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Properties of thermoluminescence glow curves from tunneling recombination processes in random distributions of defects

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ABSTRACT

Localized electronic recombination processes in donor–acceptor pairs of luminescent materials have been recently modeled using a new kinetic model based on tunneling. Within this model, recombination is assumed to take place via the excited state of the donor, and nearest-neighbor recombinations take place within a random distribution of centers. An approximate semi-analytical version of the model has been shown to simulate successfully thermally and optically stimulated luminescence (TL and OSL), linearly modulated OSL (LM-OSL) and isothermal TL processes. This paper presents a detailed analysis of the geometrical properties of the TL glow curves obtained within three different published versions of the model. The dependence of the shape of the TL glow curves on the kinetic parameters of the model is examined by allowing simultaneous random variations of the parameters, within wide ranges of physically reasonable values covering several orders of magnitude. It is found that the TL glow curves can be characterized according to their shape factors μ_g, as commonly done in TL theory of delocalized transitions. The values of the shape factor are found to depend rather weakly on the activation energy E and the frequency factor s, but they have a strong dependence on the parameter ρ' which characterizes the concentration of acceptors in the model. It is also shown by simulation that both the variable heating rate and initial rise methods are applicable in this type of model and can yield the correct value of the activation energy E. However, the initial rise method of analysis for the semianalytical version of the model fails to yield the correct E value, since it underestimates the low temperature part of the TL glow curves. Two analytical expressions are given for the TL intensity, which can be used on an empirical basis for computerized glow curve deconvolution analysis (CGCD).

1. Introduction

Over the past twenty years there has been considerable experimental and modeling work trying to understand the nature and properties of luminescence signals from feldspars, especially in connection with the associated phenomenon of "anomalous fading" based on quantum mechanical tunneling ([1–15]).

Recently Jain et al. [14] presented a new general kinetic model which quantifies localized electronic recombination of donor–acceptor pairs in luminescent materials. Recombination is assumed to take place via the excited state of the donor, and to take place between nearest-neighbors within a random distribution of centers. Two versions of the model were presented by these authors, an exact model that evolves in both space and time, and an approximate semi-analytical model evolving only in time. Good agreement was found between the two versions of the model, and simulated successfully both thermally stimulated luminescence (TL) and optically stimulated luminescence (OSL). The model also demonstrated the power law behavior for OSL signals simulated within the model.

A third version of the model was published by Pagonis et al. [16], who examined the full model by Jain et al. [14] and obtained analytical expressions for the distribution of remaining donors at any time t during several experimental situations. These authors gave examples for the derived distributions of donors in each experimental case, and similarities and differences between the different experimental modes of stimulation were pointed out.

Kitis and Pagonis [17] showed that the initial system of simultaneous differential equations developed by Jain et al. [14] can be approximated to a very good precision by a single differential equation describing stimulated luminescence emission in this system. These authors were able to obtain analytical solutions of this single differential equation for several possible modes of stimulation, namely TL, OSL, linearly modulated OSL (LM-OSL) and isothermal TL (ITL). They also derived the exact analytical form for the power law behavior in this system, and demonstrated how typical experimental TL glow curves and infrared stimulated luminescence signals (IRSL) can be

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analyzed using the derived analytical equations, and what physical information that can be extracted from such experimental data.

The goals of the present paper are as follows.

(a) To carry out a detailed analysis of the geometrical properties of the TL glow curves obtained within the three published versions of the model by Jain et al. [14], for a wide range of the kinetic parameters.
(b) To investigate how the parameters in the model affect the geometrical shape factor μ_g and to develop empirical equations relating μ_g to the parameters in the model, similarly to what has been previously done in TL theory of delocalized transitions.
(c) To investigate by simulation whether the variable heating rate method and initial rise methods of TL analysis are applicable in the TL glow curves of this model.
(d) To develop different types of analytical expressions for the TL intensity, that can be used for computerized glow curve deconvolution analysis (CGCD).

2. Overview of the model by Jain et al. [14]

In this section we briefly review the three different versions of the model by Jain et al. [14] available in the literature, for the case of TL processes.

2.1. The original full model of Jain et al. [14]

The physical assumptions in the model of Jain et al. [14] are summarized in Table 1 of their paper. The main physical assumption in the model is the presence of a random distribution of hole traps in the luminescent volume, and an associated range of random nearest-neighbor recombination probabilities. Furthermore, stimulated recombination takes place only via the excited state of the electron trap, by either optical or thermal stimulation. The concentration of holes is assumed to be much larger than the concentration of electron traps, and an electron can tunnel only to its nearest hole. In the exact form of the model presented by Jain et al. [14], the differential equations for a TL process are as follows:

$$\frac{\partial n_g(r',t)}{\partial t} = -An_g(r',t)+Bn_e(r',t) \tag{1}$$

$$\frac{\partial n_e(r',t)}{\partial t} = An_g(r',t)-Bn_e(r',t)-\frac{n_e(r',t)}{\tau(r',t)} \tag{2}$$

$$L(t) = -\frac{dm}{dt} = \int_0^\infty \frac{n_e(r',t)}{\tau(r',t)}dr' = -\int_0^\infty \left(\frac{\partial n_g(r',t)}{\partial t}+\frac{\partial n_e(r',t)}{\partial t}\right)dr' \tag{3}$$

$$\frac{dT}{dt} = \beta \tag{4}$$

$$\tau = s^{-1}\exp\left(\frac{r'}{(\rho')^{1/3}}\right). \tag{5}$$

The following parameters and symbols are used in the model: $n_g(r',t)$and $n_e(r',t)$are the instantaneous concentrations of electrons in the ground state and in the excited state correspondingly. These concentrations depend on both time t and on the dimensionless separation distance parameter r' which is defined by $r'=(4\pi\rho/3)^{1/3}r$, where r represents the actual donor–acceptor separation distance. The dimensionless number density of acceptors parameter ρ' is defined by $\rho'=(4\pi\rho/3)\alpha^{-3}$, where ρ represents the actual number density of acceptors and α is the potential barrier penetration constant (Huntley, [5]). m is the instantaneous concentration of acceptors (holes), n is the instantaneous concentration of all the donors, and if N represents the instantaneous concentration of electrons in thermally disconnected states such that charge is conserved, then $m=n+N=(n_g+n_e)+N$. The parameter A represents the thermal excitation rate from the ground to the excited state, and is equal to $A=s\exp(-E/kT)$ where $E=$ thermal activation energy, s is the frequency factor, β is the linear heating rate, T is the temperature of the sample and τ is the tunneling lifetime. B is the relaxation rate from the excited into the ground state, and $L(t)$ is the instantaneous luminescence resulting from recombination taking place via the excited state. If the equivalence principle is assumed to be valid, one also has $B=s$.

In this full version of the model of Jain et al. [14] the TL intensity $L(t)$ is calculated from the numerical solution of the system of differential equations (1)–(5).

2.2. The approximate version of the model by Pagonis et al. [16]

Pagonis et al. [16] examined the full model by Jain et al. [14] and obtained partial analytical solutions of the system of differential equations (1)–(5). These authors obtained the following analytical expressions for the distribution of remaining donors at any time t:

$$n_g(r',t) = 3n_0(r')^2\exp[-(r')^3]\exp[-\exp(-(\rho')^{-1/3}r')\int_0^t Adt']. \tag{6}$$

This analytical equation describes the evolution of the distribution of electrons in the ground state as a function of the time t elapsed since the beginning of the optical or thermal stimulation. It is valid for several types of excitation used in typical TL or OSL experiments.

The TL luminescence intensity $L(t)$ is found from the expression

$$L(t) = \int_0^\infty A\exp(-(\rho')^{-1/3}r')n_g(r',0)\exp[-\exp(-(\rho')^{-1/3}r')\int_0^t Adt']dr'. \tag{7}$$

This integral expression allows a numerical calculation of the luminescence intensity L(t), by integrating numerically over the possible range of the dimensionless variable $r'=0$ to $r'=\infty$.

Although it is not possible to obtain a closed analytical form for the luminescence intensity as a function of time in this version of the model, $L(t)$ can be easily evaluated by numerically integrating Eq. (7) over the distance r'.

2.3. The analytical form of the semianalytical version of the model [17]

Jain et al. [14] presented a semianalytical version of their model, in which one uses a critical tunneling lifetime τ_c. Kitis and Pagonis [17] were able to obtain the following analytical expressions for the concentration of electrons in the ground state $n_g(t)$and for the luminescence intensity $L(t)$ at time t:

$$n_g(t) = n_o e^{-\rho'\left[\ln\left(1+z\int_0^t Adt'\right)\right]^3} = n_o e^{-\rho'[F(t)]^3} \tag{8}$$

$$L(t) = -\frac{dn_g}{dt} = 3n_o\rho' F(t)^2 zAe^{-F(t)}e^{-\rho'[F(t)]^3} \tag{9}$$

with the quantity $F(t)$ defined by

$$F(t) = \ln(1+z\int_0^t Adt'). \tag{10}$$

Eqs. (8)–(10) are very general, and are applicable for several different types of thermal and optical stimulation. In the special case of TL with a linear heating rate β, the temperature T varies with time t as $T=T_o+\beta t$ where T_o is the room temperature. The excitation probability for the TL process is given by $A=s\exp(-E/kT)$ and the integral in Eq. (10) can be approximated by its well-known series approximation (see for example the book

by Chen and Pagonis, [18], Chapter 15),

$$\int_0^t A dt' = \int_0^t s\exp(-E/kT)dt' = \frac{skT^2}{\beta E}e^{-\frac{E}{kT}}\left(1-\frac{2kT}{E}\right) \quad (11)$$

and by inserting (11) into Eq. (10) one finds

$$F(T) = \ln\left(1+\frac{zskT^2}{\beta E}e^{-\frac{E}{kT}}\left(1-\frac{2kT}{E}\right)\right). \quad (12)$$

The accuracy of this series approximation was tested during the simulations carried in this paper, and it was found that it provides accurate values for $L(T)$ and $F(T)$ in Eqs. (9) and (10), with an accuracy of 1% or better.

The analytical expressions (9) and (12) give the instantaneous TL intensity $L(t)$ during a TL experiment. As discussed in a later section of this paper, these two equations can be programmed into a least squares fitting function in order to analyze experimental TL data using a least squares fitting procedure. The four fitting parameters in this case are the energy E, initial occupancy constant n_o, frequency factor s, and dimensionless concentration ρ'. It is important to note that Eq. (9) can be used as is to fit experimental data, while in the full model the original set of Eqs. (1)–(5) needs to be solved numerically before any attempted fitting of experimental data is carried out.

3. Results from the simulations

3.1. Geometrical shape factors of the TL glow curves

Fig. 1 shows a comparison of TL glow curves calculated using the three versions of the model discussed in the previous section. The simulated results in Fig. 1 show that the TL intensity obtained from the original full model by Jain et al. [14] (dashed line) agrees to an excellent degree with the version of the model presented by Pagonis et al. [16] (open circles), with the two versions of the model producing indistinguishable results. However, Fig. 1 shows a clear discrepancy between the full model (dashed line), and its semianalytical approximation which is based on Eq. (9) (solid line). Significant differences between these two formulations of the model are clearly seen at the low temperature side of the glow curve, as well as near the maximum TL intensity. These discrepancies are clearly due to the critical tunneling lifetime approximations used in the semi-analytical version of the model. Similar differences between these two versions of the model were also shown clearly in Fig. 4 of Ref. [14].

Fig. 2(a)–(c) shows several simulated TL glow curves obtained by varying the parameter ρ', E and s correspondingly, while keeping the rest of the parameters fixed. All simulated results in

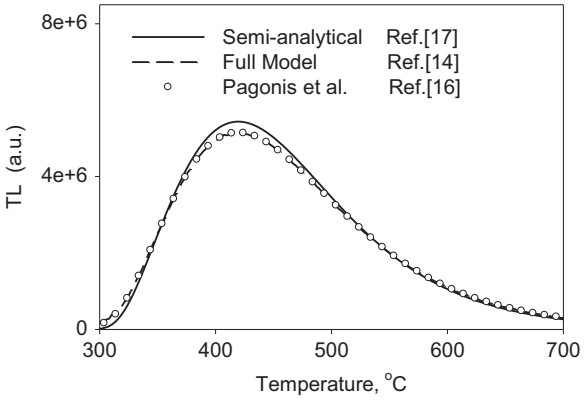

Fig. 1. Comparison of TL glow curves simulated using the three published versions of the model by Jain et al. [14]. The differences between the semi-analytical and the full version of the model are clearly seen at the low temperature side and near the maximum of the glow curve.

Figs. 2–4 are obtained using the original full model of Jain et al. [14]. Fig. 2a shows TL glow curves for several values of the donor concentration parameter $\rho' = 6-12\times10^{-4}$and with $E=1.2$ eV and $s=10^{12}$ s^{-1}. Fig. 2b shows the TL glow curves for different values of $E=1.0-1.2$ eV, with $s=10^{12}$ s^{-1} and $\rho'=3\times10^{-4}$. Similarly Fig. 2c shows TL glow curves for different values of s, while $E=1.2$ eV and$\rho'=3\times10^{-4}$. For comparison purposes the same glow curves are also shown in Fig. 2(d)–(f), normalized to the maximum TL intensity and also shifted along the temperature axis so that their maxima coincide in order to show more clearly the changes taking place in the shape of the curves. The examples in Fig. 2 show that the shape of the glow curves depends rather strongly on the concentration of acceptors ρ', while it has a weaker dependence on the activation energy E and on the frequency factor s.

The changes of the shape of the glow curves in Fig. 2 are quantified by calculating the geometrical shape factor $\mu_g=\delta/\omega$, where $\delta=T_2-T_m$, $\omega=T_2-T_1$ and T_1 and T_2 represent the temperatures corresponding to the half-maximum intensities on the low and high temperature sides of the TL peak respectively. Fig. 3a shows the dependence of $\mu_g=\delta/\omega$ on the activation energy E, for value of the frequency factor $s=10^8$ s^{-1}, and for several values of the donor concentration parameter ρ' in the model between 3×10^{-4} and 2×10^{-2} (with increasing value of ρ' in the direction of the arrow). Fig. 3b shows the dependence of μ_g on the frequency factor s, for a fixed value of the activation energy $E=0.8$ eV, and for the same range of ρ' values. Similarly Fig. 3c shows the dependence of μ_g on ρ', while the E value varies between 0.8 and 1.6 eV, and the frequency factor $s=10^8, 10^{12}$ s^{-1}. The results of Fig. 3 show that the shape factor μ_g depends strongly on ρ', while it has a much weaker dependence on the parameters E and s.

The dependence of these results on the chosen values of the kinetic parameters is further studied in a systematic manner, by allowing random variations of the kinetic parameters in the model within physically reasonable values. In a real luminescent material one can expect random variations of the recombination and retrapping coefficients, as well as random variations in the concentrations and filling of the traps. Such random variations would lead to statistical variations between different samples of the same material, and even in significant differences between aliquots of the same sample. This method of analysis based on random parameter combinations was used recently by Pagonis and Kitis [19] to explain the prevalence of first order kinetics in TL dosimetric materials. The main advantage of this method of random variations is that the average behavior of a natural material can perhaps be simulated more accurately, and for a very wide range of the kinetic parameters.

Pagonis and Kitis [19] simulated the random natural variations of the recombination and retrapping coefficients and of the initial concentrations of traps in the interactive multitrap system of TL, by allowing these parameters to vary between physically reasonable minimum and maximum values. The three parameters ρ', E and s in the model are varied randomly as follows. The E value was varied randomly between 0.8 and 1.6 eV, while the frequency factor s was chosen randomly in the interval $s=10^6$–10^{14} s^{-1}. The density parameter ρ' was chosen in the interval $\rho'=1\times10^{-4}$–2×10^{-2}. Since the values of ρ' and s represent a span of several orders of magnitude, one should allow random uniform variations in their *logarithms*, rather than in the values of themselves. The only criterion of acceptance imposed during the simulation on the values of these parameters, was that they produce a TL glow curve with a peak located between room temperature and 700 °C, the upper limit of temperatures reached by TL readers.

Fig. 4 shows the results of simulating $M=1000$ random variants of the model calculated in this manner. The scattering in the simulated data is due to the random variations of E and s. The results of Fig. 4 verify the conclusion that the shape factor μ_g depends strongly on ρ', while it has a much weaker dependence on the parameters E and

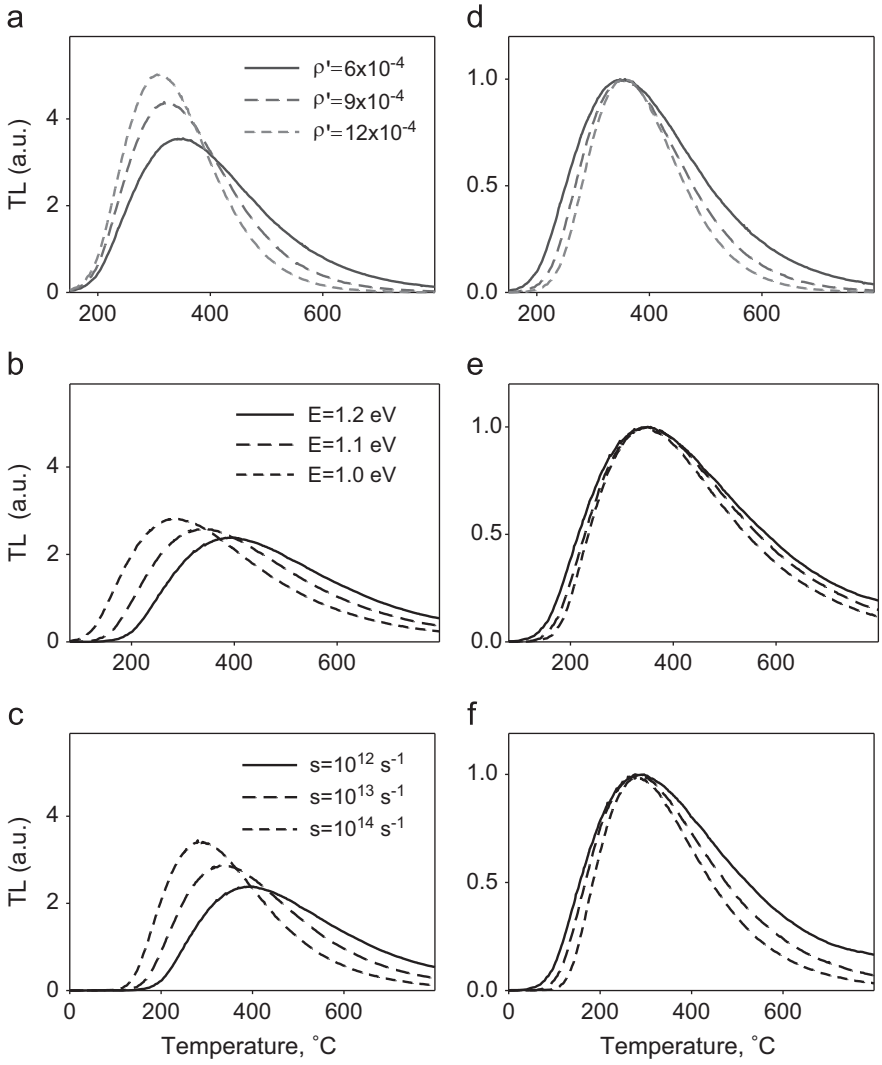

Fig. 2. Simulated TL glow curves obtained by (a) varying the parameter ρ' while $E=1.2$ eV and $s=10^{12}$ s^{-1}, (b) varying activation energy E with $s=10^{12}$ s^{-1} and $\rho'=3\times10^{-4}$ and (c) varying frequency factor s, while $E=1.2$ eV and $\rho'=3\times10^{-4}$. The same glow curves are also shown in (d)–(f) for comparison purposes, normalized to the maximum TL intensity and also shifted along the temperature axis so that their maxima overlap.

s. The solid line through the simulated data in Fig. 4 represents an empirical fit to the simulated data with the equation

$$\mu_g = 0.42113(\rho')^{-0.05395} \tag{13}$$

and its inverse empirical equation is as follows:

$$\rho' = 1.0910\times10^{-7}(\mu_g)^{-18.5368} \tag{14}$$

Fig. 4 shows that at large ρ' values the model always produces a glow curve which is nearly symmetric, with μ_g approaching a value of $\sim$0.50. This simulated data shows that the shape of the TL glow curves in this model is nearly independent of the parameters of the model for ρ'values larger than $\sim$0.006.

Two important methods of analyzing experimental TL glow curves are the variable heating rate method (VHR) and the initial rise (IR) method of analysis. The validity of these two methods of analysis within the model of Jain et al. [14] is examined in the next two sections.

3.2. Variable heating rate method – derivation of the condition for the maximum TL intensity

The variable heating rate method of TL analysis (VHR) consists of measuring the glow curves using a variable heating rate β, and studying the resulting variation of the temperature T_m corresponding to maximum TL intensity L_m. The mathematical condition for applying this method in the case of first order kinetics is the well-known expression for delocalized luminescence models ([18]):

$$\frac{\beta E}{kT_m^2} = s\exp\left(-\frac{E}{kT_m}\right). \tag{15}$$

This type of expression is very useful in practical situations, because it allows the determination of the activation energy E and the frequency factor s. In this section it is shown that a similar condition applies for the tunneling model of Jain et al. [14]. The derivation starts by taking the logarithm of Eq. (9) to obtain

$$\ln L = \ln(3n_o\rho' z) + \ln(A) + \ln(F^2) - \rho' F^3 - F. \tag{16}$$

The condition for the maximum TL intensity is found by setting the time derivative of Eq. (16) equal to zero at $T=T_m$:

$$\left(\frac{d\ln L}{dt}\right)_{T=T_m} = \left(\frac{A'}{A} + \frac{2F'}{F} - 3\rho' F^2 F' - F'\right)_{T=T_m} = 0 \tag{17}$$

or

$$\frac{(A')_m}{A_m} + \frac{2(F')_m}{F_m} - 3\rho' {F_m}^2 (F')_m - 2(F')_m = 0 \tag{18}$$

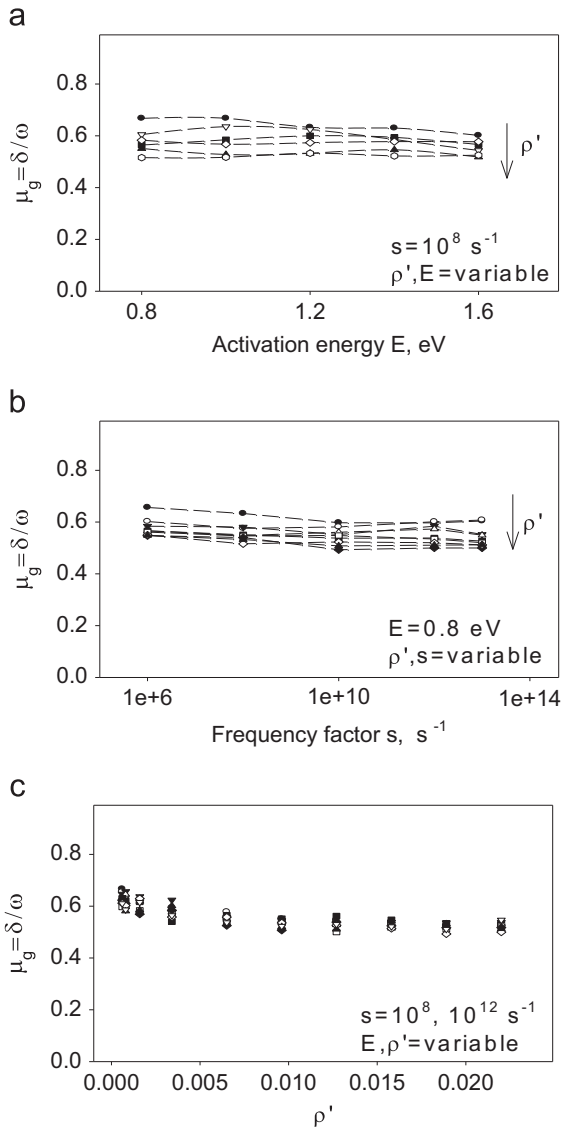

Fig. 3. The geometrical shape factor $\mu_g=\delta/\omega$ for typical ranges of the parameters. (a) Dependence of μ_g on the activation energy E for $s=10^8\ s^{-1}$, and for several values of $\rho'=3\times10^{-4}$–2×10^{-2} (with increasing value of ρ' in the direction of the arrow). (b) Dependence of μ_g on the frequency factor s for a fixed $E=0.8$ eV and for variable ρ'. (c) Dependence of μ_g on ρ', while E $=0.8$–1.6 eV, and $s=10^8$–$10^{12}\ s^{-1}$.

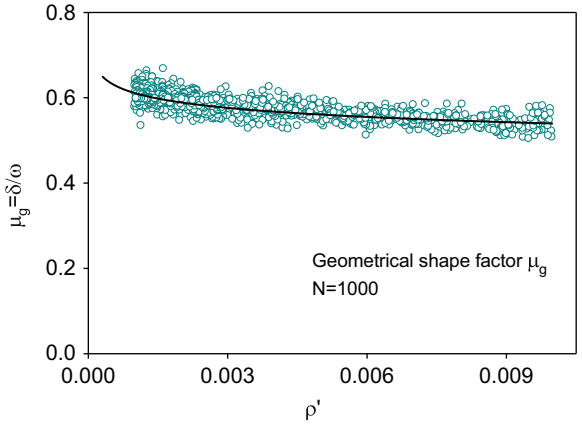

Fig. 4. The geometrical shape factor $\mu_g=\delta/\omega$ for $N=1000$ random variants, obtained from a wide range of random combinations of the parameters E, s, and ρ'. At large ρ' values one always gets a symmetric TL glow curve with $\mu_g\sim0.5$.

where the subscript m denotes the value of the parameters at $T=T_m$ and the primes indicates as usual time derivatives of the various parameters.

Next various terms in Eq. (18) are evaluated separately as follows. From the probability of thermal stimulation $A=s\exp(-E/kT)$, it is easily found that

$$\frac{(A')_m}{A_m}=\frac{\beta E}{kT_m^2}. \tag{19}$$

Using Eq. (12) it is also found after some algebra that

$$(F')_m=zA_m e^{-F_m}. \tag{20}$$

By substituting Eqs. (19) and (20) into Eq. (18), one finds after some algebra the desired condition for the maximum TL intensity, i.e.

$$\frac{\beta E}{kT_m^2}=f_m sz\exp\left(-\frac{E}{kT_m}\right) \tag{21}$$

with the dimensionless parameter f_m given by

$$f_m=\frac{3\rho' {F_m}^3+F_m-2}{F_m e^{F_m}} \tag{22}$$

and with the parameter F_m representing the value of Eq. (12) for $T=T_m$, as

$$F_m=\ln\left(1+\frac{zskT_m^2}{\beta E}e^{-\frac{E}{kT_m}}\left(1-\frac{2kT_m}{E}\right)\right). \tag{23}$$

Eq. (21) is very similar to the well-known Eq. (15) previously derived for delocalized TL models. This equation shows that a plot of kT_m^2/β versus $1/kT_m$ will be a straight line with slope E, and with a y-intercept given by $\ln(f_m sz)$. It is noted that this y-intercept will depend on both the dimensionless constant f_m and the frequency factor s, hence the y-intercept cannot be used to obtain the frequency factor s, since f_m depends on two unknown quantities (s and ρ').

An example of simulating the VHR method is shown in Fig. 5a for a specific set of parameters, with the slope of the straight line fit in the inset yielding the correct value of $E=1.0$ eV. Although an analytical expression cannot be obtained for the variable f_m, its values are easily simulated by using Eqs. (22) and (23). while Fig. 5b shows the results of simulating the values of f_m and F_m for the same random combinations of the parameters in the model as in the previous section. These simulated results indicate that the parameters f_m and F_m depend strongly on ρ', while they have a weaker dependence on the parameters E and s in the model. Typical values of the dimensionless quantity f_m are ~0.01, and for F_m the corresponding values are ~4.

Fig. 6 shows the results of running the same simulation of VHR for $M=300$ random combinations of the parameters s and ρ' and for various fixed E values, as discussed above. The solid squares in Fig. 6 represent the E values when simulating with the full model by Jain et al. [14], or the semianalytical version of the model. The dashed line in Fig. 6 represents the 1:1 line, and indicates the expected value of E. The error bars in Fig. 6 indicate the standard deviation of the $M=300$ simulated data (1σ). As seen in Fig. 6, the simulated E values lie close to this 1:1 line, indicating that the VHR method of analysis yields an accurate estimate of the activation energy E for both the full version and the semianalytical versions of the model. The results for the version of the model developed by Pagonis et al. [16] are also not shown here, since they are identical to those obtained from the full model.

It is concluded that the VHR method of analysis applies to all 3 versions of the model of Jain et al. [14].

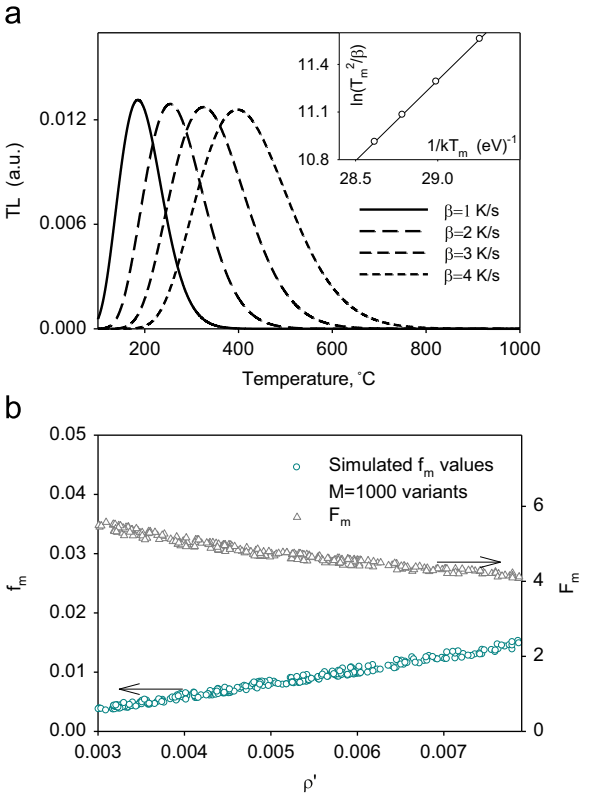

Fig. 5. (a) Example of heating rate method of TL analysis, for $\beta=1,2,3$, and 4 K/s. The inset shows a plot of $\ln(kT_m^2/\beta)$ versus $1/kT_m$ yielding a straight line with slope E, and with a y-intercept given by $\ln(f_m sz)$. (b) The results of simulating the constants f_m and F_m for $M=1000$ random variants of the model of Jain et al. [14], as described in the text.

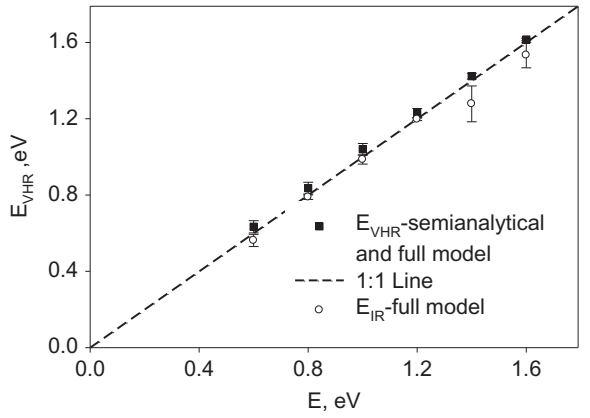

Fig. 6. Simulations of the VHR and IR methods of TL analysis obtained from a wide range of random combinations of the parameters E, s, and ρ'. The dashed line represents the 1:1 line.

3.3. Development of new TL glow curve fitting expressions based on T_m and L_m

The general analytical expressions in Eqs. (9) and (12) can be used for analyzing complex TL glow-curves. The problem with such curve fitting expressions and with any such data fitting algorithm is that it does not give a unique solution for the case of a complex glow-curve. However, it is possible to drastically reduce the number of possible solutions by transforming the general equation so that the free parameters n_o and s are replaced by the maximum TL intensity L_m and the corresponding temperature T_m. These two quantities (L_m and T_m) can be accurately evaluated from the experimental glow-curve. Using this method two of the four free fitting parameters can be fixed during curve fitting analysis, therefore decreasing the number of possible solutions. This type of transformation of the curve fitting expressions was previously developed for luminescence processes in delocalized TL models, namely for first order, general order and mixed order kinetics ([20–22]).

In this section it is shown that a similar transformed general expression can be derived for the tunneling model of Jain et al. [14]. The maximum intensity L_m of the glow peak is obtained by setting $T=T_m$ in Eq. (9) to obtain

$$L_m = 3n_o\rho' z A_m {F_m}^2 \exp[-(\rho' {F_m}^3 + F_m)]. \tag{24}$$

By taking the ratio of Eqs. (9) and (24) one obtains

$$L(T) = L_m \frac{A}{A_m}\left(\frac{F}{F_m}\right)^2 \frac{\exp\left[-(\rho' {F_m}^3 + F_m)\right]}{\exp\left[-(\rho' F^3 + F)\right]}. \tag{25}$$

Eq. (25) is a new general curve fitting equation in which the parameter n_o has been replaced by L_m. The complete transformation requires also the replacement of the frequency factor s as follows. By using $A = s\exp(-E/kT)$ one obtains

$$\frac{A}{A_m} = \exp\left[-\frac{E(T_m - T)}{kTT_m}\right]. \tag{26}$$

Taking into account the condition for the maximum Eq. (21), one obtains after some algebra from Eq. (12)

$$F(T) = \ln\left(1 + \frac{1}{f_m}\frac{T^2}{{T_m}^2}\exp\left[-\frac{E(T_m - T)}{kTT_m}\right]\left(1 - \frac{2kT}{E}\right)\right) \tag{27}$$

where the dimensionless constants F_m and f_m were previously defined in Eqs. (22) and (23) respectively. It is also noted that these two parameters are related by the equation

$$F_m = \ln\left(1 + \frac{1}{f_m}\left(1 - \frac{2kT_m}{E}\right)\right). \tag{28}$$

The final equation which can be used for CCD analysis is Eq. (25) with its partial terms given by Eqs. (26)–(28). Eq. (25) is obviously a four parameter function in which the free parameters are L_m, T_m, E and F_m (or f_m).

Based on the simulation study presented in this paper, the authors of this paper recommend the following procedure for analyzing experimental TL glow curves using the model of Jain et al. [14]. Firstly, by using the VHR method a reliable value of the activation energy E is obtained. From the experimental data one also knows the values of L_m and T_m. From the geometrical shape factor μ_g of the experimental TL glow peak, one can estimate the density parameter ρ' using the empirical Eq. (14). One can then guess a reasonable initial value for $f_m \sim 0.01$, and use Eq. (28) with the estimated values of E and T_m to obtain an initial estimate of the dimensionless constant F_m. Next by using Eq. (27) and the known values of f_m, F_m, E, and T_m one can now proceed to calculate $F(T)$ at any temperature T. Finally Eq. (25) can be used as a fitting equation with all terms known, and the least squares Levenberg–Marquardt algorithm is used by adjusting E and f_m in order to get the best possible fit to the experimental data. Although this procedure may seem rather complex, it can be easily implemented in a software routine and used with a least squares algorithm of one's choice.

3.4. Failure of the initial rise method in the semianalytical version of the model

In all simulated TL glow curves based on the full model by Jain et al. [14], it was found that the IR method produced an accurate estimate of the activation energy E. Some of these simulated data are shown as solid circles in Fig. 6.

By contrast, it was found that the IR method of analysis does not apply to the simulated TL glow curves obtained from the semianalytical version of the model. The E values calculated using the IR method in this case are found to be larger than the expected E value by a factor of ~2–3. This discrepancy is not surprising in view of the differences shown in Fig. 1 between these two versions of the model, especially at the low temperature region of the TL glow curve.

4. Discussion and conclusions

In this paper three different versions of the model by Jain et al. [14] were examined, and typical differences between them were illustrated by the simulated example in Fig. 1. It was shown that it is possible to analyze TL glow curves within the model of Jain et al. [14] by using two fitting expressions for TL glow curve fitting analysis. The first method is based on Eqs. (9) and (12) and has four fitting parameters n_o, s, E and ρ'.This paper also developed a second expression Eq. (25), with its partial terms given by Eqs. (26)–(28). The four fitting parameters here are L_m, T_m, E and F_m (or f_m). This method of analysis has the advantage that the quantities L_m and T_m are known from the experimental glow curves, while the activation energy E can be obtained from a separate experiment based on the VHR method. This leaves only the fourth known parameter F_m (or f_m) to vary in the least squares routine.

Both these fitting routines can be implemented in a straightforward manner with a least squares fitting routine.

Another practical result from this study is the empirical Eq. (14) which can be used to provide an initial estimate the value of ρ' from the experimental value of the geometrical factor μ_g. Overall the shape factor μ_g was found to depend strongly on ρ', while it has a much weaker dependence on the parameters E and s. At large ρ' values above ~0.006 one can expect an almost symmetric TL glow curve with a μ_g value close to ~0.50. The VHR and IR methods of analysis can be used reliably to obtain the energy E.

It is worth to mention here also the approximate tunneling pair recombination model by Chang and Thioulouse [23]. These authors also considered the validity of the VHR and IR methods of analysis within their model, and concluded that both methods are applicable within their model.

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