed form but a set of numerical integrations has been carried out over the temperature range 350°–400°K for $E_m=0.75$ ev and for several values of σ . It was found that the slope of the early part of the $I(T)$ curve is still exponential and approaches $-E_m/k$ for large σ . The results, tabulated in Table II, show that the method is suitable for predicting an approximate value of E_0 (which is always too small) for reasonably sharp glow peaks.

It has been shown that for some crystals such as calcite the glow peaks are appreciably enhanced by annealing the sample at temperatures near its decomposition range for a few hours.⁹ The increase in intensity is accompanied by a decrease in the half width of the glow peak. The results shown in Fig. 8 indicate that this can be readily explained by an increase in σ when the sample is annealed. Since the effect of annealing is to smooth out many of the crystal distortions which were introduced during growth, such an increase in σ is to be

 TABLE III. Effect of annealing on decay parameters b and m .

Sample	Excitation time (sec)	Temperature (deg K)	b (sec)	m
Calcite: before annealing	45	325	40	1.9
	300	325	60	1.5
Calcite: after annealing	45	325	50	1.4
	300	325	100	1.4

⁹ W. L. Medlin, J. Chem. Phys. **32**, 943 (1960).

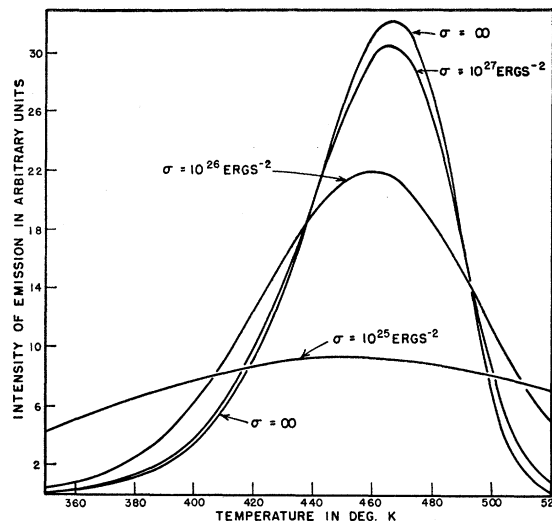


FIG. 8. Glow peak as a function of σ for $E_0=1.200 \times 10^{-12}$ ergs, $\nu=10^7$ sec⁻¹, and $\rho=0.5$ deg/sec.

expected. To test the hypothesis, a calcite sample containing 1000 ppm Mn⁺⁺ was prepared by precipitation at room temperature. A part of the sample was then annealed and values of σ were determined from the decay curves of the original and the annealed samples. The results, given in Table III, show a definite increase in σ due to annealing which indicates a larger value of σ in the annealed sample. Similar results have been observed by comparing the decay curves of samples precipitated at room temperature with samples precipitated at elevated temperatures (200–250°C) by hydrothermal techniques.⁹

In deriving the decay expression given by Eq. (8) it has been assumed that retrapping during the decay period can be neglected. If the crystal contains trapping sites at several different distribution levels then it is clear that retrapping at levels other than the one under consideration can be neglected. Retrapping in the shallower distributions has negligible effect since the electrons spend such a short time there. Retrapping in the deeper levels is in the same category as radiationless transitions; both can be neglected as long as the emptying process is the rate determining step. However, retrapping at the same level may occur to an appreciable extent and it is worthwhile to consider its effect.

Using the notation of Fig. 1, the rate of emptying traps is

$$dz/dt = -\gamma z + \alpha(N_E - z)n. \quad (16)$$

The case where an electron is immediately retrapped at the same center it has just left can be eliminated as before since this merely amounts to a reduction in the value of γ . If it is assumed that the number of conduction band electrons, n , remains approximately constant

during the period of interest, then Eq. (16) gives

$$z = \frac{1}{\lambda + \gamma} \{ \lambda N_E + [(\lambda + \gamma)z - \lambda N_E] \times \exp[-(\lambda + \gamma)(t - t_0)] \}, \quad (17)$$

where $\lambda = \alpha n$ and z_0 is the number of filled traps at $t = t_0$. Differentiating Eq. (17) with respect to t and substituting for z_0 and N_E from Eqs. (3) and (6) gives an expression for the rate of emptying traps,

$$-dz/dt = \{ (\lambda + \nu e^{-E/kT}) S \exp[-\sigma(E - E_m)^2] - \lambda N \exp[-\delta(E - E_0)^2] \} \times \exp[-(\lambda + \nu e^{-E/kT})(t - t_0)]. \quad (18)$$

The decay rate is then obtained by integrating Eq. (18) over all energies. The resulting expression can be put in the form,

$$I = \exp[-\lambda(t - t_0)] \left\{ \int_0^\infty \nu S e^{-E/kT} \times \exp[-\sigma(E - E_m)^2] \exp[-\nu e^{-E/kT}(t - t_0)] dE + \int_0^\infty \{ S \exp[-\sigma(E - E_m)^2] - N \exp[-\delta(E - E_0)^2] \} \times \lambda \exp[-\nu e^{-E/kT}(t - t_0)] dE \right\}. \quad (19)$$

The first integral in Eq. (19) is identical to the decay rate without retrapping [see Eq. (8)] multiplied by the exponential, $\exp[-\lambda(t - t_0)]$. The second integral is always negative since $\int_0^\infty z_0 dE < \int_0^\infty N_E dE$ and for long excitation times becomes negligible. Therefore the decay with retrapping is given by the decay without retrapping multiplied by the corrective factor $\exp[-\lambda(t - t_0)]$ and with another corrective term of approximately the same form in t subtracted from it. An obvious means of determining the importance of retrapping is to measure the decay rates under the two conditions: (1) $\gamma \gg \lambda$ (high temperature) and $\int_0^\infty z_0 dE \approx \int_0^\infty N_E dE$ (long excitation time), and (2) $\gamma \sim \lambda$ and $\int_0^\infty z_0 dE \ll \int_0^\infty N_E dE$. This has been done for several samples¹ without finding any apparent differences in the form of the decay curve.

The preceding developments have been derived on the basis of a single crystal of large dimensions. But since large single crystals of most of the crystals considered are not generally available, it is important to consider the effect of crystal size on the decay process.

Since the crystal boundaries act as barriers for the motion of free electrons it is clear that the crystal dimensions determine the maximum range of electrons in the conduction band. Therefore, unless the mean free path of the conduction electrons is considerably less than the dimensions of the individual crystallites, the equations based on single crystals are not valid when applied to a powdered sample (the effect of considering

TABLE IV. Effect of crystal size on decay curve.

Sample	Excitation time (sec)	Temperature (deg K)	b (sec)	m	Remarks
Natural calcite (Brewster County, Texas)	300	335	25	0.85	Single crystal
Natural calcite (Brewster County, Texas)	300	335	20	0.85	Ground sample

the contributions of a large number of crystallites to the decay process has been considered by Weyl¹⁰).

An expression for the mean free path of electrons in ionic crystals has been derived by Fröhlich and Mott¹¹ and by Seeger and Teller.¹² For electrons having an energy of a few electron volts (the energy gap in most of the crystals considered here is of the order of 10 eV), the mean free path is no greater than 10^{-5} cm. Since the crystallites in most natural samples have dimensions of the order 10^{-3} cm, it is evidently valid to apply the single-crystal results to these samples.

To verify this experimentally the decay curves for a single crystal of natural calcite containing Mn^{++} were measured before and after grinding. The maximum crystallite size after grinding was no larger than 10^{-3} cm. The results, which are given in Table IV, show that the form of the decay curve and the values of b and m were not appreciably affected by diminishing the crystal dimensions.

The choice of a Gaussian function to describe the distribution of traps with energy follows from the assumption that localized distortions as well as trapping centers are randomly distributed throughout the crystal. It is interesting to consider at this point the question of other possible distribution functions.

A form which suggests itself is one for which the rate of change in the number of traps with energy (measured on either side of a zero point energy, E_0) is proportional to the number of traps at that energy, i.e.,

$$dN_\epsilon/d\epsilon = -\mu N_\epsilon, \quad (20)$$

where $\epsilon = |E - E_0|$. From Eq. (20), $N_\epsilon(E)$ has the form,

$$\begin{aligned} N_\epsilon &= N_0 \exp[\mu(E - E_0)], & E \leq E_0, \\ N_\epsilon &= N_0 \exp[-\mu(E - E_0)], & E \geq E_0. \end{aligned} \quad (21)$$

When this distribution is substituted into the decay expression, the result is

$$\begin{aligned} I &= N_0 \nu \int_0^{E_0} \exp[\mu(E - E_0)] e^{-E/kT} \exp[-\nu t e^{-E/kT}] dE \\ &\quad + N_0 \nu \int_{E_0}^\infty \exp[-\mu(E - E_0)] e^{-E/kT} \exp[-\nu t e^{-E/kT}] dE. \end{aligned} \quad (22)$$

¹⁰ P. K. Weyl, J. Chem. Phys. **26**, 547 (1957).

¹¹ H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).

¹² R. J. Seeger and E. Teller, Phys. Rev. **54**, 515 (1938).

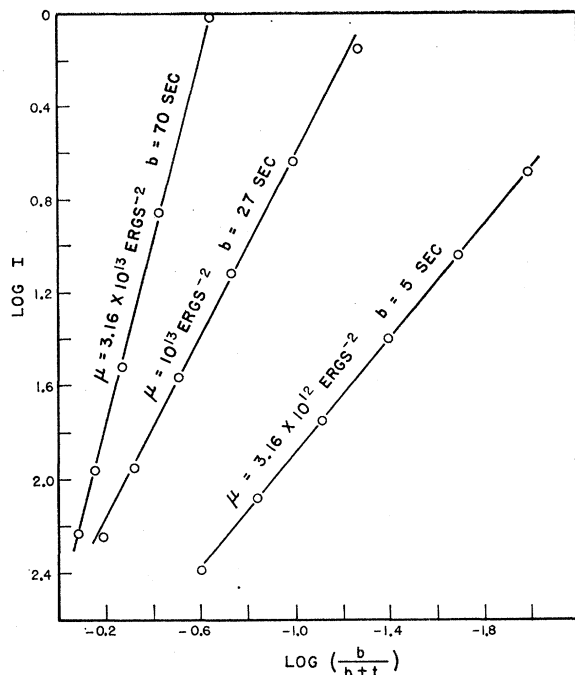


FIG. 9. Theoretical decay curves computed from Eq. (21) for an exponential distribution of trapping levels with $E_0 = 1.20 \times 10^{-12}$ ergs, $\nu = 1.40 \times 10^7 \text{ sec}^{-1}$, and $T = 440^\circ \text{K}$.

Equation (22) is nonintegrable in closed form but a set of values of I as a function of t has been computed numerically. The results fit Eq. (1) over a suitable range of $t - t_0$ as illustrated in Fig. 9. The relations between b and m and the parameters E_0 , ν , T , and μ have not been worked out in this case. Also, it has been assumed that the distribution function (21) retains its form to a good approximation as the traps are filled.

It can be concluded that a Gaussian distribution function is not the only one which will give the correct form for the decay curve. Therefore, the agreement with experiment of results based on the Gaussian distribution cannot be taken as proof that the traps are distributed in this way.

III. CONCLUSIONS

The experimentally observed form of the decay curve for all of the common thermoluminescent minerals, given by Eq. (1) can be derived by assuming that: (a) the electron traps are not confined to a discrete level but are distributed over a narrow range of energies and (b) at temperatures near the glow peak, the rates of recombination and retrapping are so much faster than the rate of emptying traps that the latter process is the rate determining step.

A Gaussian distribution of trapping levels (which is the most logical choice) results in a distribution of filled traps which can be approximated by a different Gaussian function for any excitation time. The decay curve predicted for such a distribution has the experimentally observed form and the behavior of the parameters b and m with excitation time and temperature (near the glow peak) agree with the experimental results.

Retrapping during the decay period is apparently not important in affecting the form of the decay curve. Also, the size of the individual crystallites in powdered samples is not critical above $10\text{--}100 \mu$.

The smearing out of discrete trapping levels into bands of levels results in a flattening of the associated glow peak. This broadening effect becomes extreme for distributions which are still relatively narrow and shows that the very broad, low-temperature glow peaks observed in such crystals as calcite and dolomite can be explained by quite narrow distributions of trapping levels.

It can be shown that a Gaussian distribution is not the only one which provides the observed decay form and the proper behavior of the parameters b and m with excitation time and temperature. It appears that any narrow distribution function provides the observed results.

ACKNOWLEDGMENTS

The author wishes to thank O. D. Ferris, G. E. Weatherly, J. J. McAlpin, and D. Harris for making most of the calculations, and Socony Mobil Oil Company for permission to publish this paper.