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VALIDITY OF REPEATED INITIAL RISE

THERMOLUMINESCENCE KINETIC PARAMETER DETERMINATIONS*

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ABSTRACT

The validity of thermoluminescence (TL) analysis by repeated initial rise (initial slope) measurements has been studied by computer simulation. Thermoluminescence described by 1st Order, 2nd Order, General One Trap (GOT) and Interactive TL Kinetics was investigated. In the simulation each of the repeated temperature increase and decrease cycles contains a linear temperature increase followed by a decrease appropriate for "radiative" cooling, i.e. the latter is approximated by a decreasing exponential. The activation energies computed from the simulated emission are readily compared with those used to compute the TL emission. In all cases studied, the repeated initial rise technique provides reliable results only for single peak glow curves or for glow curves containing peaks that do not overlap and, if sufficiently separated, the lowest temperature peak in multipeak curves. Also the temperatures, or temperature cycles corresponding to "correct" activation energies occur on the low temperature side of the normal glow curve, often well below the peak temperature. A variety of misleading and/or incorrect "results" can be obtained when the repeated initial rise technique is applied to TL systems that produce overlapping peaks in the usual glow curve.

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1. INTRODUCTION

The initial rise and the repeated initial rise method for determining the activation energies associated with thermoluminescence (TL) has been evaluated by simulating this technique on a computer. The initial rise method is based on the fact, for a system with one glow peak, that the initial TL from a sample is well approximated by the equation $I(T) = \text{constant}[\exp(-E/kT)]$. This is based on the assumption that the change in trapped charge concentration during heating is small enough to legitimately assume that the trapped charge concentration is constant during the temperature excursion (Garlick and Gibson, 1948). The data from an initial rise measurement is usually used to obtain an activation energy, by constructing an Arrhenius plot. Furthermore, the approximation described above applies to all of the commonly used kinetics that describe TL emission. A repeated initial rise measurement, sometimes called a fractional glow measurement (Gobrecht and Hofmann, 1966), is the luminescence measured during repeated heating and cooling of a sample, with the maximum temperature increasing by some fixed amount (e.g. 5 or 10 K) for each successive cycle. To simulate a repeated initial rise measurement one computes the TL emission from specified kinetic equations using selected values for the activation energy, E , attempt to escape frequency, s , trapped charge concentration, n , initial trapped charge concentration, n_0 , etc. Thus, one knows in advance the parameter value(s), e.g. the activation energy, that should be reproduced by the repeated initial rise simulation. It is reasonable to conclude that the repeated initial rise method would apply to single peak glow curves but it is not apparent that it applies to TL systems containing overlapping glow peaks and/or those where retrapping is non-negligible.

As will be demonstrated, in some TL systems the repeated initial rise method supplies erroneous conclusions. In others, a mixture of correct and erroneous results is obtained. The validity of the repeated initial method was tested for TL systems described by 1st Order, 2nd Order, General One Trap (GOT), and Interactive TL Kinetics.

2. THERMOLUMINESCENT KINETICS

All the computations in this paper utilize the differential equation forms of the 1st Order, 2nd Order, General One Trap (GOT), and Interactive TL Kinetic equations. These are Equations (1)-(4), respectively,

$$-\frac{dn}{dt} = nse^{-E/kT} \quad (1)$$

$$-\frac{dn}{dt} = n^2s'e^{-E/kT} \quad \text{where } s' = s/N \quad (2)$$

$$-\frac{dn}{dt} = nse^{-E/kT} \left[1 - \frac{\sigma_t(N-n)}{\sigma_t n + \sigma_t(N-n)_t} \right] \quad (3)$$

$$-\frac{dn_i}{dt} = n_i s_i e^{-E/kT} - \sum_{j=1}^m n_j s_j e^{-E/kT} \left[\frac{\sigma_u(N_i - n_i)}{\sigma_t n_r + \sum_{j=1}^m \sigma_{t,j}(N_j - n_j)} \right] \quad (4)$$

$$\text{and } n_r = \sum_{j=1}^m n_j$$

where E is activation energy, s is attempt to escape frequency, n is the trapped charge (i.e. electron) concentration at time t, n_0 is initial trap charge (i.e. electron) concentration, k is Boltzmann's constant, T is absolute temperature (K), N is trap concentration, σ_t is the cross section for charge

trapping or retrapping, σ_r is the cross section for radiative (light emitting) electron-hole recombination at recombination centers, and m is the number of different types of electron traps.

The Interactive kinetics case used for all examples applies to a system which contains one type of recombination center (i.e. hole trap) and more than one type of charge trap (i.e. electron trap) which "compete" for thermally released electrons. Each electron-hole recombination at recombination centers creates one photon. If an electron is retrapped at an electron trap, light is not emitted but the electron may again be thermally released. An electron may be thermally released and retrapped many times before recombining with a hole at a recombination center. The parameters N_i , n_i , σ_i , s_i , and E_i are those described above but for the i th type of electron trap. Also, n_r is the trapped hole concentration (and equals the recombination center concentration in this model). The condition that n_r equals the sum of the trapped electron concentrations of each type of trap results from the requirement that the material be electrically neutral (i.e. the total number of trapped holes equals the total number of trapped electrons). A more detailed discussion of these equations and further references may be found in Levy (1984a,1984b).

Furthermore, to simulate the normally used linear temperature dependence, a linear relation between time and temperature is used. Specifically, $T = T_0 + \beta t$, where T_0 is the initial temperature and β is the heating rate (i.e. a constant). During each cycle the linear temperature increase is followed by radiative cooling approximated by a decreasing exponential. In other words, during cooling, $T = T_0 + (T_m - T_0)\exp[-Ct]$, where T_m is the highest temperature reached in each cycle, C is a constant, and time, t , is measured from the onset of cooling. The value of C chosen was based on the cooling rate observed in typical thermoluminescent measurements.

3. SIMULATION PROCEDURE

The TL kinetics for 1st Order, 2nd Order, General One Trap (GOT) and Interactive Kinetics were simulated on a Vax 11/785 Computer using a Fortran program and the differential equation solving routine, DIVPAG, from the IMSL Library (IMSL Inc. 1987). The TL emission curves were then computed using specified (i.e. known) parameter values. In all computations only E , the activation energy, was varied. Other parameters have the fixed values: $s = 10^{10}/\text{second}$, $N = 10^{16}/\text{cm}^3$, $n_0 = 10^{15}/\text{cm}^3$ for each trap, $\sigma_t/\sigma_r = \sigma = 0.1$, $\beta = 1^\circ\text{C}/\text{second}$, a starting temperature, T_0 of 300°K , and a cooling time constant C of 0.2 . Also, an integration time of 1 second/point was used. In each successive cycle the final temperature (T_m) was increased by a fixed increment, T_{inc} , which was set at 5 K. The differential equation solving routine DIVPAG is equipped with an internal test of the "accuracy" of the computation. This is a user selectable parameter called the "tolerance". For all computations reported the tolerance was set at 10^{-10} . It was demonstrated that this is adequate for the computations described here.

A typical set of repeated initial rise measurements is generated in the following manner. The desired kinetics, number of traps, and activation energy(ies) for the trap(s) are selected. To simulate a signal just large enough to emerge "out of the noise", the light output is numerically computed and retained in the calculation at all temperatures but is not included in the (simulated) data unless 1 part in a million of the total initial trapped charge is released in the time/temperature interval producing one data point (1 second/ 1°C). This condition was applied to all computed emission, i.e. the simulated TL. It emulates the response from a detector (i.e. a phototube)

during an actual measurement.

During the first cycle the light emission (i.e. the change in trapped charge concentration) is computed from 300 K until 0.1% of the trapped charge in the lowest temperature trap is released. The next higher temperature (in K) evenly divisible by T_{inc} (i.e. 5 K) is defined as T_{mo} , the maximum temperature of the first heating cycle. The portion of the computation, for the first heating cycle, that is used as simulated data on an Arrhenius plot lies between the temperature of the first point in which 1 part in a million of the total initial trapped is released and T_{mo} . After reaching T_{mo} the temperature is assumed to decrease exponentially to room temperature. T_m , the maximum temperature in each cycle, is given by $T_m = T_{mo} + T_{inc}(n - 1)$ where T_{mo} and T_{inc} are defined above and n is the heating cycle number (e.g. where $T_{inc} = 5$, $n = 1$ implies $T_m = T_{mo}$, $n = 2$ implies $T_m = T_{mo} + 5$, etc...). The emission during cooling is computed, retained in the calculation, but not included in the "results". The emission during cooling in the range $T = T_o$ to $T_o + 5$ was assumed to be negligible and was not computed. These steps describe the first heating cycle. The cycling procedure is continued until less than 0.5% of the total initial trapped charge remains trapped.

Arrhenius Plots (Fig. 1) were constructed for each heating cycle. The activation energy, E_T , was calculated from a portion of the data curve that is midway between the minimum and maximum of the intensity values (in the usual log plot) and usually includes a one order of magnitude portion of the data. The temperature assigned to the computed E_T value is the temperature at the midway point.

This choice, for the temperature assigned to each heating cycle, appears to correspond to that used in some published initial rise measurements, e.g. see Strickertsson, 1985. It could be argued that the temperature assigned to each

cycle should be the initial temperature. If the temperature change in each cycle is small this would not change the published results as well as those given below in any important way. A list of the cases investigated and a summary of the results is contained in Table 1.

4. RESULTS AND DISCUSSION

Typical results for single trap, i.e. single peak glow curves for 1st Order, 2nd Order and GOT kinetics (curves) are shown in Figures 2, 3, and 4. In all 3 cases the computed E_T values appear as a plateau and agree with the value used to compute the TL emission. However, the temperature for each computed series for 1st order and GOT kinetics is shifted to the lower temperature side of the corresponding normal glow curve. This was observed by Strickertsson (1985) who attributed the shift to an effective lowering of the heating rate due to the repetitive heating by the repeated initial rise technique. However, it is apparent that this shift is a property of the method and is not an artifact. Also, the shift might be slightly exaggerated by the method used to assign temperatures to each cycle. The agreement between the selected (i.e. known) E value and the computed E_T values is very good. This can be regarded as a verification of the computer model. Also, the existence of a well defined plateau supports the use of the repeated initial rise technique but, as explained later, only for single peak glow curves.

The results obtained by simulating a 1st order system with three types of traps, with activation energies of 1.0, 1.25, and 1.5 eV, are shown in Fig. 5. The computed E_T values agree with the known starting values and appear in the simulations as well defined plateaus with sharp transitions between plateaus. However, the plateaus occur at temperatures that are distinctly lower than the

corresponding glow peaks for 1st order and GOT kinetics. In the 2nd order case, Fig. 6, the initial rise activation energies are in good agreement in value and occur at temperatures corresponding to the peak of the normal glow curve. However, the transition from one plateau, with one activation energy, to the next is not sharply delineated. In the interactive case (Fig. 7) the computed E_T values agree with the known values for the 1.0 eV and 1.5 eV peaks. This is not true for the 1.25 eV peak (Fig. 7). Furthermore, the simulation contains two plateaus that do not correspond to any trap in the system. In general, in the interactive kinetic case, both the computed E_T values and plateau positions are inconsistent with known E values and the temperature positions of the normal glow peaks, except for the lowest temperature peak of the system. Thus, the electron retrapping kinetics plays a crucial role in the application of the repeated initial rise method. In an actual measurement the kinetics would have to be known to use this technique reliably.

Simulations for 1st order, 2nd order, and interactive kinetics for a system of 5 traps with activation energies of 1.0, 1.1, 1.2, 1.3, and 1.4 eV are shown in Figs. 8 - 10. The 1st order and interactive systems give rise to inflection points (i.e. changes in the rate of change of slope) in the plots of activation energy versus temperature but well defined plateaus (i.e. constant E_T values) are not obtained. The dominant pattern of the curves is a gradual increase in activation energy with temperature. In the second order kinetics case the E_T values change smoothly from the lowest value (i.e. 1.0 eV) to the highest value (i.e. 1.4 eV). The existence of the intermediate traps is not apparent in the simulated initial rise analysis.

This model is identical, at least in principle, with one of the methods used by Strickertsson (1985) in which the sample is heated and allowed to cool

to room temperature without controlling the temperature during cooling. An important variation on this technique is obtained when the temperature is controlled during cooling (e.g. decreasing the temperature linearly). If a linear temperature decrease is employed and if the trapped charge concentration did not change significantly the curves for heating and cooling should be nearly identical. It has been stated that this is a necessary condition for the repeated initial rise method to apply (Gobrecht and Hofmann, 1966). However, it should be emphasized, that even if this condition is satisfied, if there are different types of electron traps with different activation energies (and/or s values) that release electrons at the same temperature the activation energy obtained would be an (unspecified) average value weighted by the relative contribution from each type of trap. A study, similar to that reported here, in which the linear temperature rise is followed by a linear temperature decrease, is underway.

5. SUMMARY

The repeated initial rise (initial slope) technique for determining the activation energy(ies) associated with TL emission has been studied by simulating this process on a computer. TL emission that would normally give rise to both single and multiple peak glow curves described by 1st, 2nd, GOT and Interactive kinetics were investigated. For each case studied, Arrhenius plots were constructed for each temperature cycle. An activation energy, E_T , was computed from the central portion of each Arrhenius plot curve and assigned the temperature, T , of the midpoint of the curve. In turn, the activation energy values, E_T , were superimposed on normal (continuous) glow curves, for the same system, computed with the same heating rate. Thus the activation energy, E_T , vs temperature plots and the normal glow curves have

the same temperature axis. The principle results include:

(1) The activation energies, E_T values, obtained from all single peak glow curves are in good agreement with the known values. However, on the superposition plots the reliable activation energies (as indicated by plateaus of constant value) usually occur only on the low temperature side of the normal glow peak. Occasionally, the signal has disappeared--the trap is empty--at temperatures below the peak of the normal glow curve.

(2) Multipeak systems:

A) The "correct" activation energy was always obtained for the lowest temperature peak, provided that it is sufficiently separated from the other peaks.

B) In some systems reasonable energies are obtained for the lowest and highest temperature peaks but not the intermediate temperature peak(s).

C) Occasionally there are indications of activation energies, e.g. a plateau of constant activation energies, that do not correspond to any of the energies inserted into the simulations. In other words, entirely misleading values can be obtained from repeated initial slope measurements.

D) In cases where the glow peaks are widely separated reasonable values can be obtained from multipeak curves.

E) Systems with overlapping glow peaks are not likely to be analyzable by the repeated initial rise method. For example, systems with overlapping peaks in normal glow curves may yield a curve of activation energy vs temperature that suggests there is a continuous distribution of energies. If the system contains a "plateau" of activation energies they may not correspond to any actual energy and/or occur at temperatures other than those corresponding to peak temperatures in normal glow curves.

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TABLE I
CASES INVESTIGATED AND RESULTS

No. of peaks (Energy, eV)	Kinetics	Results
1 (1.0)	1st order	good E value agreement, See Note 1
1 (1.0)	2nd order	good E value agreement
1 (1.0)	GOT	good E value agreement, see Note 1
3 (1.0, 1.25, 1.5)	1st order	good E value agreement, see Note 1
3 (1.0, 1.25, 1.5)	2nd order	good E value agreement, see Note 2
3 (1.0, 1.25, 1.5)	Interactive	good E value agreement for 1st and 3rd peaks, not 2nd peak
3 (1.0, 1.1, 1.2, 1.3, 1.4)	1st order	See Notes 2 and 3
5 (1.0, 1.1, 1.2, 1.3, 1.4)	2nd order	See Notes 2 and 3
5 (1.0, 1.1, 1.2, 1.3, 1.4)	Interactive	See Notes 2 and 3

Note 1: The computed series of E_T values lies to the low temperature side of the normal glow peak.

Note 2: The transition of E_T values from one plateau to the next is not sharp.

Note 3: The computed E_T values agree only for the lowest temperature peak.

FIGURE CAPTIONS

Fig. 1. Arrhenius plot for a typical initial rise measurement. The section between the arrows is used to determine the initial rise activation energy, E .

Fig. 2. Glow curve computed with 1st order kinetics and specified activation energy, E , of 1.0 eV. Also shown are the computed initial rise measurements and the computed initial rise E_T values. Both plots have the same temperature scale. The computed E_T values agree well with the known E value. However, in this case, the computed E_T series spans the normal glow peak.

Fig. 3. Glow curve computed with 2nd order kinetics and specified activation energy, E , of 1.0 eV. Also shown are the computed initial rise measurements and the computed initial rise E_T values. Both plots have the same temperature scale. There is good agreement in both value and temperature between the selected (i.e. known) E value and the computed E_T values.

Fig. 4. Glow curve computed with general one trap (GOT) kinetics with selected activation energy, E , of 1.0 eV. Also shown are the computed initial rise measurements and the computed initial rise E_T values. Both plots have the same temperature scale. There is good agreement between the selected (i.e. known) E value and the computed E_T values. However, the computed E_T series lies on the low temperature side of the normal glow peak.

Fig. 5. Computed glow curve describe by 1st order kinetics with selected activation energies of 1.0, 1.25, and 1.5 eV. Also shown are the computed

initial rise measurements, the computed initial rise E_T values, and the individual glow peaks. All plots have the same temperature scale. The computed E_T values agree with the known starting values and are distributed in well defined plateaus with sharp transitions. However, the plateaus are shifted to the low temperature side of the corresponding glow peak.

Fig. 6. Computed glow curve described by 2nd order kinetics with selected activation energies of 1.0, 1.25, and 1.5 eV. Also shown are the computed initial rise measurements, the computed initial rise E_T values, and the individual glow peaks. All plots have the same temperature scale. The computed E_T values are in good agreement with the known E values. However, the transition from one plateau to the next is not sharply defined.

Fig. 7. Computed glow curve described by Interactive kinetics with selected activation energies of 1.0, 1.25, and 1.5 eV. Also shown are the computed initial rise measurements, the computed initial rise E_T values. All plots have the same temperature scale. The computed E_T values agree with the known E values for the 1.0 and 1.5 eV peaks but do not agree for the 1.25eV peak. Note particularly that there are two plateaus which do not correspond to any specified E values. Furthermore, the plateaus are shifted to the low temperature side of the corresponding glow peak.

Fig. 8. Computed glow curve described by 1st order kinetics with selected activation energies of 1.0, 1.1, 1.2, 1.3, and 1.4 eV. Also shown are the computed initial rise measurement, the computed initial rise E_T values, and the individual glow peaks. All plots have the same temperature scale. The E_T values gradually increase in value with temperature and inflection points

replace well defined plateaus.

Fig. 9. Computed glow curve described by 2nd order kinetics with selected activation energies of 1.0, 1.1, 1.2, 1.3, and 1.4 eV. Also shown are the computed initial rise measurement, the computed initial rise E_T values, and the individual glow peaks. All plots have the same temperature scale. The E_T values gradually increase with temperature from 1.0 eV to 1.4 eV.

Fig. 10. Computed glow curve described by Interactive kinetics with selected activation energies of 1.0, 1.1, 1.2, 1.3, and 1.4 eV. Also shown are the computed initial rise measurement, the computed initial rise E_T values. All plots have the same temperature scale. The E_T values gradually increase with temperature and well defined plateaus are replaced by inflection points.

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FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

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FIGURE 10

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