Semi-localized transitions model for thermoluminescence

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Abstract
A new model for thermoluminescence (TL) kinetics is presented, which is a
natural generalization of the standard localized transition model. The model
of semi-localized transitions (SLTs) allows trapped charge carriers to be
excited to the conduction band. Analytic equations for SLTs are constructed
using an enumeration technique which transforms concentrations of carriers
to concentrations of states of localized trap–recombination centre pairs.
Solving numerically the set of equations, we demonstrate some basic
features of the SLT model. It is shown that SLT is able to produce so-called
TL displacement peaks that were previously found in one-dimensional TL
simulations.

1. Introduction

Thermoluminescence (TL) is a relaxation process of emitting
light during thermal stimulation. Initially, the solid under study
has to be excited at an appropriately low temperature to fill
charge carriers' traps with carriers. The TL phenomenon is
widely applied in dosimetry [1] and dating [2]. In dosimetric
applications the non-equilibrium initial occupation of traps is
generated by high-energy radiation. Trapped charge carriers
are released during heating. A series of peaks appearing on the
TL glow curve may be attributed to trap levels characterized
by different activation energies. The theoretical description of
TL usually assumes uniform spatial distribution of traps and
recombination centres (RCs) (the simple trap model (STM)—
for a review see [3]). Another extreme case is the model of
localized transitions (LTs) of Halperin and Braner [4] regarding
hole–electron pairs trapped close to each other. The model
was later modified by Land [5]. Only for the two cases was it
possible to formulate differential equations describing charge
carriers' kinetics.

A spatial correlation between traps and RCs in
thermoluminescent detectors was suggested by many
authors [6–8]. However its influence on TL kinetics could
be studied only by using Monte Carlo methods [9–11]. It
was shown that in these cases one gets unusual TL spectra
that cannot be described in terms of the above standard
models. Consequently, the spatial arrangement of traps could
change the kinetics of trapping and recombination of charge
carriers. Applying Monte Carlo simulation to a system
of linearly arranged localized hole–electron pairs with the
possibility of the charge carrier's transport along the chain,
it was found that the main TL curve is accompanied by an
additional small peak. Since the peak relates to the charge
carrier's movement between localized sites it was called the
displacement peak [12, 13].

An existence of metastable hole–electron pairs in irradi-
ated TL detectors is normally assumed in TL dose–response
studies [14, 15]. However, the consequences for TL kinetics
have never been theoretically assessed. This paper presents
the semi-localized transitions (SLTs) model that is a natural
generalization of LT. Fully analytic formulation allows easier
numerical modelling of such systems. Some examples demon-
strate that in a monoenergetic trap system SLT generates a
two-peak TL structure resembling displacement peaks.

2. Theory

2.1. Two standard models

In dielectrics with randomly distributed traps and RCs, where
all transitions go through the conduction band, the kinetics of
trapping and recombination can be described well by the STM
model [3]. Assuming that within a given temperature range
only one trap level and one type of RC are 'active', the charge
carrier's kinetics is described by the following set of equations:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT}\right) - n_{c}A(N-n), \quad (1a)$$

$$-\dot{m} = Bmn_{c}, \quad (1b)$$

$$m = n + n_{c} + M. \quad (1c)$$

Here E stands for the activation energy and N, n and m denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in RCs, respectively. M stands for the number of electrons in the thermally disconnected traps (deep traps), i.e. traps that are not emptied during the experiment. A and B stand for the trapping and recombination probability coefficients, respectively, and ν is the frequency factor. The sample is usually heated at a constant rate β, i.e. $T = T_0 + \beta t$, where T_0 is the initial temperature.

In general, the set of equations (1) has no analytic solutions. However, in many cases it was found that the following approximation applies:

$$\mathcal{L} = n_0 \nu \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{\nu}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{k\theta}\right) d\theta\right], \quad (2)$$

which is known as the Randall–Wilkins (RW) solution [16] or the first order kinetics equation. Here, n_0 denotes the initial concentration of trapped carriers and $\mathcal{L}$ is the TL intensity, defined as

$$\mathcal{L} \equiv -\frac{dm}{dt} \simeq -\frac{dn}{dt}. \quad (3)$$

Another situation (the LT model) was considered by Halperin and Braner [4]. They assumed that traps and RCs are closely correlated in space forming pairs that can be considered as independent units—i.e. all charge transfer takes place within groups of one kind, each having one trapping state, one excited state and one RC. Correct equations for this case were given by Land [5]:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT}\right) - \bar{A} n_e, \quad (4a)$$

$$-\dot{m} = \bar{B} n_e, \quad (4b)$$

$$m = n + n_e, \quad (4c)$$

where n_e denotes the concentration of electrons in the excited state. Because the transport of charge carriers does not take place through the conduction band, the TL peak should not be accompanied by thermally stimulated conductivity. It is assumed that $\bar{A}$ and $\bar{B}$ are constants. It was found [17] that the solution of (4) is very well approximated by the RW equation with the frequency factor, ν, replaced by

$$\bar{\nu} = \frac{\nu}{1 + \bar{A}/\bar{B}}. \quad (5)$$

2.2. The model of SLTs

In the LT model all trapped carriers will recombine with adjacent RCs at an appropriately high temperature. However, we can enrich the model by adding the possibility of separation of trapped hole–electron pairs in a way similar to that for the most popular LiF : Mg, Ti detector: for example, Nail *et al* [14] and Horowitz *et al* [15] considered that only peak 5a relates to the geminate recombination (i.e. the LT). The main peak, peak 5, relates to charge carriers that escaped from their native hole–electron pair systems.

Constructing the kinetic model, we will consider additional transitions between the local excited state and the conduction band. The appropriate energy diagram is shown in figure 1. Unfortunately, it is not possible to
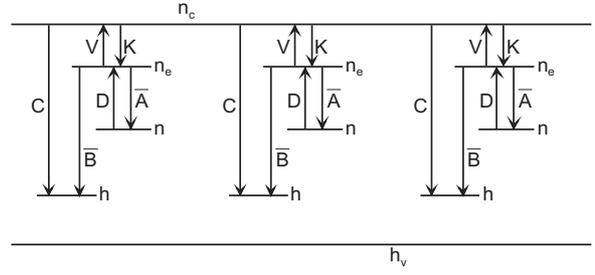
Figure 1. TL kinetics for the SLT model. Intra-pair transitions are denoted by $\bar{A}$, trapping; D, detrapping; and $\bar{B}$, recombination. Other transitions are denoted as follows: V, excitation to the conduction band; K, capture of a free electron to the excited state of a hole–electron pair and C, recombination process directly from the conduction band.
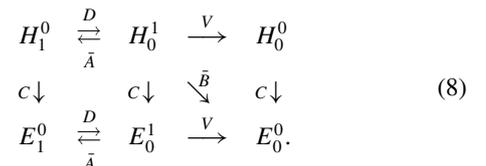
write kinetic equations using solely global concentrations of charge carriers in each level, because some of the transitions depend on the current number of carriers occupying traps and RCs. For that reason, to describe the system analytically we will enumerate the concentrations of all elementary states of trap–recombination centre (T–RC) pairs using the following notation:

$$H_0^0 \equiv \begin{Bmatrix} 0 \\ 0 \\ 1 \end{Bmatrix}, \quad H_1^0 \equiv \begin{Bmatrix} 0 \\ 1 \\ 1 \end{Bmatrix}, \quad H_0^1 \equiv \begin{Bmatrix} 1 \\ 0 \\ 1 \end{Bmatrix}, \quad H_1^1 \equiv \begin{Bmatrix} 1 \\ 1 \\ 1 \end{Bmatrix},$$

$$E_0^0 \equiv \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix}, \quad E_1^0 \equiv \begin{Bmatrix} 0 \\ 1 \\ 0 \end{Bmatrix}, \quad E_0^1 \equiv \begin{Bmatrix} 1 \\ 0 \\ 0 \end{Bmatrix}, \quad E_1^1 \equiv \begin{Bmatrix} 1 \\ 1 \\ 0 \end{Bmatrix},$$

$$(6)$$

where the numbers inside brackets,

$$\begin{Bmatrix} \bar{n}_e \\ \bar{n} \\ \bar{h} \end{Bmatrix}, \quad (7)$$

denote occupation of all states in a single (T–RC) unit, i.e. $\bar{n}_e$ is the number of electrons in the local excited level, $\bar{n}$ is the number of electrons in a trap level and $\bar{h}$ denotes the number of holes in the RC level. The symbol (7) is a time-dependent variable denoting concentration (in cm^{-3}) of all T–RC units having $\bar{n}_e$, $\bar{n}$ and $\bar{h}$ charge carriers in the respective trap levels. Therefore, the variables $H_m^n(t)$ and $E_m^n(t)$ denote the concentrations of states (i.e. corresponding T–RC units) with full and empty RCs, respectively. The initial excitation generates only H_1^0 states, i.e. trapped hole–electron pairs. All other states are set to 0 (the initial concentration of E_0^0 is not significant). For simplicity, in present calculations, we will consider the SLT model (figure 1) without K transitions, i.e. $K = 0$. Additionally, we will assume that creation of states with two active electrons, i.e. H_1^1 and E_1^1, is unlikely. It reduces the number of variables (6) and allows us to write the following diagram illustrating transitions between all states:

$$\begin{array}{ccccc} H_1^0 & \underset{\bar{A}}{\overset{D}{\rightleftharpoons}} & H_0^1 & \xrightarrow{V} & H_0^0 \\ c\downarrow & & c\downarrow \quad \searrow^{\bar{B}} & & c\downarrow \\ E_1^0 & \underset{\bar{A}}{\overset{D}{\rightleftharpoons}} & E_0^1 & \xrightarrow{V} & E_0^0. \end{array} \quad (8)$$

Using the diagram, we can derive a set of differential equations for these processes. For the sake of demonstration, we will consider transitions for the H_1^0 states, i.e. T–RC pairs having one hole in an RC with empty trap and excited levels. The concentration of these states can be changed due to transitions involving H_0^1 and E_0^0 states. The first process is the excitation of an electron from the excited local level to the conduction band. This process transforms H_0^1 states to H_0^0 with the rate $V H_0^1$, where the excitation coefficient, V, will be defined later. The second process converts H_0^0 states to E_0^0 due to recombination of the hole in the RC with an electron from the conduction band. The total rate for this process is $(-C n_c H_0^0)$. Similarly, considering the other transitions, we can derive the following set of equations:

$$\dot{H}_1^0 = -(D + C n_c) H_1^0 + \bar{A} H_0^1, \qquad (9a)$$

$$\dot{H}_0^1 = D H_1^0 - (\bar{A} + \bar{B} + V + C n_c) H_0^1, \qquad (9b)$$

$$\dot{H}_0^0 = V H_0^1 - C n_c H_0^0, \qquad (9c)$$

$$\dot{E}_1^0 = C n_c H_1^0 - D E_1^0 + \bar{A} E_0^1, \qquad (9d)$$

$$\dot{E}_0^1 = C n_c H_0^1 + D E_1^0 - (\bar{A} + V) E_0^1, \qquad (9e)$$

$$\dot{E}_0^0 = \bar{B} H_0^1 + C n_c H_0^0 + V E_0^1, \qquad (9f)$$

$$\dot{n}_c = -C n_c (H_1^0 + H_0^1 + H_0^0) + V (H_0^1 + E_0^1). \qquad (9g)$$

Here $\bar{B}$ and C denote the coefficients for direct (intra-pair) and band-to-RC recombination, respectively. $\bar{A}$ denotes the coefficient for trapping. We will assume that the excitation coefficients, D and V, are thermally activated:

$$D(t) = \nu \exp\left(\frac{-E}{kT(t)}\right), \qquad (10)$$

$$V(t) = \nu_V \exp\left(\frac{-E_V}{kT(t)}\right), \qquad (11)$$

where E, E_V, ν and ν_V are constants. The connection with standard variables used in STM (1) and LT (4) models is the following:

$$n = H_1^0 + E_1^0, \qquad (12)$$

$$n_e = H_0^1 + E_0^1, \qquad (13)$$

$$n_c = H_0^0 - E_0^1 - E_1^0, \qquad (14)$$

$$h = H_1^0 + H_0^1 + H_0^0. \qquad (15)$$

The SLT system has two possible radiative transitions, $\bar{B}$ and C, that could be responsible for TL. The first one relates to direct recombination within the hole–electron pair. The second one denotes recombination from the conduction band. The corresponding TL intensities are defined by

$$\mathcal{L}_{\bar{B}} = \bar{B} H_0^1, \qquad (16)$$

$$\mathcal{L}_C = C n_c (H_1^0 + H_0^1 + H_0^0). \qquad (17)$$

3. Numerical examples

Analytic formulation of the SLT model eliminates the necessity for performing Monte Carlo simulations. Here the solution may be obtained by solving the set of nonlinear equations (9). For these purposes we used the *Mathcad* procedures *stiffr( )* and *stiffb( )* for stiff differential equations. Average computing times for solving the set of equations (9) for a given set of parameters were less than half an hour on a typical personal computer. Below, we will show some examples demonstrating basic properties of the SLT model.

To solve the set of equations (9), we have to fix the initial values of seven variables, $H_m^n(0)$, $E_m^n(0)$ and $n_c(0)$, and nine parameters, $\bar{A}$, $\bar{B}$, C, E, E_V, ν, ν_V, β and T_0. As said before, only H_1^0 states are initially generated, i.e. $H_1^0(0) = n_0$, where n_0 is the initial concentration of trapped carriers. All other variables are set to 0. We will assume typical trap parameters, i.e. $E = 0.9$ eV, $\nu = \nu_V = 10^{10}$ s^{-1} and the heating rate $\beta = 1$ K s^{-1}. Some parameters have a minor influence on TL, e.g. the initial temperature, T_0 (provided that T_0 is low enough, e.g. 100 K below the maximum peak temperature). Numerical calculations show also that the recombination coefficients $\bar{B}$ and C do not change the resulting TL significantly. To characterize the relative recombination probabilities, we introduce a new coefficient,

$$\delta \equiv \frac{CN}{\bar{B}}, \qquad (18)$$

where N denotes the global concentration of traps. Here we assume the full initial filling $N = n_0$. Considering a solid with the concentration of traps $N = 10^{17}$ cm^{-3} and recombination coefficients $C = 10^{-10}$ cm^3 s^{-1}, $\bar{B} = 10^3$ s^{-1}, we get $\delta = 10^4$. The influence of the retrapping coefficient $r \equiv \bar{A}/\bar{B}$ and the energy barrier, E_V, on the TL kinetics is demonstrated in figures 2–4.

The TL curves presented in figure 2 were calculated for $E_V = 0.7$ eV and various retrapping coefficients: $r = 0$, $r = 1$ and $r = 10^2$. Three TL intensities were calculated: intra-pair luminescence, $\mathcal{L}_{\bar{B}}$ (LTs, equation (16)), radiative recombination from the conduction band, $\mathcal{L}_C$ (delocalized transitions, equation (17)), and the sum $\mathcal{L}_{tot} = \mathcal{L}_{\bar{B}} + \mathcal{L}_C$. Using spectrally resolved TL, it is possible to distinguish between $\mathcal{L}_{\bar{B}}$ and $\mathcal{L}_C$, since these transitions should typically have different spectral distributions. $\mathcal{L}_{tot}$ is given for reference only. The standard solution for the LT model (which corresponds in SLT to $V(t) = 0$) is drawn (with black dots) to show the discrepancy between LT and SLT. We can note an increase in delocalized transitions with increasing r. To explain this dependence, one may note that the delocalization (i.e. excitation probability, $V(t)$) is thermally activated (11). Strong retrapping shifts the TL to higher temperatures where the delocalization is more probable.

Figure 3 presents the influence of the energy barrier height, E_V, on the TL intensities. The calculations were made assuming $r = 10^2$. As expected, for high values of E_V, SLT is limited to LTs ($\mathcal{L}_{\bar{B}}$) which coincide with the LT model. As the barrier decreases, the delocalized recombination path becomes more probable and the main TL peak occurs at a lower temperature than does the relevant LT peak.
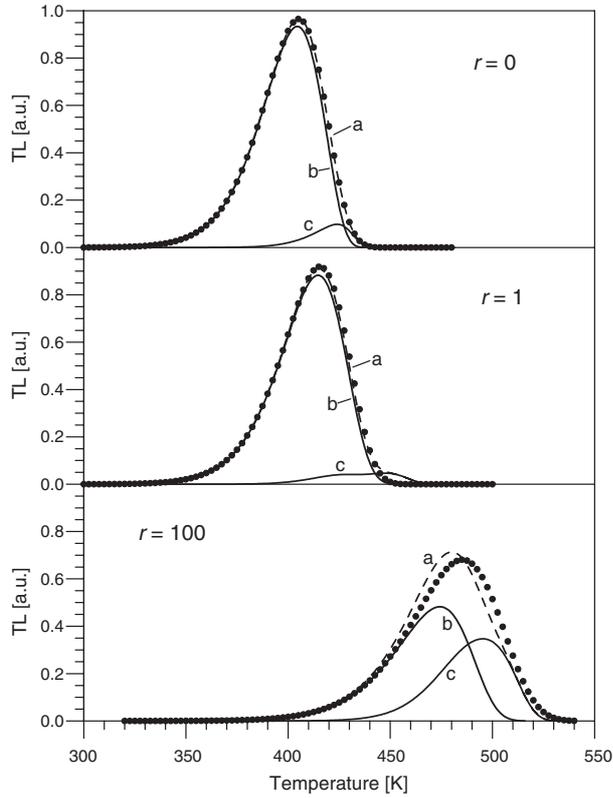
Figure 2. TL curves calculated in the framework of the SLT model for various retrapping coefficients: $r = 0$, $r = 1$ and $r = 10^2$. The curves 'b' correspond to the TL intra-pair direct transition intensity, $\mathcal{L}_{\bar{B}}$ (16), and the curves 'c' corresponds to radiative transitions from the conduction band, $\mathcal{L}_C$ (17). The curves 'a' correspond to the sum of the two intensities, $\mathcal{L}_{\text{tot}} = \mathcal{L}_{\bar{B}} + \mathcal{L}_C$. The calculations were performed for the following parameters: $E = 0.9\,\text{eV}$, $E_V = 0.7\,\text{eV}$, $\nu = \nu_V = 10^{10}\,\text{s}^{-1}$, $\delta = 10^4$ and the heating rate $\beta = 1\,\text{K}\,\text{s}^{-1}$. The K transition is neglected. Relevant solutions for the LT model (setting $V = 0$) are shown as full circles (●).

Figure 3. TL curves calculated in the framework of the SLT model for various energy barrier heights, E_V, assuming the retrapping coefficient $r = 10^2$. Other parameters and symbols are the same as in figure 2.

Figure 4. Illustration of displacement peaks calculated for three activation energies, E_V. Other parameters and symbols are the same as in figure 3.

On the middle diagram in figure 2 ($r = 1$) and the upper diagram in figure 3 ($E_V = 0.8\,\text{eV}$) one can observe the nontypical double-peak structure of the $\mathcal{L}_C$ curve. To study this effect more carefully, three $\mathcal{L}_C$ curves were calculated for $r = 10^2$ and different energy barriers, E_V. The results are presented in figure 4. The shape of $\mathcal{L}_C$ resembles the TL displacement peaks which were found in various spatially correlated systems using Monte Carlo simulation [12, 13]. The first $\mathcal{L}_C$ peak corresponds to an increasing concentration of charge carriers on the excited local level undergoing intra-pair recombination, and the second one relates to carriers wandering in the system in search of free RCs.

The resulting TL intensities were fitted numerically to RW equation (2). Usually, the fit of LTs, $\mathcal{L}_{\bar{B}}$, was unsatisfactory when both transitions took place simultaneously. However the intensity of delocalized transitions, $\mathcal{L}_C$, in most cases may be well fitted by one or two RW peaks. The results of the curve fitting are shown in table 1. Despite successful fitting by the first order kinetics equation, the obtained values of energies, E_C, and frequency factors, ν_C, do not relate directly to the real values assumed for the calculation, i.e. $E = 0.9\,\text{eV}$ and $\nu = 10^{10}\,\text{s}^{-1}$. Nevertheless, one may note that for the first case studied, $r = 0$ and $E_V = 0.7\,\text{eV}$, the deconvolution for two peaks leads to very high activation energies and frequency factors.
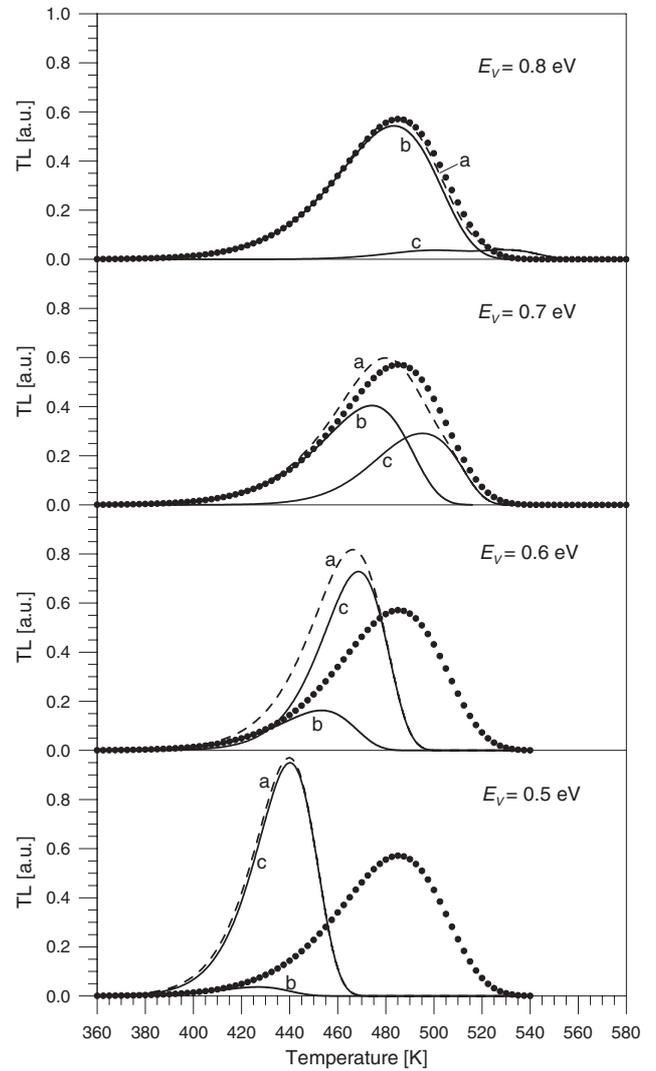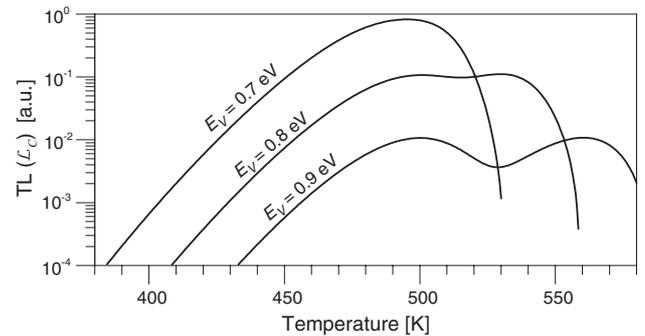
4. Conclusions

Recent dosimetric models of TL consider T–RC pairs involving both localized and delocalized (via conduction band)

Table 1. Results of fitting of $\mathcal{L}_C$ curves with the activation energy $E = 0.9$ eV and $\nu = 10^{10}$ s^{-1} to the RW equation (2) with the parameters E and ν replaced by E_C and ν_C, respectively. The SLT model was used for various r and E_V values. Other parameters of the model are the same as in figure 2. Numbers (1) and (2) relate to deconvolution for two peaks.

SLT parameters			Fitted parameters	
r	E_V (eV)		E_C (eV)	ν_C (s^{-1})
0	0.7	(1)	1.41	6.5×10^{15}
		(2)	2.48	3.6×10^{28}
1	0.7	(1)	1.32	4.9×10^{14}
		(2)	1.47	3.1×10^{15}
10^2	0.7		1.27	4.6×10^{11}
10^2	0.6		1.41	9.8×10^{12}
10^2	0.5		1.33	1.2×10^{14}

recombination [14, 15]. Until now, no kinetic model for this kind of composite transitions has been considered. This paper presents a new kinetic model for SLTs. A set of differential equations describing SLT is derived by enumeration of all T–RC states. Fully analytic formulation allows easier calculation, eliminating the necessity for performing Monte Carlo simulations. Numerical examples demonstrate some interesting properties of the SLT model. For example, it is able to account for the existence of displacement peaks, predicted previously by Monte Carlo calculations [12, 13]. From a mathematical point of view the SLT is much more complex than the standard models, LT and STM. Therefore, further comprehensive studies are necessary to know its properties and relate the kinetic parameters to dosimetric ones.

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