THERMOLUMINESCENCE AND PHOSPHORESCENCE WITH A CONTINUOUS DISTRIBUTION OF ACTIVATION ENERGIES *

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Some theoretical features of phosphorescence decay curves and thermoluminescence (TL) glow curves have been investigated with some select depth distributions. In early studies a t^{-1} (inverse-time dependence) behaviour for isothermal decay was found assuming a uniform distribution of activation energies ranging from 0 to infinity. Additional studies explored the TL features resulting for Gaussian distributions of activation energies. For broad enough distributions the t^{-1} behavior for isothermal luminescent decay again followed. It thus appears that broad distributions will quite generally result in t^{-1} phosphorescence behavior. We have addressed the more mathematically tractable situation of a continuous uniform distribution within a finite range of energies, from E_1 to E_2. The circumstances under which the t^{-1} law can be accepted as a valid approximation, as well as the deviations from this law, are discussed using numerical calculations. Also, the expected features of TL glow curves under similar conditions for continuous trap distributions are discussed. In particular the effective values of the activation energies one can calculate using different known methods for its evaluation are studied. The relationship of these derived effective values to the distributions actually used in the calculations is discussed.

The near-t^{-1} time dependence of phosphorescence resulting from a model of electrons and holes recombining through tunneling is contrasted to that for the standard first-order kinetics model with a broad excitation energy distribution also giving a near-t^{-1} dependence. The distinction appears in the curvature of yield curve with time during the onset of phosphorescence.

1. Introduction

Most works dealing with the kinetics of the thermoluminescence (TL) process are based on the assumption that in a given temperature range, only one trapping state and one kind of recombination center are active. When a series of TL peaks is seen, it is still usually assumed that each individual peak results from the transition from a single trapping state to a single kind of recombination center. Right from the very beginning of the study of TL, the possibility of having a continuous distribution of trapping states has been taken into consideration. Randall and Wilkins [1],

who were the first to give a theoretical account of the TL phenomenon suggested this possibility and studied the behavior of TL glow curves and iso-thermal decay behavior (phosphorescence) assuming uniform and exponential trap depth distributions. For reasons discussed below, these authors as well as most other investigators limited their work to cases of first-order kinetics or, in other words, cases in which thermally released charge carriers can only interact with trapped recombination centers and cannot undergo retrapping into empty trap sites. Under this assumption and assuming that the distribution extends uniformly from 0 to ∞, they showed that the expected time dependence of phosphorescence should behave as t^{-1}. When the trap distribution is exponential, namely $N_E = A e^{-\alpha E} \, dE$ where N_E is the concentration of trapping states with energies between E and $E + dE$, they showed that phos-

phorescence decays obeying a $t^{-(\alpha\kappa T+1)}$ law, where κ is Boltzmann's constant.

Medlin [2] investigated the TL behavior associated with activation energy distributions obeying a Gaussian form $N_E = C \exp[-a(E - E_0)^2]$. He showed that isothermal decay following the law $I(t) = I_0(1 + bt)^{-m}$ results over a reasonable time range and related the constants b and m to the distribution width and other relevant parameters.

Hornyak and Franklin [3] extended the TL behavior studies of Gaussian-shaped trap distributions taking retrapping into account in first-order approximation. The possibility of retrapping did not materially alter the conclusion that broad distributions lead to isothermal luminescent decay having a t^{-1} dependence.

Experimentally a $t^{-\beta}$ behavior is rather common, except for the early time portion of the decay curve, and β is quite often found to be close to unity. It is to be noted that although in crystalline samples the occurrence of discrete energy levels seems to be plausible, in amorphous organic materials (see Pender and Fleming, [4]) as well as amorphous inorganic materials (e.g. glassy materials, see Kikuchi [5]), continuous or quasi-continuous distributions of activation energies seem more likely to occur.

A number of researchers have investigated TL glow peaks that possibly result from a continuum of activation energies. These include Bosacchi et al. [6,7] who studied "quasi-disordered" materials, and Pender and Fleming [4] who were interested in organic materials such as polystyrene. The general phenomenon was studied by Hagekyriakou and Fleming [8] and Rudolf et al. [9]. The latter authors utilized the fractional glow technique (FGT) devised by Gobrecht and Hofmann [10] to try to retrieve the energy distribution from a TL glow curve. This technique comprises a repeated "initial rise" measurement performed in small temperature range heating and cooling cycles yielding the activation energies as function of, say, the middle of each small temperature range.

Kikuchi [5] studied the TL glow and phosphorescence behavior of glasses. He derived the expression for phosphorescence decay with a uniform energy distribution of traps between the energies E_1 and E_2. In the present work we carry

this idea further, partly in order to get a measure for how broad the energy range $\Delta E = E_2 - E_1$ should be so that the Randall and Wilkins t^{-1} result can be considered a good approximation. In view of the results of the theoretical investigations cited above, which show quite generally that broad distributions with or without retrapping can lead to a t^{-1} form of phosphorescence, this very simple and mathematically tractable energy distribution should provide a reliable criterion for determining when this type of time dependence will result.

In the present work, in addition to the study of calculated phosphorescence decay curves, we have also calculated TL glow curves under similar conditions. TL glow peaks clearly showed a broadening which reflected the effect of the assumed width ΔE. Some standard methods were then used for evaluating activation energies from these broadened glow peaks. Comparisons are made contrasting the effective activation energy obtained using these methods with the given energy distribution of activation energies actually used in the calculations.

2. Phosphorescence decay

As mentioned above, Randall and Wilkins [1] wrote the phosphorescence decay function as

$$I(t) = \int_0^\infty N_E s \ e^{-E/\kappa T} \exp[-st \ e^{-E/\kappa T}] \ dE, \quad (1)$$

where T is the absolute temperature and s and frequency factor assumed to be the same for all the activation energies. N_E is the number of traps between energies E and $E + dE$. It should be mentioned that this approach is limited to first-order kinetics. As has been discussed by many authors, first-order kinetics results from assuming a situation in which retrapping is negligible compared to recombination. It is quite obvious that taking the integral from zero to infinity is questionable because the range of possible energies is actually limited. More realistically we assume a uniform trap distribution between E_1 and E_2 and write (see also ref. [5])

$$I(t) = \int_{E_1}^{E_2} N_E s \ e^{-E/\kappa T} \exp[-st \ e^{-E/\kappa T}] \ dE. \quad (2)$$

Here $N_E = n_0/\Delta E$ where $\Delta E = E_2 - E_1$ and n_0 stands for the total number of traps. Integrating eq. (2), one gets

$$I(t) = \frac{n_0 \kappa T}{t \Delta E} \Big[\exp(-st\ e^{-E_2/\kappa T})$$
$$- \exp(-st\ e^{-E_1/\kappa T}) \Big]. \tag{3}$$

We now turn to finding the circumstances under which the t^{-1} law approximates the more general case of eq. (3). In order to do this, we calculated decay curves, all with $n_0 = 5 \times 10^9$ cm^{-3}, $s = 10^{10}$ s^{-1}, $T = 300$ K, and $E_0 = 0.7$ eV, E_0 being the center of the energy distribution. The results are plotted on a log–log scale in fig. 1. Curve (a) which corresponds to $\Delta E = 0.01$ eV is in fact indistinguishable from a simple exponential decay. This shows up more clearly when the same results are plotted on a semi-log graph. Curves (b) and (c) result from choosing $\Delta E = 0.05$ eV and $\Delta E = 0.1$ eV respectively, and have shapes which are neither exponential nor following the t^{-1} law. Curves (d), (e) and (f) are essentially straight lines with a slope of -1 which, of course, shows that the $0-\infty$ Randall and Wilkins approximation is a reasonably good one for $E_0 = 0.7$ eV and $\Delta E \geqslant 0.2$
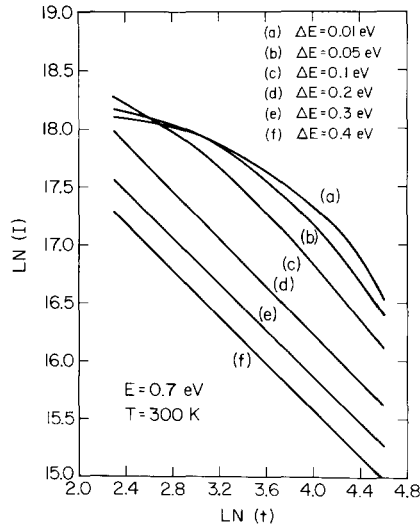

Fig. 1. Calculated phosphorescence decay curves with $n_0 = 5 \times 10^9$ cm^{-3}, $s = 10^{10}$ s^{-1}, $E_0 = 0.7$ eV and $T = 300$ K, plotted on a log–log graph. The widths of the distribution are (a) $\Delta E = 0.01$ eV, (b) $\Delta E = 0.05$ eV, (c) $\Delta E = 0.1$ eV, (d) $\Delta E = 0.2$ eV, (e) $\Delta E = 0.3$ eV, (f) $\Delta E = 0.4$ eV.

eV. The parameter playing an important role in this changing behavior pattern is the quantity $y = \kappa T/\Delta E$.

For these truncated uniform distribution examples the criterion for the onset of the t^{-1} dependence is $\Delta E \geqslant 0.2$ eV in the chosen example or $y \leqslant 0.13$. Nearly exponential decay results when $\Delta E \leqslant 0.01$ eV and the value of y is $y \geqslant 2.5$. As expected, these results are quite consistent with those found by Hornyak and Franklin [3] for Gaussian-shaped activation energy distributions as cited above. In the absence of retrapping the general phosphorescence behavior was found by them to be of the form $I = I_0 y G(x, y)$, where $y = \kappa T \sqrt{a}$ and $x = \lambda_0 t$ with $\lambda_0 = s e^{-E_0/\kappa T}$. It was found that for very narrow distributions, i.e. $y > 1.5$ the decay was essentially an exponentially decreasing function of time. For broad distributions, i.e. $y \leqslant 0.15$ the t^{-1} dependence prevailed. For value $0.15 < y < 1.5$ the time dependence slowly transformed from the one extreme dependence to the other as y ranged from the lower to the higher value.

For both the Gaussian and truncated uniform distribution of trap energies the critical parameter controlling the change from exponential to inverse time dependence is the quantity $y = \kappa T \sqrt{a} = 1.66$ $\kappa T/\text{FWHM}$ for the Gaussian case and $y = \kappa T/\Delta E$ for the truncated uniform distribution. Although the function $G(x, y)$ is available in tabulated form in Jahnke and Emde's *Tables of Functions* and in an approximate analytic form for $G(x, y)$ (see ref. [3]), the truncated uniform distribution is considerably simpler to work with.

For the initial time dependence we adopt the method suggested by Avouris and Morgan of plotting I^{-1} as a function of time, in order to check the t^{-1} behavior and deviations therefrom. Figure 2 depicts such a presentation of a calculated phosphorescence curve with $E_0 = 0.7$ eV, $\Delta E = 0.3$ eV, and $T = 300$ K. The results show practically a straight line for times greater than about 1.5 s. For times less than 1.5 s a deviation from the straight line behavior is evident and exhibits an initial portion with a concave upward curvature. Similar results have been found by Avouris and Morgan [11] for some of their decay curves, which could not be explained by their tunneling model. Tun-
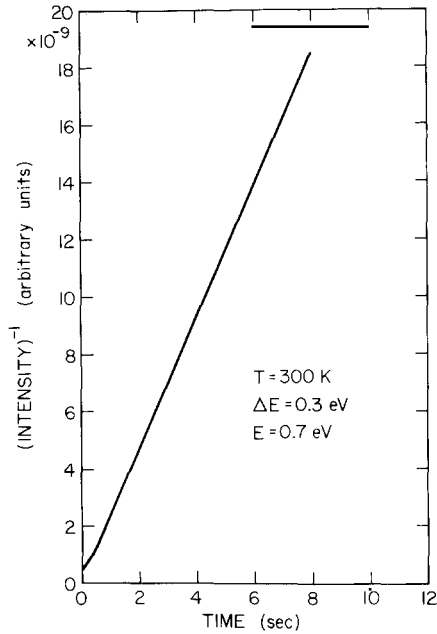
Fig. 2. Calculated I^{-1} vs. time for $n_0 = 5 \times 10^9\,\mathrm{cm}^{-3}$, $s = 10^{10}$ s^{-1}, $E_0 = 0.7$ eV, $T = 300$ K and $\Delta E = 0.3$ eV.

neling could account only for a convex behavior. Indeed this type of behavior was seen in some other experimental results (see also the discussion below).

Changing the parameters (E_0, ΔE, T or s) did not vary the basic dependence, namely, the curve had a positive intercept with the y-axis, it was concave in its initial range and got linear at higher values of t. A comparison between the tunneling model and the continuous distribution model will be made in the discussion below.

To sum up this section, we would like to re-write the decay curve given by eq. (3) using the two dimensionless quantities $z = st\ \exp(-E_0/\kappa T)$ and $w = \exp(-\Delta E/2\kappa T)$ where $\Delta E = E_2 - E_1$ and $E_0 = (E_2 + E_1)/2$. Equation (3) transforms into

$$I(z, w) = \frac{n_0 \kappa T}{\Delta E \cdot t}(\mathrm{e}^{-zw} - \mathrm{e}^{-z/w}). \tag{3'}$$

As pointed out by Randall and Wilkins the study of $I \cdot t$ should yield useful information concerning the kinetics involved. For example, for decay curves resulting from a single narrow trapping state, the plot of $I \cdot t$ as a function of $\log(t)$

should yield a nearly TL-like glow peak [12]. In the other limit of an extremely broad uniform trap distribution (essentially from 0 to ∞) $I \cdot t$ should be a constant as a function of t which is, of course, a manifestation of the t^{-1} behavior of phospherescence. Equation (3') can be written as

$$I \cdot t = \frac{n_0 \kappa T}{\Delta E}(\mathrm{e}^{-zw} - \mathrm{e}^{-z/w}). \tag{3''}$$

For any value of z which is not too small (i.e. excluding the very beginning of the decay curve), and for values of ΔE large enough so that W is a very small number, there follows $\mathrm{e}^{-zw} \approx 1$ and $\mathrm{e}^{-z/w} \approx 0$ and therefore

$$I \cdot t \approx \frac{n_0 \kappa}{\Delta E}.$$

From fig. 1 one can deduce that the t^{-1} decay applies for $\Delta E/\kappa T \ge 6$ excluding, again, the very initial period of time.

3. Thermoluminescence

Thermoluminescence (TL) glow peaks have also been calculated assuming first-order kinetics and a continuous distribution of trapping states uniformly distributed over a finite energy range $\Delta E = E_2 - E_1$. The expression for $I(T)$ under these circumstances is

$$I(T) = \frac{n_0 s}{\Delta E} \int_{E_1}^{E_2} \mathrm{e}^{-E/\kappa T}$$

$$\times \exp\left[-\frac{s}{\beta}\int_{T_0}^{T}\mathrm{e}^{-E/\kappa T'}\mathrm{d}T'\right]\,\mathrm{d}E, \tag{4}$$

where β is the (constant linear) heating rate.

In contrast to the phosphorescence energy integral this integration cannot be performed analytically. Two alternative methods have been utilized in order to calculate $I(T)$ using eq. (4). One approach is to divide ΔE into 50 or 100 intervals, calculate the first order glow curves and add them up at each temperature, ending up with the total glow curve for the entire energy distribution (see also ref. [9]). The other approach consists of using the asymptotic series for evaluating the

temperature interval in eq. (4) (see e.g. the appendix in refs. [13,3]),

$$\int^T e^{-E/\kappa T'}\, dT'$$

$$\simeq T \exp(-E/\kappa T) \sum_{n=1} (\kappa T/E)^n (-1)^{n-1} n!$$

(5)

Thus eq. (4) can be approximated

$$I(T) \approx \int_{E_1}^{E_2} \exp\left[-\frac{E}{kT} - \frac{s\kappa T^2}{\beta E} e^{-E/\kappa T} \right.$$

$$\left. \times \left(1 - \frac{2\kappa T}{E} + \frac{6\kappa^2 T^2}{E^2} - ... \right) \right] dE.$$

(6)

The first term in the square bracket is much larger than the second term. Furthermore the main variation of the second term is through the exponential factor $e^{-E/\kappa T}$. Thus, an approximation in which the second term is simply written

$$\frac{-s\kappa T^2}{\beta E_0} e^{-E/\kappa T} \left(1 - \frac{2\kappa T}{E_0} + ... \right),$$

is not expected to effect the results very much. With this change the integration is straightforward resulting in

$$I(T) = \frac{\kappa T}{\gamma \Delta E} \left[\exp(-\gamma\, e^{-E_2/\kappa T}) \right.$$

$$\left. - \exp(-\gamma\, e^{-E_1/\kappa T}) \right],$$

(7)

where

$$\gamma = \frac{s\kappa T^2}{\beta E_0} \left(1 - \frac{2\kappa T}{E_0} + \frac{6\kappa^2 T^2}{E_0^2} - ... \right).$$

Using these two approximations in deriving $I(T)$ resulted in practically the same curves provided that ΔE was subdivided into a large enough number of intervals in the first method and for $\Delta E \lesssim 0.1$ eV. Once this was established, the second method using eq. (7) was usually employed since it was appreciably less time-consuming. However, for $\Delta E > 0.1$ eV only the method of dividing ΔE into a large number of sub-ranges was judged to yield satisfactory results. An example of the calculated results is shown in fig. 3. Curve (a) represents the calculated peak found with $\Delta E = 0.01$ eV. This peak looks very much
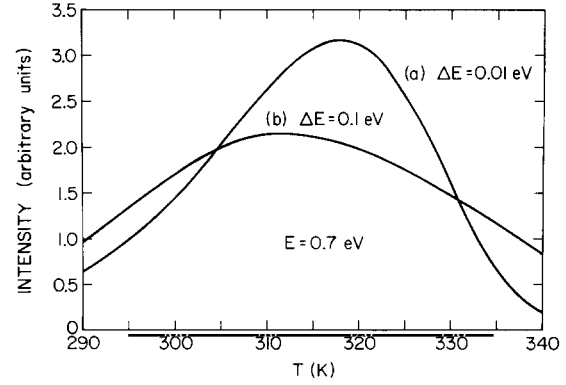

Fig. 3. Calculated glow curves for $n_0 = 10^{10}$ cm^{-3}, $s = 10^{10}$ s^{-1}, $E_0 = 0.7$ eV, and (a) $\Delta E = 0.01$ eV, (b) $\Delta E = 0.1$ eV.

like a "normal" first-order peak as far as its symmetry properties are concerned. This should, of course, be expected due to the narrow energy range, i.e. $\Delta E/E = 1/70$. In curve (b), however, we have $\Delta E = 0.1$ eV for which $\Delta E/E = 1/7$. The resulting peak is much broader than that in curve (a). The peak became even broader for larger values of ΔE. As will be discussed below, this feature of the peak being broad, in particular at the high temperature half can be misinterpreted as indicating a second or higher order kinetics operating for a single trapping level. The peak shape characteristics have been studied by computing TL peaks with different values of the parameters E_0, ΔE and s. The shape factor $\mu_g = \delta/\omega$ where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$ where T_m is the maximum temperature and T_1 and T_2 the low and high half intensity temperatures respectively. It has been found that μ_g was rather strongly dependent on $\Delta E/E$ whereas the dependence on ΔE and E_0 separately was insignificant. For example, taking $E_0 = 0.7$ eV and $\Delta E = 0.1$ eV resulted in practically the same value of μ_g as $E_0 = 0.35$ eV and $\Delta E = 0.05$ eV. For a given value of $\Delta E/E_0$, the results for μ_g depended only weakly on the given values of the frequency factor s. The values of μ_g as a function of $\Delta E/E_1$ with s as a parameter are shown in fig. 4. The same results as a function of $\Delta E/E_0$ could of course also be shown. The reason for the chosen presentation will become evident in the discussion below. The solid line represents the values of μ_g for $s = 10^{10}$ s^{-1}
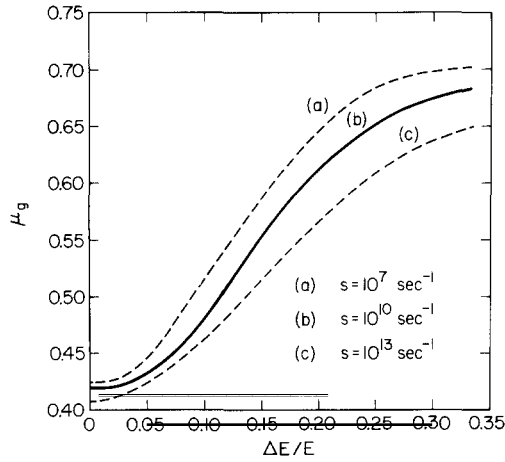
Fig. 4. The shape factor $\mu_g = \delta/\omega$ as a function of $\Delta E/E_1$ for curves calculated with $E_0 = 0.7$ eV, $n_0 = 10^{10}$ cm^{-3}, and $s = 10^7$ s^{-1} in curve (a), $s = 10^{10}$ s^{-1} in (b), and $s = 10^{13}$ s^{-1} in (c).

(curve b), whereas curves (a) and (c) show the dependence of μ_g on $\Delta E/E_1$, for $s = 10^{13}$ s^{-1} and $s = 10^7$ s^{-1}, respectively.

Two methods have been widely used to determine the activation energy distribution. These are the "initial rise" method, and the Hoogenstraaten method of various heating rates [14]. In the original initial rise method, the logarithm of the TL-intensity I is plotted as a function of $(1/T)$, in the low-temperature region of the glow curve. The activation energy is evaluated from the slope of this curve which is expected to be $-E/\kappa$. Gobrecht and Hofmann [10] further developed the technique by using subsequent heating and cooling cycles to obtain the "spectroscopy of traps". As shown by Rudolf et al. [9], this procedure does not yield accurately the correct continuous distribution. Halperin et al. [15] improved the method by plotting $\ln(I/n^b)$ vs. $1/T$, where n is the concentration of electrons still remaining trapped at temperature T, and b is the effective order of kinetics (which in our case is unity). We have used this improved initial rise method for our simulated glow curves although, strictly speaking, the correction of dividing by n (in the first-order case) was devised for TL peaks resulting from a discrete energy level. Figure 5 depicts some representative results. Curve (a) is seen to be a straight line

through a very broad temperature range, which directly results from the very narrow energy range used in this case, $\Delta E = 0.01$ eV for $E_0 = 0.7$ eV. The activation energy evaluated from the slope is $E_e = 0.715$ eV, within 2% of the mean value. As shown below, it is evident that having $E_e > E_0$ has to do with a slight inaccuracy of the method of evaluating the activation energy rather than being a result of the energy range involved. In all the cases where larger values of ΔE were utilized in the simulation of the TL peak, the slope-evaluated effective energy E_e was found to be smaller than the actual average energy E_0. Curve (b) is the plot on the same scale of I/n when the simulated curve is calculated with the same s and E_0 parameters but $\Delta E = 0.1$ eV. After an initial straight-line portion, the curve bends over as if the order of kinetics was larger than unity, although at higher temperatures (lower values of $1/T$) the slope increases again. The activation energy evaluated from the initial straight line is 0.66 eV. In curve (c), the results for $\Delta E = 0.2$ eV are shown. The bending over of the curve occurs earlier in $1/T$, but the general behavior is similar to that in curve (b). The slope of the initial straight line portion yields an activation energy of $E_e = 0.603$ eV. In this example as well as in other cases studied, the
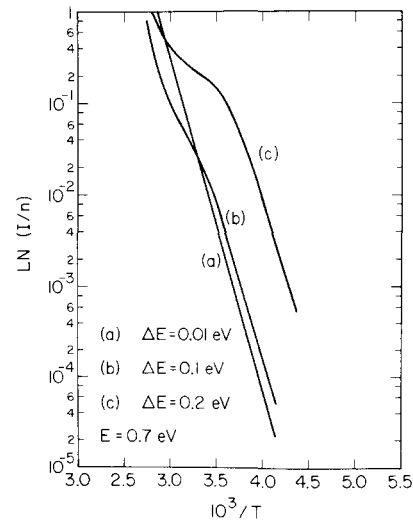

Fig. 5. Plot of $\ln(I/n)$ as a function of $1000/T$. The given parameters are $s = 10^{10}$ s^{-1}, $n_0 = 10^{10}$ cm^{-3}, $E_0 = 0.7$ eV, and (a) $\Delta E = 0.01$ eV, (b) $\Delta E = 0.1$ eV, and (c) $\Delta E = 0.2$ eV.
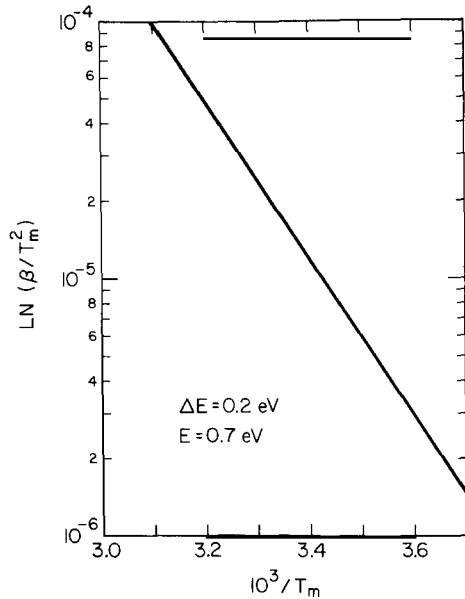
Fig. 6. Plot of $\ln(\beta/T_{\rm m}^2)$ vs. $1000/T_{\rm m}$ for calculated glow curves with $s = 10^{10}$ s^{-1}, $n_0 = 10^{10}$ cm^{-3}, $E_0 = 0.7$ eV, $\Delta E = 0.2$ eV, and heating rates varying by factors of 2 from 0.125 K/s to 8 K/s.

evaluated energy $E_{\rm e}$ is in better agreement with the low end of the distribution E_1 rather than with E_0, the average energy.

The slope of $-E_{\rm e}/k$ which yields the activation energy has more easily been evaluated by the use of linear regression of the points of $\ln(I/n)$ vs. $1/T$. As a by-product, one can get the y-intercept which, in the simple single-level cases corresponds to $\ln(\beta s)$. The value obtained for βs in the present study leads to an effective value of $s_{\rm e}$ which appears to be always lower than the value used in generating the glow curves. This deviation from the value of s used in the calculated glow curve increases for larger values of $\Delta E/E_0$. Typically,

for $\Delta E = 0.2$ eV and $E_0 = 0.7$ eV, the effective value found was $s_{\rm e} = 2 \times 10^{-9}$ s^{-1}. Although always on the lower side, $s_{\rm e}$ is a reasonably good estimate for s, at least to within an order of magnitude.

The general heating rate method consists of running a number of glow curves using different heating rates β for samples given the same excitation dose. One plots $\ln(\beta/T_{\rm m}^2)$ vs. $1/T_{\rm m}$ and evaluates the activation energy from the slope which is expected to be $-E/\kappa$. Figure 6 shows such a graph found by using different heating rates in the simulated glow peaks with $E_0 = 0.7$ eV and $\Delta E = 0.2$ eV. The line obtained has a slope yielding $E_{\rm hr} = 0.603$ eV. For $\Delta E = 0.1$ eV and $\Delta E = 0.01$ eV straight lines were also obtained using semi-log plots yielding $E_{\rm hr} = 0.667$ and $E_{\rm hr} = 0.707$, respectively.

4. Discussion

Phosphorescence decay curves and thermoluminescence glow curves have been numerically simulated assuming first-order kinetics and a uniform continuous distribution of activation energies in the energy range ΔE centered on energy E_0. In the case of phosphorescence, the required width ΔE necessary for a broad energy distribution in order to obtain the t^{-1} Randall and Wilkins result, has been tested. Although Randall and Wilkins obtained the t^{-1} behavior by assuming a uniform continuous distribution from zero to infinity we found practically the same behavior for a distribution with a width of $\Delta E = 0.2$ eV with $E_0 = 0.7$ except for times at the very early stages of the process. The t^{-1} behavior extends

Table 1
Shape parameters and calculated activation energies from simulated glow curves relating to a truncated uniform distribution of activation energies

E (eV)	ΔE (eV)	T_1 (K)	$T_{\rm m}$ (K)	T_2 (K)	$\mu_{\rm g}$	E_τ (eV)	E_ω (eV)
0.7	0.01	301.1	317.9	330.2	0.423	0.699	0.697
0.7	0.05	298.5	316.3	331.3	0.457	0.691	0.707
0.7	0.10	291.4	311.4	336.3	0.555	0.684	0.672

further into the early stages as ΔE increases beyond 0.2 eV.

It would appear that for activation energy distributions more or less bell-shaped (including the truncated uniform distribution), the t^{-1} dependence sets in when the ratio $\kappa T/\Delta E$ is less than about 0.15. On the other hand narrow distributions with $\kappa T/\Delta E$ greater than about 1 or 2 result in essentially exponentially decaying phosphorescence with time.

It is interesting to compare the present results for wide distributions generating the essentially t^{-1} behavior of phosphorescence with those obtained by Avouris and Morgan who reported experimental phosphorescence decay behavior in Zn_2SiO_4: Mn as well as theoretical results based on a model of electrons and holes recombining through tunneling from shallow traps or from excited states of deeper traps [11]. It would appear that one could distinguish between the tunneling and the continuum models by which direction the I^{-1} vs. t curve deviates from a straight line at early times. The tunneling model proposed by Avouris and Morgan [11] requires a downward or convex bending curve for small t. However, their experimental results yield a curve which bends upward or is concave at small t and therefore does not agree with their model. Rather, the observed behavior agrees better with the shapes generated in the present work involving simple first-order processes. It is to be noted, however, that our treatment is based on a symmetric distribution of activation energies. In this respect, it seems plausible that had we taken another symmetric distribution, e.g. a Gaussian, a similar time dependence would have resulted. As for asymmetric distributions, the expression given by Randall and Wilkins has been mentioned in the introduction namely $I \propto t^{-(\alpha\kappa T+1)}$ for an exponential distribution with $N_E = A e^{-\alpha E} dE$. This distribution may yield deviations from the straight line that curves either way depending on whether α is positive or negative. Although this latter possibility (i.e. $\alpha < 0$) might appear unlikely, it could hold for a limited range of activation energies. It therefore seems that it is not possible unambiguously to tell the trap distribution model from the tunneling one by merely studying the decay curves. Considering this prob-

lem from a slightly different point of view, it appears that the near-t^{-1} time dependence is directly related to the fact that we sum different exponential decay curves over a wide range of time constants. This is also the case in the tunneling model where the different time constants are related to the different distances between the donor and acceptor. These spacings are usually imagined to span a large range of distances. In the energy distribution model, the different constants in the time-dependent exponents are related to the different activation energies. In fact, one can think of other mechanisms involving different time constants such as a quasi-continuum of recombination centers with varying recombination probability which could also result in a near-t^{-1} dependence.

Concerning the TL glow curves appropriate for a broad range of activation energies, it is obvious from the numerical calculations that the main result is the broadening of the glow peak particularly that of the high temperature half. It is to be emphasized that our present treatment is limited to the first-order kinetics which means that possible retrapping is assumed to be negligible. Work is underway now which includes such retrapping. This is significantly more complicated since once retrapping is allowed, a free carrier can retrap to any level in the continuous range, not necessarily only to one at the same energy as that at the site it left. Furthermore, the features described above of broadening the glow curve due to the distribution (as compared to a single level), namely, the broadening of the high temperature half of the curve, is similar to the effect of retrapping on the glow peak. Therefore, the occurrence of a continuum of trapping states would result in a peak in which the presence of retrapping may be masked by the features related to the continuous distribution of energies. It is interesting to note that experimental data resembling curves (b) and (c) of fig. 5 have been successfully fitted assuming a single trap site with no spread in activation energies but with the presence of retrapping [16]. This further emphasizes the ambiguities present in TL processes.

Applying the simple methods for evaluating the activation energy to the simulated peaks with a range of energies as described above tended to

yield values which were close to the lower end of the energy distribution. Concentrating on the broadest range of 0.2 eV reported above, and a mean energy $E_0 = 0.7$ eV, we found an activation energy of 0.603 eV for the modified initial rise method, 0.657 eV for the shape method based on the low temperature half of the glow peak and 0.603 eV for the various heating rates method. The main lesson to be learned is that if there is evidence of a distribution of activation energies, e.g. by the shape of the decay curve and by the breadth of the glow peak, in particular at the high temperature half, then the activation energy one evaluates is going to be on the low side of the distribution. This conclusion may, of course, vary somewhat with the details of the distribution, but it seems that such a general rule applies.

Finally, if one encounters a t^{-1} decay curve, the occurrence of a finite uniform distribution of activation energies should be considered. Particularly if this is accompanied by a TL glow curve which is unusually broad as indicated by the calculated shape factor μ_g with its corresponding value of the effective ratio $\Delta E/E_1$. In general, the initial rise activation energy should be evaluated, and if possible, the different heating rate analysis should be performed. These two measurements should yield a reasonable value of E_1. The width ΔE of the distribution can then be estimated from curves such as in fig. 4. As explained above, an estimate of the value of s can also be determined using the initial rise method. Using this value the evaluation of $\Delta E/E_1$ can be refined by moving to the left or right of the central curve shown in fig. 4 (with $s = 10^{10}$ s^{-1}).

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