MODELLING EXCITATION KINETICS IN THE FRAMEWORK OF SEMI-LOCALIZED TRANSITIONS MODEL

J. Orzechowski[1], A. Mandowski[2]

*[1]Stanislaw Staszic High School
ul. Szkolna 12, 27-200 Starachowice, POLAND
[2]Institute of Physics, Jan Długosz University
Armii Krajowej 13/15, 42-200 Czestochowa, POLAND
email: a.mandowski@ajd.czest.pl*

Recently the model of semi-localized transitions (SLT) was proposed combining both localized and delocalized transitions occurring in thermoluminescence (TL) and related phenomena. This paper presents formulation and exemplary application of the SLT model to the analysis of excitation processes, which are very important in constructing dose dependence characteristics of TL. It shows how various factors determine initial conditions for TL. Possible consequences for the analysis of TL and related phenomena in terms of standard kinetic models are discussed also.

Key words: thermoluminescence, semi-localized transition, traps, recombination.

Thermoluminescence (TL) is a widely known technique, frequently used for characterization of traps and recombination centers (RCs) in insulating materials [1]. Commercial applications include dosimetry of ionizing radiation and dating of archaeological and geological objects. Prior to the measurement a sample is excited at appropriately low temperature to fill traps and RCs with charge carriers. Then, the sample is heated, usually with a constant rate. During heating emitted luminescence is recorded. The luminescence is related to recombination of charge carriers, which were thermally released from traps and then moved to RCs.

Theoretical description TL is usually based on two models: the model of localized transitions (LT) and the simple trap model (STM). The first one (the LT model) allows trapped charge carriers to recombine solely to adjacent RC. The second one (STM) assumes transition of charge carriers via conduction band. These transitions are delocalized. Recently [2] a more general model was proposed combining both localized and delocalized transitions. This is the model of semi-localized transitions (SLT). Analytic equations for SLT are constructed using enumeration technique which transforms concentrations of carriers to concentrations of states of localized trap - recombination centre (T-RC) pairs. The model allows explaining some unusual properties observed in TL measurements (e.g. the occurrence of very high frequency factors [3]).

This paper discussed the possibility of applying SLT model to the analysis of excitation processes, which is performed before the main TL measurement. This stage of

measurement is very important for dose dependence characteristics. Example approach of this kind is proposed. Possible consequences for TL will be analysed.

Typical TL experiment is performed with linear heating rate scheme, i.e. the temperature $T = T_0 + \beta t$, where T_0 is the initial temperature, t denotes time and β is the heating rate. The first "classical" model – STM – assumes spatially uniform distribution of separate traps and recombination centres (RCs). Charge carrier transitions taking place during heating occur via conduction band after thermal release. The kinetics of trapping and recombination is governed by the following set of differential equations [1]:

$$-\dot{n}_i = n_i \nu_i \exp\left(\frac{-E_i}{kT}\right) - n_c A_i (N_i - n_i), \qquad i=1..p, \qquad (1a)$$

$$-\dot{m}_s = B_s m_s n_c, \qquad s=1..k, \qquad (1b)$$

$$\sum_{s=1}^{k} m_s = \sum_{i=1}^{p} n_i + n_c + M, \qquad (1c)$$

where N_i, n_i, and m_s denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in recombination centres, 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_i and B_s stand for the trapping and recombination probabilities, respectively, and ν is the frequency factor. Luminescence intensity is proportional to $(-\dot{m})$, i.e.

$$L = -\frac{dm}{dt}. \qquad (2)$$

Another important case is the model of laclized transitions (LT). 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]:

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

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

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

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.

The SLT model for TL kinetics was first introduced in [2] (some earlier attempts were erroneous and will be not mentioned here). The model unifies STM and LT models. The basic rules are the following: it is assumed that a solid consists of trap–recombination centre (T–RC) pairs. The energy band diagram representing the general SLT model is given in figure 1 (for detailed description cf. [2] and [3]).
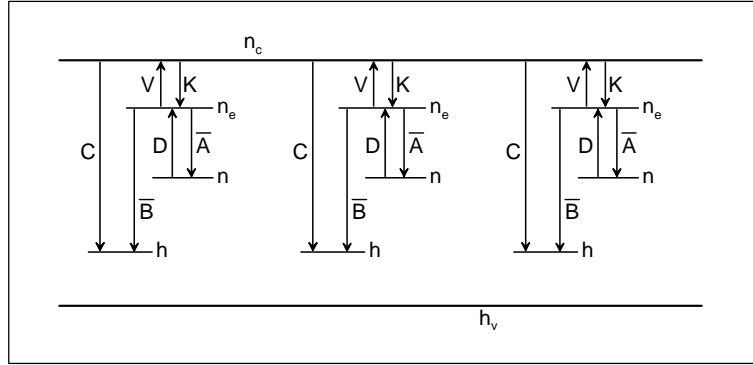
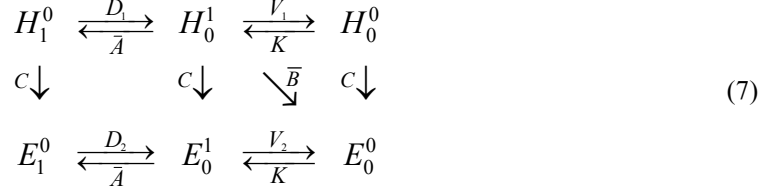Fig. 1. Energy band diagram for the SLT model for heating stage

Each pair may contain not more than one electron and one hole. Traps have two localized energy levels: the ground level and the excited level. Therefore, we have the following set of the allowed states of T–RC pair:

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

$$(5)$$

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

Where the numbers inside brackets

$$\begin{Bmatrix} \overline{n}_e \\ \overline{n} \\ \overline{h} \end{Bmatrix}$$

$$(6)$$

denote occupation of all states in a single T–RC unit, i.e. $\overline{n}_e$ is the number of electrons in the local excited level, $\overline{n}$ is the number of electrons in trap level and $\overline{h}$ denotes the number of holes in RC level. The symbol (6) is a time-dependent variable denoting concentration (in cm^{-3}) of all T–RC units having $\overline{n}_e$, $\overline{n}$ and $\overline{h}$ 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. Due to previous assumption the states H_1^1 and E_1^1 will not be taken into account. Allowed transitions between various states of a single T–RC pair may be represented here by the following diagram:

$$H_1^0 \xrightleftharpoons[\overline{A}]{D_1} H_0^1 \xrightleftharpoons[K]{V_1} H_0^0$$

$$C\downarrow \qquad\quad C\downarrow \qquad \searrow \overline{B} \quad C\downarrow \tag{7}$$

$$E_1^0 \xrightleftharpoons[\overline{A}]{D_2} E_0^1 \xrightleftharpoons[K]{V_2} E_0^0$$

The bar variables $\overline{A}$ and $\overline{B}$ denote probability densities (in s^{-1}) of localized transitions for trapping and recombination, respectively. Similarly, K and C denote probability densities (in cm^{3}s^{-1}) of delocalized transitions for trapping from the conduction band to the excited state of a trap and recombination, respectively. Thermal activation probabilities for transition of a single charge carrier from the ground trap level to the excited level, and subsequent transition from the excited level to the conduction band are given by D and V, respectively (all in s^{-1}). The difference between D_1 and D_2 as well as between V_1 and V_2 will be discussed later. The corresponding set of differential equations is written below:

$$\dot{H}_1^0 = -\left(D_1 + Cn_c\right)H_1^0 + \overline{A}H_0^1 \tag{8a}$$

$$\dot{H}_0^1 = D_1 H_1^0 - \left(\overline{A} + \overline{B} + V_1 + Cn_c\right)H_0^1 + Kn_c H_0^0 \tag{8b}$$

$$\dot{H}_0^0 = V_1 H_0^1 - \left(K + C\right)n_c H_0^0 \tag{8c}$$

$$\dot{E}_1^0 = Cn_c H_1^0 - D_2 E_1^0 + \overline{A}E_0^1 \tag{8d}$$

$$\dot{E}_0^1 = Cn_c H_0^1 + D_2 E_1^0 - \left(\overline{A} + V_2\right)E_0^1 + Kn_c E_0^0 \tag{8e}$$

$$\dot{E}_0^0 = \overline{B}H_0^1 + Cn_c H_0^0 + V_2 E_0^1 - Kn_c E_0^0 \tag{8f}$$

$$\dot{n}_c = -Cn_c\left(H_1^0 + H_0^1 + H_0^0\right) + V_1 H_0^1 + V_2 E_0^1 - Kn_c\left(H_0^0 + E_0^0\right) \tag{8g}$$

The coefficients D and V are responsible for thermal activation, i.e.

$$D(t) = \nu \exp\left(\frac{-E}{kT(t)}\right) \tag{9}$$

$$V(t) = \nu_V \exp\left(\frac{-E_V}{kT(t)}\right) \tag{10}$$

where E, E_V, ν and ν_V are constants. When the states H_m^n and E_m^n have different activation energies, the coefficients split up into D_1 (with E_1, ν_1), V_1 (with E_{V1}, ν_{V1}) and D_2 (with E_2, ν_2), V_2 (with E_{V2}, ν_{V2}). It leads to the 'cascade detrapping' phenomenon [3] resulting in very narrow TL peaks characterized by enormously high frequency factors and overestimated activation energies. Luminescence intensities related to recombination from localized excited levels ($L_{\overline{B}}$) and from the conduction band (L_C - delocalized) are defined as follows:

$$L_{\overline{B}} = \overline{B}H_0^1 \tag{11}$$

$$L_C = Cn_c(H_1^0 + H_0^1 + H_0^0) \tag{12}$$

As the luminescence comes from different transitions it may be characterized by different spectral distribution. Any differences may be observed by applying spectrally resolved measurements. Classical limits of SLT and 'downconversion' to STM and LT was discussed in [6]. A comparison of these three models is shown in fig. 2.
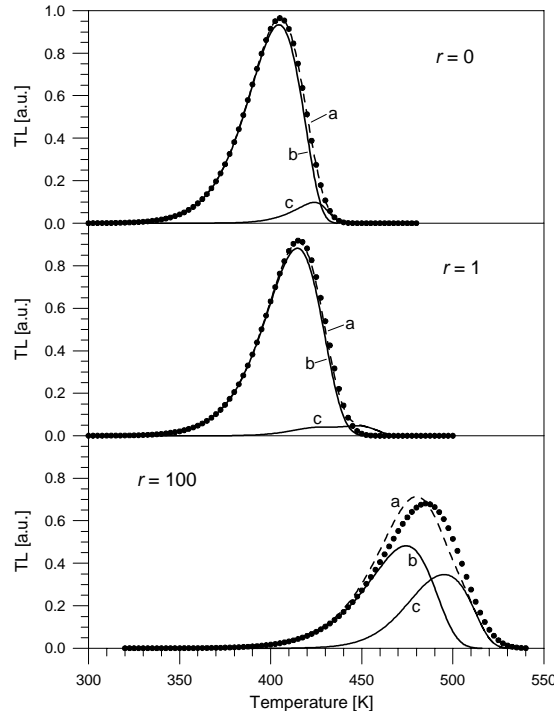

Fig. 2. TL curves calculated in the framework of SLT model for various retrapping coefficients: $r = 0$, $r = 1$ and $r = 10^2$. The curves b correspond to TL intra-pair direct transitions intensity $L_{\bar{B}}$ (11), the curves c corresponds to radiative transitions from the conduction band L_C (12). The curves a correspond to the sum of both intensities $L_{\text{tot}} = L_{\bar{B}} + L_C$. The calculations were performed for the following parameters: $E = 0,9\,\text{eV}$, $E_V = 0,7\,\text{eV}$, $\nu = \nu_V = 10^{10}\,\text{s}^{-1}$, and the heating rate $\beta = 1\,\text{K/s}$. Relevant solutions for the LT model (setting $V = 0$) were shown as full circles (•)

Typically, excitation of TL samples is performed at constant, 'low' temperature. The term 'low' means that all charge carrier transitions from trap/recombination levels to transport bands may be neglected. This assumption simplifies the kinetics, however some additional issues have to be taken into account. First of all, the high-energy radiation generates band-to-band transitions creating free electrons and holes. We denote the transitions as G. Free charge carriers moving through transport bands are captured by traps and RC's. There are several possible transitions of this kind, supplementary to that shown in fig. 1. However, to keep the calculations as simple as possible, we limit

ourselves to two hole transitions from the valence band: K_v represents trapping of free hole to RC for electrons and K_e represents trapping of free hole to deeper electron trap. The diagram is shown in fig. 2.
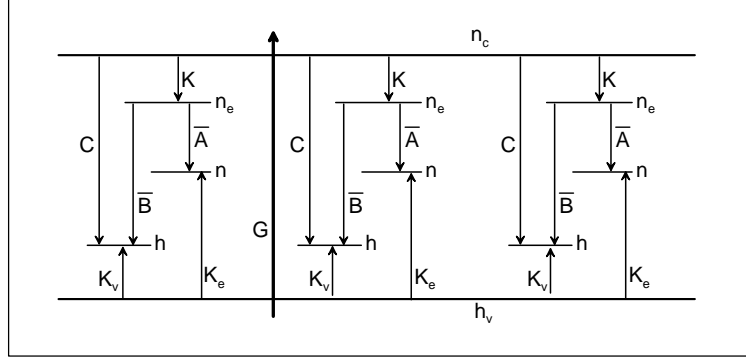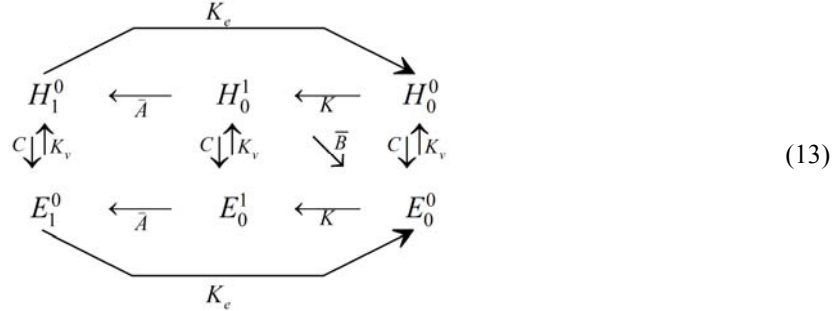

Fig. 2. Energy band diagram for the SLT model for excitation stage

To construct differential equations for the excitation stage, first we have to write a diagram illustrating transitions between various states of T-RC pairs take into account K_v and K_e transitions. The diagram is shown below:

$$
\begin{array}{ccccc}
 & & K_e & & \\
H_1^0 & \xleftarrow{\bar{A}} & H_0^1 & \xleftarrow{K} & H_0^0 \\
C\Updownarrow K_v & & C\Updownarrow K_v & \searrow^{\bar{B}} & C\Updownarrow K_v \\
E_1^0 & \xleftarrow{\bar{A}} & E_0^1 & \xleftarrow{K} & E_0^0 \\
 & & K_e & &
\end{array}
\tag{13}
$$

The diagram allows to write corresponding set of differential equations:

$$\dot{H}_1^0 = -(Cn_c + K_e h_V)H_1^0 + \bar{A}H_0^1 + K_V h_V E_1^0 \tag{14a}$$

$$\dot{H}_0^1 = -(\bar{A} + \bar{B} + Cn_c)H_0^1 + Kn_c H_0^0 + K_V h_V E_0^1 \tag{14b}$$

$$\dot{H}_0^0 = K_e h_V H_1^0 - (C+K)n_c H_0^0 + K_V h_V E_0^0 \tag{14c}$$

$$\dot{E}_1^0 = Cn_c H_1^0 - (K_V + K_e)h_V E_1^0 + \bar{A}E_0^1 \tag{14d}$$

$$\dot{E}_0^1 = Cn_c H_0^1 - (\bar{A} + K_V h_V)E_0^1 + Kn_c E_0^0 \tag{14e}$$

$$\dot{E}_0^0 = \bar{B}H_0^1 + Cn_c H_0^0 + K_e h_V E_1^0 - (K_V h_V + Kn_c)E_0^0 \tag{14f}$$

$$\dot{n}_c = G - Cn_c H_1^0 - Cn_c H_0^1 - (C+K)n_c H_0^0 - Kn_c E_0^0 \tag{14g}$$

$$\dot{h}_V = G - K_e h_V H_1^0 - (K_V + K_e)h_V E_1^0 - K_V h_V E_0^1 - K_V h_V E_0^0 \tag{14h}$$

After excitation, the term $G = 0$ and the system goes in the state of fast relaxation. After some time (typically very short) it stays in metastable equilibrium.

Numerical calculations solving the set of eqs. (14) for excitation and relaxation stages were performed for various parameters. For example, assuming the following

parameters: $G=5 \cdot 10^{13}$ cm^{-3}s^{-1}, t=200s, $\overline{A} = \overline{B} = 10^{10}$ s^{-1}, $N=10^{16}$ cm^{-3}, $C=10^{-12}$ cm^{3}s^{-1}, $K=10^{-14}$ cm^{3}s^{-1}, $K_v=K_e=10^{-15}$ cm^{3}s^{-1}, we get the final concentrations of T-RC pairs shown in table 1.

<div align="right">*Table 1*</div>

Population of various states of T-RC pairs after excitation with the rate
$G=5 \cdot 10^{13}$cm^{3}s^{-1} during t=200 s

State name	H_1^0	H_0^1	H_0^0	E_1^0	E_0^1	E_0^0
Population [%]	14,0	0,0	24,5	24,5	0,0	36,9

What is meaning of these results? First of all, we are dealing with two classes of charge carriers - these are 'singlets'. i.e. T-RC pairs - each populated with a single charge carrier and 'doublets', i.e. T-RC pairs populated with electron and hole together. The first class comprises mainly two states: H_0^0 and E_1^0. Population of other state E_0^1 is negligible. The second class comprises mainly of state H_1^0. Population of the other doublet state H_0^1 is also negligible. Such distribution may have significant consequences for TL kinetics. Detailed studies will be given in a separate paper.

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МОДЕЛЮВАННЯ КІНЕТИКИ АКТИВАЦІЇ В НАБЛИЖЕННІ НАПІВЛОКАЛІЗОВАНОЇ МОДЕЛІ ПЕРЕХОДІВ

Й. Оржеховський[1], А. Мандовський[2]

*[1]Вища фахова школа Станіслава Стачіца
вул. Шкільна 12, 27-200 Старачовіце, Республіка Польща
[2]Інститут фізики, Університет Яна Длугоша
вул. Армії Крайової 13/15, 42200 Ченстохова, Республіка Польща*

У статті сформульовано та застосовано моделі напівлокалізованих переходів для аналізу процесів активації, важливих у конструкційній дозовій залежності характеристик термолюмінесценції. Показано, як різноманітні чинники визначають початкові умови для термолюмінесценції. Обговорено можливі наслідки аналізу термолюмінесценції в межах стандартної кінетичної моделі.

Ключові слова: термолюмінесценція, напівлокалізований перехід, пастки, рекомбінація.

МОДЕЛИРОВАНИЕ КИНЕТИКИ АКТИВАЦИИ В ПРИБЛИЖЕНИИ ПОЛУЛОКАЛИЗИРОВАННОЙ МОДЕЛИ ПЕРЕХОДОВ

И. Оржеховский[1], А. Мандовский[2]

*[1]Вищая профессиональная школа Станислава Стачица
ул. Школьная 12, 27-200 Старачевице, Республика Польша
[2]Институт физики, Университет Яна Длугоша
ул. Армии Краевой 13/15, 42200 Ченстохова, Республика Польша*

В статье сформулированы и использованы модели полулокализи-рованных переходов для анализа процессов активации, важных в конструкционной дозовой зависимости характеристик термолюминесценции. Показано, как разнообразные факторы определяют начальные условия для термолюминесценции. Обсуждаются возможные последствия анализа термолюминесценции в пределах стандартной кинетической модели.

Ключевые слова: термолюминесценция, полулокализированный переход, ловушки, рекомбинация.