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Evaluated thermoluminescence trapping parameters—What do they really mean?



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HIGHLIGHTS

- Double TL peak may look like a single peak.
- Simulated double peak analyzed by peak-shape methods and by deconvolution.
- Determination of effective activation energies and frequency factors.
- Effect of anomalous stability predicted.

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ABSTRACT

The main two trapping parameters in thermoluminescence (TL), the activation energy and the frequency factor, are often calculated and used for the evaluation of the stability of the TL signal at a given temperature. In several cases, “anomalous” values of these parameters, either very high or very low have been reported in the literature. In practically all of these cases, the values reported have been recognized to be effective values which resulted from some special circumstances related to the specific materials in hand. Obviously, these effective values are not associated directly with the real rate of thermal release of carriers from traps at the ambient temperature, prior to heating, and therefore, they do not indicate the real decay time of the TL signal or, in other words, the stability of the signal which may be used in TL dosimetry or dating of archaeological or geological samples. In the present paper, we discuss briefly some of these cases and add, in more detail, a rather elementary situation of very low effective activation energy and frequency factor. A model with two trapping states and one kind of recombination center is used and the simulation includes the numerical solution of the relevant sets of coupled differential equations in the three stages of the measurement, namely, excitation, relaxation and heating for a given set of the trapping parameters. The parameters are chosen in such a way that two overlapping TL peaks occur, which look together like a single first-order peak, but with anomalously low evaluated effective activation energy and frequency factor. Implications regarding the possible results in glow curve deconvolution are discussed.

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1. Introduction

In the study of thermoluminescence (TL), one may be interested in the values of the relevant trapping parameters. These parameters and the relation between them are of importance in determining the temperatures of the TL peaks, their dose dependence as well as

other properties, in particular their stability at ambient temperature. The main parameters mentioned in the literature are the activation energy, the escape frequency factor and the recombination and retrapping probability coefficients. The activation energy has to do with the energy required to release thermally a trapped electron into the conduction band. As for the frequency factor, according to Mott and Gurney (1948), the frequency factor s (s^{-1}) should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons. Also mentioned a lot

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in the literature is the order of kinetics of the peak; whereas first- and second-order kinetics have rather simple physical meaning, the intermediate order cases are always heuristic simplified presentations of more complex situations determined by all the relevant trapping parameters.

A number of methods for evaluating the basic trapping parameters from a TL peak are based on the peak-shape. A simple example (see [Chen, 1969](#)), yielding the activation energy for a first-order peak is

$$E = 2.52kT_m^2/\omega - 2kT_m, \quad (1)$$

where T_m is the temperature at the maximum and $\omega = T_2 - T_1$, the full width at half intensity and where T_1 and T_2 are, respectively, the low and high half-width temperatures and k (eV/K) is the Boltzmann constant. Note that the order of kinetics of a peak is usually determined by its symmetry factor, defined as

$$\mu_g = \delta/\omega, \quad (2)$$

where $\delta = T_2 - T_m$.

As shown by [Randall and Wilkins \(1945\)](#), once the activation energy of a first-order peak is determined, the frequency factor can be easily determined by using the maximum condition

$$s = \frac{\beta E}{kT_m^2} \exp(E/kT_m), \quad (3)$$

where β (K/s) is the constant heating rate. In the present work, we discuss some difficulties in the use of conventional peak-shape and curve fitting in evaluating the parameters, in particular in cases where two or more TL peaks occur in close vicinity to each other. Previously presented cases of very high apparent activation energy and non-physically high frequency factor, the models of which are based on the concept of competition, will briefly be mentioned ([Chen and Hag-Yahya, 1996](#); [Chen and Pagonis, 2014](#)). The effect of anomalous fading has also been explained in the past by a similar model of competition ([Chen and Hag-Yahya, 1997](#)). In the present work, we demonstrate, using numerical simulations, that very low effective values of the activation energy and frequency factor may be evaluated due to the occurrence of two or more TL peaks in close vicinity to each other. When this situation takes place, an apparent anomalous stability may be deduced. Also will be discussed the possible implications on the results obtained when numerical deconvolution of a glow curve is used for separating individual glow peaks and determining their trapping parameters.

2. Previous work on anomalous effective activation energies and frequency factors

As pointed out above, according to [Mott and Gurney \(1948\)](#), the frequency factor s should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons. Indeed, many results reported by various authors over the years gave values of s in the range of 10^{10} – 10^{13} s⁻¹. In some cases, anomalously high values of the frequency factor, accompanied by high values of the activation energy, were reported. [Taylor and Lilley \(1978\)](#) reported a frequency factor of 2×10^{20} s⁻¹ and an activation energy of 2.06 eV of peak V of LiF:Mg, Ti (TLD-100). Even larger values were reported by [Gorbics et al. \(1967\)](#) and by [Pohlit \(1969\)](#). [Fairchild et al. \(1974\)](#) suggested that the kinetics of this peak and other peaks with unusually large s might be complicated and the apparent first-order behavior is an approximation of a more complex kinetics

situation. One should note that peak V in LiF:Mg, Ti is part of a complex glow curve, usually separated by some kind of deconvolution.

[Chen and Hag-Yahya \(1996, 1997\)](#) presented a model of one trap and three recombination centers, one radiative and two non-radiative, to explain the possibility of high activation energy and very high frequency factor. They wrote the relevant sets of simultaneous differential equations for the excitation and heating stages and solved them numerically. As a result of the competition of the two radiationless centers, the apparent curve which simulates the measurable TL peak looks like a very narrow first-order peak. With regard to Eq. (1), this means that ω is very small and, as a result, the apparent activation energy is very high, around twice as large as the value inserted into the simulations. Once this high value is inserted into Eq. (3), the effective frequency factor is many orders of magnitude higher than the one used for the simulation. In an example given by [Chen and Hag-Yahya \(1996\)](#), the inserted parameters are $E = 1.2$ eV and $s = 2.5 \times 10^{11}$ s⁻¹ and the evaluated parameters are $E_{eff} = 2.24$ eV and $s_{eff} = 9.3 \times 10^{21}$ s⁻¹. [Mandowski \(2006\)](#) has offered another possible explanation to the occurrence of very high frequency factors and high activation energies in first-order-shaped TL peaks, which is based on the concept of cascade detrapping (CD).

In the literature, there are also reports on very small frequency factors, accompanied by small activation energies. [Haake \(1957\)](#) reported results of activation energies and frequency factors of TL in ZnS·ZnO-Cu, Pb, Cl and ZnS-Cu, Cl, in which values of the frequency factor between 1 and 2×10^3 s⁻¹ were found. He also mentions previously found values of the frequency factor of TL in ZnS determined by [Hoogenstraaten and Klasens \(1953\)](#) and [Dropkin \(1954\)](#), in which the frequency factor s was found to be between 300 and 5×10^4 s⁻¹, again non-physically low values. [Hickmott \(1972\)](#) studied a TL peak at ~380 °C in sputtered SiO₂ films and found an activation energy of $E = 0.66$ eV and a frequency factor of $s = 10^4$ s⁻¹. Unusually low values of the activation energy and frequency factor have been reported for the associated effect of thermally stimulated conductivity (TSC). [Bräunlich \(1967\)](#) and [Sunta et al. \(1999\)](#) pointed out that within the one-trap-one-recombination-center model (OTOR), if retrapping is strong and if the traps are filled to saturation, the standard initial-rise method as well as the peak-shape methods and glow peak fitting yield very low effective values of the activation energy. [Bräunlich \(1967\)](#) showed by numerical solution of the relevant set of differential equations that for saturated trap and $A_n/A_m \sim 1000$ where A_n is the retrapping probability coefficient and A_m the recombination probability coefficient, the initial-rise method yields a value of $\sim 0.43E$ where E is the real activation energy. [Sunta et al. \(1999\)](#) tested two models, OTOR and interactive multitrapping system (IMTS) in which the occurrence of an additional thermally disconnected deeper trap (TDDT) is assumed. Using peak shape methods (similar to Eq. (1) above) as well as a best-fit method, they found for cases of saturated trap and high retrapping low values of the effective activation energy down to $\sim 0.466E$. These authors have not dealt with the effective frequency factor, but it is obvious that in this case, the effective frequency factor found by Eq. (3) would be several orders of magnitude lower than the “real” one. Also should be mentioned the work by [Kierstead and Levy \(1991\)](#) who simulated a series of rather closely located TL peaks, due to a series of activation energies, and analyzed them using the repeated initial-rise method. Their conclusion is that the first and sometimes last activation energies in the series could be accurately determined. As for the other peaks, the analysis yielded a continuum of activation energies, usually in the same range as the inserted discrete ones.

3. Simulation with the present model

Fig. 1 depicts the energy level diagram of a model with two trapping states and one kind of recombination center. The meaning of the different magnitudes is given in the caption. The differential equations governing the flow of carriers during the excitation, relaxation and heating stage are as follows

$$\frac{dn_1}{dt} = A_{n1}n_c(N_1 - n_1) - s_1n_1 \exp(-E_1/kT), \quad (4)$$

$$\frac{dn_2}{dt} = A_{n2}n_c(N_2 - n_2) - s_2n_2 \exp(-E_2/kT), \quad (5)$$

$$\frac{dm}{dt} = B(M - m)n_v - A_mmn_c, \quad (6)$$

$$\frac{dn_v}{dt} = X - B(M - m)n_v, \quad (7)$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} + \frac{dn_v}{dt} - \frac{dn_1}{dt} - \frac{dn_2}{dt}. \quad (8)$$

Equations (4)–(8) govern the three stages of the process. During excitation, a constant ambient temperature is used (e.g. room temperature) and the value of X is associated with the dose-rate of the irradiation. In the second stage of relaxation, the temperature is still kept constant and X is set to zero. The final values of the concentration functions in the excitation stage are used as initial values of the relaxation stage and the process continues until n_c and n_v decrease to practically zero. Finally, the final values of the relaxation stage are used as initial values for the heating stage. The equations are solved, still with $X = 0$ using a linear heating function $T = T_0 + \beta t$ where T_0 (K) is the initial temperature, T (K) the variable temperature, t (s) is the time and β (K/s) is the constant heating rate. As implied from Fig. 1, the emitted TL light during heating is proportional to the rate of recombination of free electrons with trapped holes, i.e.

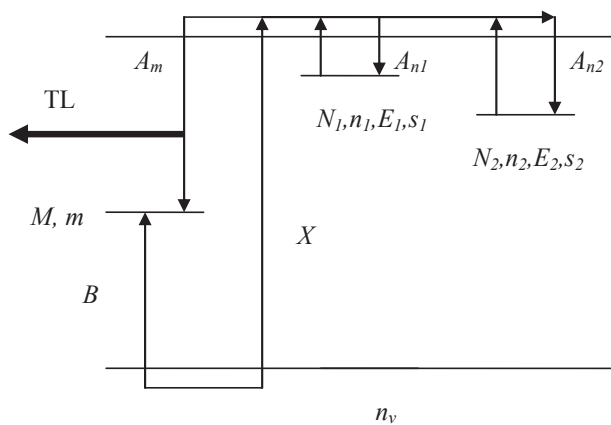


Fig. 1. Energy-level diagram of the model with two traps and one center. N_1 (cm^{-3}) and N_2 (cm^{-3}) are the concentrations of the shallow and deeper electron traps, respectively, with occupancies of n_1 (cm^{-3}) and n_2 (cm^{-3}). E_1 (eV) and E_2 (eV) are the activation energies and s_1 (s^{-1}) and s_2 (s^{-1}) are, respectively, the frequency factors. M (cm^{-3}) is the concentration of hole centers with occupancy of m (cm^{-3}). n_c (cm^{-3}) and n_v (cm^{-3}) are the instantaneous concentrations of free electrons and free holes. A_{n1} ($\text{cm}^3 \text{s}^{-1}$) and A_{n2} ($\text{cm}^3 \text{s}^{-1}$) are the trapping/retrapping probability coefficients. B ($\text{cm}^3 \text{s}^{-1}$) is the trapping probability coefficient of holes from the valence band into the centers and A_m ($\text{cm}^3 \text{s}^{-1}$) the recombination probability coefficient of free electrons with holes in centers. X ($\text{cm}^{-3} \text{s}^{-1}$) is the rate of production of electron-hole pairs by the irradiation, proportional to the dose rate.

$$I(T) = A_mmn_c. \quad (9)$$

3.1. Analysis with the peak-shape method

The results of such simulation with the chosen parameters given in the caption are shown in Fig. 2. Although the glow curve results from two traps, the curve looks like a single peak. Its symmetry factor μ_g is 0.425, typical of a first-order peak (see e.g., Chen, 1969). However, when Eq. (1) is used, one gets $E_{\text{eff}} = 0.78$ eV, significantly lower than the inserted values of $E_1 = 1.21$ eV and $E_2 = 1.39$ eV. Using Eq. (3) we get $s_{\text{eff}} = 5.72 \times 10^5 \text{ s}^{-1}$, orders of magnitude lower than the inserted values of s_1 and s_2 of 10^{12} s^{-1} . A note should be made regarding the choice of the parameters. As seen in the caption of Fig. 2, N_1 is somewhat larger than N_2 and A_{n1} is 100 times larger than A_{n2} . The reason for this choice is that had we chosen the probabilities of the two traps to be of the same order of magnitude, with the given choice of the other parameters, more or less equal numbers of electrons would have been trapped in the two traps. However during the heating stage most of the electrons released from N_1 would have been trapped in N_2 and, as a result, the second component would have been very significantly stronger than the first one. With the present choice of these parameters, the two components come out to have about the same size and therefore, the combined curve may look like a single broad peak. An interesting feature of the results of the simulation with the given set of parameters is shown in Fig. 3 in which the concentration of electrons in trap #2 is shown as a function of temperature. The unusual behavior here is that due to the given set of parameters, with electrons released thermally from trap #1 and retrapping several times before trapping into #2 or performing recombination, a sizeable number of electrons are preferably trapped in trap #2 during heating. Only at higher temperatures, the rate of release of electrons from trap #2 increases. The concentration of electrons in trap #2 reaches a maximum and starts to decrease at higher temperatures, showing a peak-shaped curve. The electrons released from trap #2 obviously contribute to the recombinations with trapped holes, thus contributing to the emitted TL light. Note that

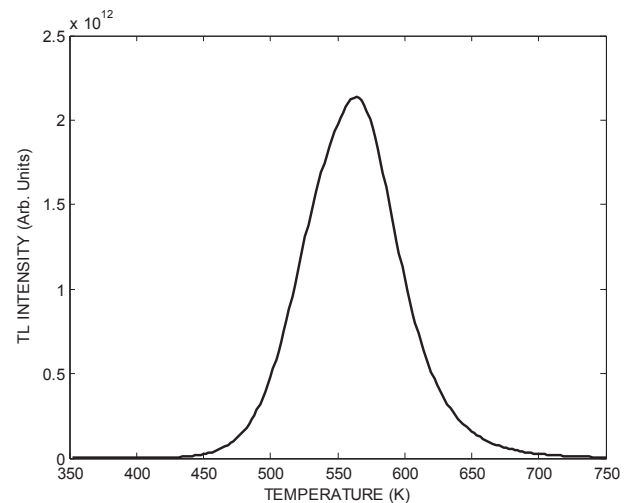


Fig. 2. Glow curve simulated with the three stages of excitation, relaxation and heating, using the simultaneous differential equations pertaining to the model in Fig. 1 and using the following set of parameters: $E_1 = 1.21$ eV; $E_2 = 1.39$ eV; $s_1 = 10^{12} \text{ s}^{-1}$; $s_2 = 10^{12} \text{ s}^{-1}$; $N_1 = 10^{17} \text{ cm}^{-3}$; $N_2 = 9 \times 10^{16} \text{ cm}^{-3}$; $M = 10^{19} \text{ cm}^{-3}$; $X = 10^{14} \text{ cm}^{-3} \text{ s}^{-1}$; $A_m = B = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$; $A_{n1} = 10^{-13} \text{ cm}^3 \text{ s}^{-1}$; $A_{n2} = 10^{-15} \text{ cm}^3 \text{ s}^{-1}$; the heating rate used was $\beta = 2$ K/s; the excitation time was $t_D = 1$ s and the relaxation time was 100 s.

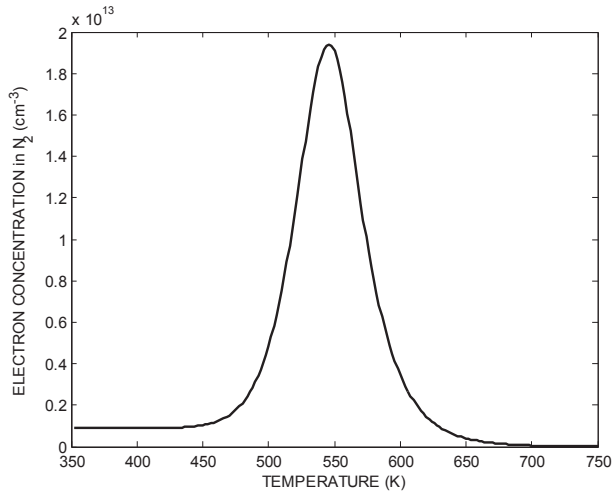


Fig. 3. The temperature dependence of the concentration of electrons in the trap N_2 in the simulation with the same parameters as in Fig. 2.

up to ~ 430 K, the concentration of electrons in N_2 is constant before electrons released from N_1 are trapped in trap #2 in significant numbers.

3.2. Analysis with glow-curve deconvolution

A method rather broadly used in the analysis of TL is the numerical deconvolution of the glow curve in hand. To describe it briefly (see e.g. Chen and McKeever, 1997, p. 272), let us assume that we know (or guess) the number of individual glow peaks present in the glow curve; the glow curve can be represented as

$$I(T) = \sum_{i=1}^{\nu} \alpha_i f_i(T), \quad (10)$$

where α_i are scaling constants, $f_i(T)$ is the chosen mathematical function of the individual glow peaks, e.g., first order or general order, and ν is the assumed number of individual peaks. The fitting parameters for each peak are α_i , s_i , E_i and possibly, the kinetic orders b_i . A total of 4ν fitting parameters are thus involved. One starts by guessing the values of the parameters, evaluates $I(T)$ by Eq. (10) and compares with the experimental glow curve. The parameters are now changed until a minimum error is reached between the evaluated and experimental signals. A rather popular routine used is the Marquardt nonlinear least squares fitting.

Let us consider a proposed fitting function

$$y = f(x, \mathbf{a}), \quad (11)$$

where $\mathbf{a} = (a_1, a_2, a_3, \dots, a_m)$ is a vector of the m adjustable parameters. We aim at the best fit of this function to the n data points $(x_1, y_1, \dots, x_n, y_n)$. We therefore wish to minimize the function

$$S = \sum_{i=1}^n (f(x_i, \mathbf{a}) - y_i)^2. \quad (12)$$

From here, we choose any minimization method and get the “best” values of the parameters, \mathbf{a}^* . It should be noted, however, that there is no known way of reaching a global minimum of such a function, and in most cases, the algorithm gets stuck in a local minimum. One way of dealing with this is to run the procedure several times with different initial guesses of the parameters and choose the best result.

In order to check the goodness of the final result, one often uses the Figure of Merit (FOM) defined as

$$FOM = \sum_{j_{\text{initial}}}^{j_{\text{final}}} \frac{100|f(x_i, \mathbf{a}^*) - y_i|}{\Delta}, \quad (13)$$

where Δ is the integral over the region of interest, from j_{initial} to j_{final} . FOM values of a few percent usually indicate acceptable fit.

We have analyzed the curve shown in Fig. 2 by two deconvolution programs, GlowFit prepared by Puchalska and Bilski (2005), which assumes that all the individual components are of first order and a program by Kitis et al. (1998) which allows the individual peaks to be of general order. In both cases, the procedure has been run several times with different initial guesses for the parameters, and the best results reached are reported. With GlowFit, we have tried to fit the “experimental” glow to one, two, three and four first-order components. The best result with $FOM = 1.40\%$ includes four components and is shown in Fig. 4. Note that for deconvolution into one, two and three components, the values of FOM are 14.40%, 5.76%, and 3.80%, respectively. These rather unexpected results will be discussed below. It should be mentioned that in very many papers, the routine use of deconvolution into first-order components only has been reported; a list of such papers can be found at: <https://scholar.google.com/scholar?q=GlowFit>.

The analysis of the same curve using the method allowing for general-order peaks is seen in Fig. 5. The agreement with the sum of two peaks seems to be quite convincing here. The parameters reached by the Kitis et al. (1998) method are given in the caption. The E and s values here are rather close to those used in the simulation, and the effective orders of kinetics of the first and second components are rather close to first and second orders, respectively. This point will also be discussed below.

3.3. Analysis with the $T_{\text{max}}-T_{\text{stop}}$ method

As pointed out before, the deconvolution method is sometimes limited in particular if one tries to separate rather close peaks. Since all minimization algorithms used for deconvolution do not guarantee global minima, the minimum reached is usually a local optimum only, which is dependent on the initial guess of the relevant parameters. One strategy used frequently is to repeat the runs several times with different starting guesses and choose the best

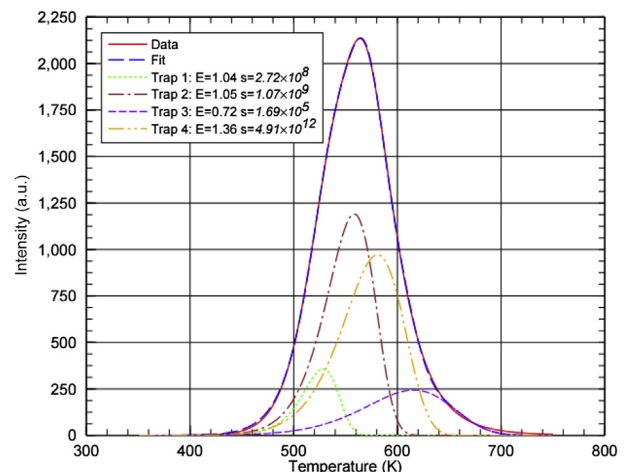


Fig. 4. Deconvolution of the curve given in Fig. 2 using GlowFit into four components. $E_1 = 0.72$ eV; $s_1 = 1.69 \times 10^5 \text{ s}^{-1}$; $E_2 = 1.04$ eV; $s_2 = 2.72 \times 10^8 \text{ s}^{-1}$; $E_3 = 1.05$ eV; $s_3 = 1.07 \times 10^9 \text{ s}^{-1}$; $E_4 = 1.36$ eV; $s_4 = 4.91 \times 10^{12} \text{ s}^{-1}$; $FOM = 1.40\%$.

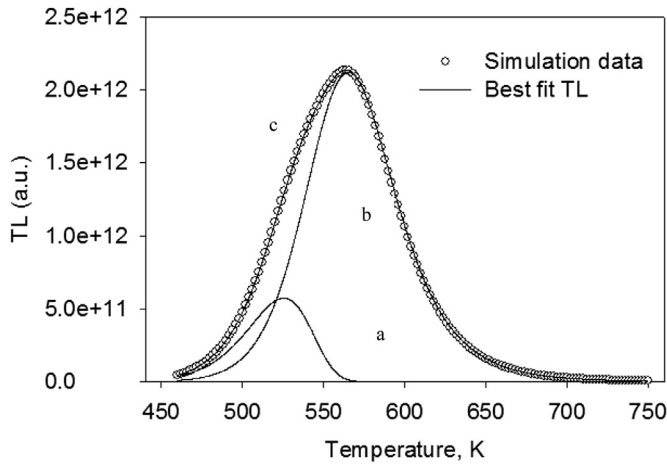


Fig. 5. Deconvolution of the curve given in Fig. 2 using the general-order based program into two components. $E_1 = 1.17$ eV; $s_1 = 5.65 \times 10^{11} \text{ s}^{-1}$; $T_{1max} = 525.1$ K; $b_1 = 1.0$; $E_2 = 1.43$ eV; $s_2 = 2.12 \times 10^{12} \text{ s}^{-1}$; $T_{2max} = 564.9$ K; $b_2 = 2.14$; $FOM = 2.4\%$. (a) and (b) are the first and second order components, respectively. In (c), the circles are the simulated data and the solid line is the best fit.

solution. Another method which can be used has to do with partial bleaching of the low component or components in a complex glow curve, thus increasing the likelihood of getting better values of the parameters of the higher temperature components. The method is called the $T_{max}-T_{stop}$ method, also termed the E- T_{stop} method (see e.g., [McKeever, 1980](#) and [Pagonis et al., 2006](#)). This is an experimental procedure that we can simulate in the numerical work. In the present case, it consists of irradiation, then relaxation and then heating from room temperature (RT) to a chosen temperature T_{stop} . The next step is cooling the sample to RT and then heating it all the way to 750 K. This procedure is repeated for different values of T_{stop} . Results of such simulations are shown in Fig. 6 where the “unheated” curve is the same as in Fig. 5 and the other three curves are for $T_{stop} = 543, 558$ and 600 K. Fig. 7 shows the curve for $T_{stop} = 600$ K on an enlarged scale and it is quite obvious that it looks like a single second-order peak. The figure also shows its best fitted second-order curve. Fig. 8 depicts the activation energies reached by this analysis as a function of T_{stop} . It can be seen that up to $T_{stop} \sim 540$ K, the deconvolution yields two activation energies, not too far from the inserted values of 1.21 and 1.39 eV. The single peak received following heating to T_{stop} yields, quite surprisingly an

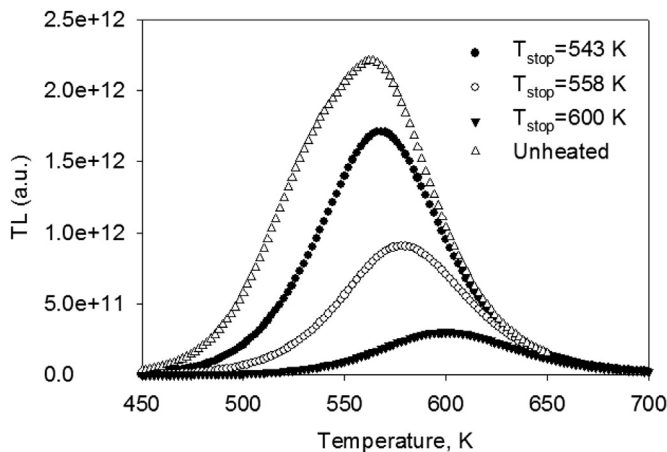


Fig. 6. The glow curves simulated with the same parameters, but following heating to different T_{stop} temperatures.

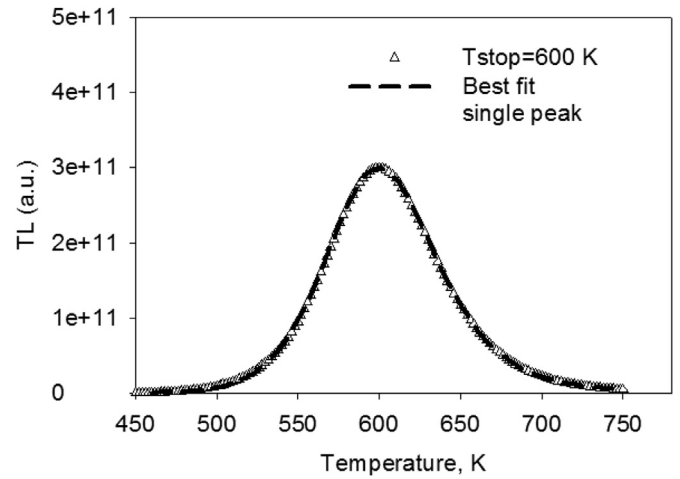


Fig. 7. The single glow peak reached following heating to $T_{stop} = 600$ K and its best fitted curve which turned out to be of second order.

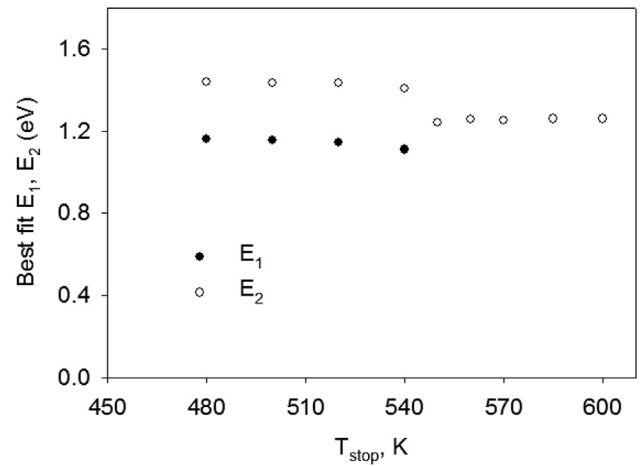


Fig. 8. The evaluated activation energies following heating-simulation to different T_{stop} temperatures. Note that as of $T_{stop} \sim 550$ K, only the high-temperature peak is seen and therefore, only one activation energy is found.

activation energy of ~ 1.26 eV, not much higher than that of the inserted shallower trap. This occurs because the parameters strongly favor electron retrapping into the first trap and consequently it is the shallower trap’s activation energy that dominates.

4. Discussion

In this work, we have shown, by the use of a simple two-trap-one-center model that a curve which looks like a single TL peak may be observed. The peak may have the typical symmetry of a first-order peak and may be mistaken to be a single peak. However, this peak can be, as shown in the given example, rather broad and therefore, if one uses one of the peak-shape methods (e.g. Eq. (1) above), a low effective activation energy, E_{eff} , significantly lower than the inserted energies, E_1 and E_2 , may be evaluated. Insertion of this value into Eq. (3) would yield an effective frequency factor which may be (as in the given example) orders of magnitude lower than the physically acceptable values. This may explain the occurrence of such low values of the frequency factor as reported in the literature and mentioned above. This may possibly account for an effect of “anomalous stability” of TL peaks. In the simple first-order

situation, one would expect the mean lifetime τ (namely, the time it takes to the intensity to reduce to $1/e$ of its initial value) to be related to the measured activation energy and frequency factor by

$$\tau = (1/s)\exp(E/kT). \quad (14)$$

Inserting E_{eff} and s_{eff} in Eq. (14) and using the ambient temperature (~ 300 K) at which the sample is held following excitation, one gets the time τ_{eff} which may be expected to be the mean lifetime of the measured peak. Inserting into Eq. (14) the values of E_{eff} and s_{eff} evaluated from Fig. 2, we get $\tau_{eff} = 2.5 \times 10^7$ s or ~ 10 months. Using the same equation (14) for the inserted values of E_1 and s_1 yields $\tau_1 = 2.13 \times 10^8$ s ~ 6.75 years and for E_2 , s_2 , one gets $\tau_2 = 2.25 \times 10^{11}$ s ~ 7130 years. Thus, the decay time is much longer than that expected by the evaluation of the E_{eff} and s_{eff} values from the measured glow curve. This may predict an effect of “anomalous stability”, namely, the TL signal may be much more stable at room temperature than expected. Note that the values of τ_1 and τ_2 have actually to do only with the release of electrons from the traps. However, due to retrapping, the mentioned values of τ_1 and τ_2 are actually only lower bounds on the mean lifetimes. Furthermore, with regard to the results presented in Fig. 3, it is obvious that once electrons are freed from trap #1, they preferably get trapped in trap #2. The figure shows this for the heating stage, however, it is obvious that the same effect occurs when the sample is held at ambient temperature, which further increases the effective value of τ_2 . It should be noted that another possible explanation of anomalous stability, being due to a two-stage thermal excitation of electrons into the conduction band has been proposed by Chen et al. (2012).

It should be mentioned that although the method used to evaluate the activation energy was a peak-shape method, the same features of the curve are used with any curve-fitting method. Therefore, since the simulated peak is artificially broad, the evaluated effective activation energy will be low with any curve-fitting method and as a result the effective frequency factor will also be very low.

We have also studied the possible impact on the results of the broadly used methods of glow curve deconvolution. The underlying assumption in these methods is that the glow curve is a superposition of several single peaks each of which is of first-order, general order or mixed order. However, due to trapping/retrapping, it is quite obvious that in many cases, the components in a glow curve resulting from two or more trapping states are coupled to each other in a more complex way than mere superposition. It is worth mentioning that Yukihiro and McKeever (2011, p.45), while discussing the deconvolution of an optically stimulated luminescence (OSL) curve, have pointed out that due to interaction between trapping centers, the principle of superposition is not valid. Sakurai (2001) has indicated the difficulty in using computerized glow curve deconvolution when the relevant traps are coupled by the occurrence of trapping/retrapping during the heating stage, and termed this difficulty “fatal defect”. Note that the Sakurai model slightly differs from the present one because he assumes the existence of a disconnected deep trap. Note also that in the example given in Sakurai’s paper, the parameters are such that in the glow curve, the two separate peaks are seen whereas here, the envelope curve looks like a single peak. Anyway, the results in the present work partly support the “fatal defect” observation. The fact that with the GlowFit program a satisfactory result with small FOM occurs with four first-order components is intriguing. The situation appears to be much better in the results of the program based on general order where two components deconvolution yields rather good results. Here, the first peak is very close to first order and the second peak to second order, and the evaluated trapping

parameters are not too far from those inserted to the initial simulation. The result also agrees with the conclusion by Pagonis and Kitis (2012) and by Chen and Pagonis (2013) that in a series of peaks resulting from a system with one center and a number of traps, the last peak tends to be of second order whereas the previous peaks tend to be of first order.

It should be mentioned that in the present example, at the end of irradiation and relaxation, $\sim 99\%$ of the electrons are in trap #1. It is only during readout that a significant population is transferred to trap #2 and this transfer happens in a way that makes the resulting thermoluminescence quite deceptive. Note that Sakurai (2001) has not included the excitation and relaxation stages and just made an arbitrary choice of the carriers’ occupancy at the beginning of readout. In this sense, the present work has a more realistic distribution of the occupancies at the beginning of the heating stage.

Note also that in complex glow curves such as that of LiF:Mg, Ti (TLD-100) the number of components is large (see e.g., Horowitz and Yossian (1995)) and it is not always possible to determine their number. If in the deconvolution process, the envelope of two adjacent components is considered to be a single peak, the conclusion concerning the trapping parameters may be entirely wrong since the effective values of E and s may be very far from the real ones as demonstrated in the present work. Anyway, the present work along with that by Sakurai (2001) indicates that in complex situations, the results of the trapping parameters reached by peak-shape methods and by deconvolution should be taken as just a first step. In order to get more reliable results, it is crucial to analyze many TL glow curves measured under different irradiation conditions, different heating rates, different pre-heatings etc. If deconvolution of several such TL curves gives a consistent set of parameters, one can have confidence in them. As pointed out above, in order to get initially a good idea on the number of components in the glow curve one may use the $T_{max}-T_{stop}$ method, which consists of repeating the thermal cleaning process in small increments. By graphing the activation energy E obtained by this process as a function of T_{stop} , one usually obtains a “staircase” type of graph which may provide a good set of initial values of the activation energies to the deconvolution process. Note that with the present simulation results Fig. 8 has an apparent anomaly where for high values of T_{stop} , where only a single peak is seen the evaluated single activation energy is closer to that of the inserted shallow trap than to the deeper one. By examining the concentrations of the electrons and holes in the model during the heating from room temperature up to $T_{stop} = 600$ K, the following qualitative explanation was found for the mechanism producing the broad TL peak during the final heating stage. During heating up to $T_{stop} = 600$ K, trap #1 is thermally emptied only partially, and some of these thermally released electrons are trapped in trap #2. Even though one might expect that trap #1 would be completely empty and only some electrons will survive in trap #2, it was found that the concentrations remaining in both traps after heating to $T_{stop} = 600$ K are comparable. This is clearly due to the presence of a strong retrapping probability for both traps, even at these high temperatures. During the final heating/readout stage from room temperature up to 750 K, electrons from both traps are released thermally, and both traps contribute to the simulated TL signal shown in Fig. 8.

We are currently developing an analytical model describing these strong retrapping effects which take place at high temperatures during the readout stage of the TL process.

In conclusion, we strongly recommend great caution in the analysis of TL curves. When the peak-shape methods are used, one should make sure that the peak in hand is really a single peak. When deconvolution is utilized, it is crucial that the correct number of components be considered and that a reasonable first guess of

the values of parameters of the individual component peaks be in hand.

References

- Bräunlich, P., 1967. Comment on the initial rise for determining trap depths. *J. Appl. Phys.* 38, 2516–2519.
- Chen, R., 1969. On the calculation of activation energies and frequency factors from glow curves. *J. Appl. Phys.* 40, 570–585.
- Chen, R., Hag-Yahya, A., 1996. Interpretation of very high activation energies and frequency factors in TL as being due to competition between centres. *Radiat. Prot. Dosim.* 65, 17–20.
- Chen, R., Hag-Yahya, A., 1997. A new possible interpretation of the anomalous fading in thermoluminescent materials as normal fading in disguise. *Radiat. Meas.* 27, 205–210.
- Chen, R., McKeever, S.W.S., 1997. *Theory of Thermoluminescence and Related Phenomena*. World Scientific, Singapore, p. 559.
- Chen, R., Lawless, J.L., Pagonis, V., 2012. Two-stage thermal stimulation of thermoluminescence. *Radiat. Meas.* 47, 809–813.
- Chen, R., Pagonis, V., 2013. On the expected order of kinetics in a series of thermoluminescence (TL) and thermally stimulated conductivity (TSC) peaks. *Nucl. Inst. Method Phys. Res. B* 312, 60–69.
- Chen, R., Pagonis, V., 2014. The role of simulations in the study of thermoluminescence (TL). *Radiat. Meas.* 71, 8–14.
- Dropkin, J.J., 1954. *Photoconductivity in Phosphors*. Final Report, Contract N6–26313. Polytechnic Institute of Brooklyn.
- Fairchild, R.G., Mattern, P.L., Lengweiler, K., Levy, P.W., 1974. Thermoluminescence of LiF TLD-100 dosimeter crystals. *IEEE Trans. Nucl. Sci. NS* 21, 366–372.
- Gorbics, S.G., Attix, F.H., Pfaff, J.A., 1967. Temperature stability of CaF₂:Mn and LiF (TLD-100) thermoluminescent dosimeters. *Int. J. Appl. Radiat.* 18, 625–630.
- Haake, C.H., 1957. Critical comment on a method for determining electron trap depths. *J. Opt. Soc. Am.* 47, 649–652.
- Hickmott, T.W., 1972. Thermoluminescence and color centers in rf-sputtered SiO₂ films. *J. Appl. Phys.* 43, 2339–2351.
- Hoogenstraaten, W., Klasens, H.A., 1953. Some properties of zinc sulfide activated with copper and cobalt. *J. Electrochem. Soc.* 100, 366–375.
- Horowitz, Y.S., Yossian, D., 1995. Computerised glow curve deconvolution: application to thermoluminescence dosimetry. *Radiat. Prot. Dosim.* 60, 1–114.
- Kierstead, J.A., Levy, P.W., 1991. Validity of repeated initial rise thermoluminescence kinetic parameter determinations. *Nucl. Tracks Radiat. Meas.* 18, 19–25.
- Kitis, G., Gomez-Ros, J.M., Tuyn, J.W.N., 1998. *J. Phys. D. Appl. Phys.* 31, 2636–2641.
- Mandowski, A., 2006. Topology-dependent thermoluminescence kinetics. *Radiat. Prot. Dosim.* 119, 23–28.
- McKeever, S.W.S., 1980. On the analysis of complex thermoluminescence glow-curves: resolution into individual peaks. *Phys. Stat. Sol. A* 62, 331–340.
- Mott, N.F., Gurney, M.A., 1948. *Electronic Processes in Ionic Crystals*, second ed. Dover Publications Inc., NY, p. 275.
- Pagonis, V., Kitis, G., Furetta, C., 2006. *Numerical and Practical Exercises in Thermoluminescence*. Springer, NY, p. 208.
- Pagonis, V., Kitis, G., 2012. Prevalence of first-order kinetics in thermoluminescence materials: an explanation based on multiple competition processes. *Phys. Stat. Sol. A* 249, 1590–1601.
- Pohlit, W., 1969. Thermoluminescence in LiF. I. Measurement of activation energy of electrons in different traps. *Biophysik* 5, 341–350.
- Puchalska, M., Bilski, P., 2005. *The Thermoluminescence Glow-curve Analysis Using GlowFit – the New Powerful Tool for Deconvolution*. Report No. 1968/D. Polish Academy of Sciences.
- Randall, J.T., Wilkins, M.H.F., 1945. The phosphorescence of various solids. *Proc. Roy. Soc. Lond. A* 184, 347–365.
- Sakurai, T., 2001. Fatal defect in computerized glow curve deconvolution of thermoluminescence. *J. Phys. D. Appl. Phys.* 34, L105–L107.
- Sunta, C.M., Feria, A.W.E., Pifers, T.M., Watanabe, S., 1999. Limitation of peak fitting and peak shape methods for determination of activation energy of thermoluminescence glow peaks. *Radiat. Meas.* 30, 197–201.
- Taylor, G.C., Lilley, E., 1978. The analysis of thermoluminescence glow peaks in LiF (TLD-100). *J. Phys. D. Appl. Phys.* 11, 567–581.
- Yukihara, E.G., McKeever, S.W.S., 2011. *Optically Stimulated Luminescence: Fundamentals and Applications*. Wiley, Chichester, UK, p. 362.