Radiation Measurements 125 (2019) 78–84

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Simulation of TL kinetics in complex trap cluster systems: Some new approaches

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ARTICLE INFO

Keywords:
Thermoluminescence kinetics
Cluster system
Monte Carlo method
Deep traps
Competition effects

ABSTRACT

This paper presents an improved Monte Carlo algorithm for calculating thermoluminescence (TL) curves for complex cluster systems, which contain a large number of localized levels. The new algorithm is based on generation of two random numbers, instead of the many random number generations used in previous approaches. The first random number generation is associated with the choice of which type of energy transition takes place in the model, while the second random number generation is connected with the choice of a cluster group for which this transition occurred. The proposed new algorithm was tested on a new TL model consisting of clusters containing both electron traps and deep competitor traps. The luminescence centers in the model are treated as uniformly distributed defects. Applicability of the Monte Carlo method is demonstrated by simulating for the first time in this type of model the complete TL process, including the excitation, relaxation and heating stages. The new model explains the anomalous heating rate effect of TL, and describes the effect of localized trapping processes within the cluster on the intensity and temperature position of the TL peaks.

1. Introduction

Charge transfer processes in wide-gap insulators determine their many electrical, luminescent, and optical properties. Thermoluminescence (TL) is one of the widely studied phenomena, which is based on such processes. In experimental work, TL is recorded when a sample is heated after it was previously exposed to ionizing radiation. A linear heating rate is usually employed in these experiments, and the measured curve of TL intensity as a function of temperature consists of one or several peaks, depending on the structure of the charge carrier traps.

Theoretically, the TL process is described within the framework of the band theory of solids through rate equations, which are based on the concepts of chemical reaction kinetics. Generally, simulations of the TL process include all three stages: irradiation, relaxation, and thermal stimulation (Chen and Pagonis, 2011, 2014).

Most kinetic models that describe charge transfer processes in condensed matter are based on the assumption of a uniform distribution of traps and recombination centers. In this case, the TL process is simulated by solving a system of differential kinetic equations, either numerically or analytically (McKeever and Chen, 1997). In such equations, the concentrations of free electrons and holes and the concentrations of carriers trapped at localized levels are unknown functions.

In a number of luminescence materials, theoretical explanation of the TL mechanism in a number of materials by using this differential equation approach is not possible. These materials require more complex models that take into account the possibility of the formation of clusters, consisting of several localized lattice defects (Townsend and Rowlands, 1999; Mandowski and Swiatek, 1992; Horowitz et al., 2003; Mandowski and Swiatek, 1996; Mandowski, 2008; Mandowski. and Swiatek, 1998; Mandowski, 2001). Such spatially coupled cluster systems are typical of polycrystalline materials, as well as nanostructured phosphors. In addition, intensive processes of cluster formation can be observed with high-dose irradiation of the phosphor, as well as after excitation by high-energy charged particles (Chen and Pagonis, 2011; Horowitz et al., 2001, 2003).

The main feature of cluster models is the presence of localized electron transitions *within* the cluster, which are not accompanied by their delocalization into the conduction band. In a number of papers (Mandowski, 2005; Pagonis, 2005; Kumar et al., 2006, 2007), theoretical models describing TL kinetics in cluster systems were proposed and tested. It was found that the simultaneous consideration of the localized transitions within clusters, as well as intercluster charge transfer through the conduction band, lead to anomalous TL properties. These include changing the shape of the TL curve, the appearance of

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https://doi.org/10.1016/j.radmeas.2019.04.021
Received 21 December 2018; Received in revised form 27 March 2019; Accepted 27 April 2019
Available online 30 April 2019
1350-4487/

additional peaks, abnormally high values of the activation energy (Mandowski, 2006). Furthermore, such models can explain the anomalous dependencies of TL signals on the exposure dose rate and on the heating rate used during the experiments (Orzechowski and Mandowski, 2010; Mandowski and Bos, 2011).

To calculate the TL in cluster systems, some methods have been proposed which allow a description using a system of differential equations. For instance, in Refs. (Mandowski, 2005, 2006; Orzechowski and Mandowski, 2010), a model with cluster defects which contain two types of localized levels (trap and recombination centers) was considered. Both localized electron transitions within the cluster, and delocalized transitions taking place through the conduction band were taken into account. In this type of model, the concentrations of clusters in one of the possible states were treated as continuous functions, instead of considering the concentrations of isolated defects. The state of the cluster, in its turn, was uniquely determined by the population of its localized levels. This approach to the description of the TL kinetics in a cluster system was also used by other authors to simulate various features of TL with linear and isothermal heating (Kumar et al., 2006, 2007; Pagonis and Kulp, 2010). The disadvantage of these approaches is that the number of the considered functions in the system of differential equations is equal to the number of possible cluster states. As the number of localized levels inside a cluster increases, the number of kinetic equations in these approaches increases significantly, so that it becomes difficult to solve them using the known numerical methods.

Another example of a TL model which is difficult to describe via systems of differential equations is, for example, a model of one-dimensional chains of ordered clusters described in Ref. (Mandowski, 2001). In such models, occupancy of the localized levels of any cluster depends on the occupancies of localized levels of the neighbor clusters, at the previous moments of time. The number of independent functions in such systems can be quite large and, in general, is determined by the number of clusters in the chain and the number of localized energy levels in each cluster.

The application of the Monte Carlo method is promising in simulations of complex cluster systems (Mandowski and Swiatek, 1992; Mandowski. and Swiatek, 1998; Pagonis et al., 2014; Pagonis and Chen, 2015). The essence of the method is to generate random time intervals for each possible carrier transition. At each step, the smallest time interval is selected among the generated intervals. The transition with the shortest time interval is considered to be executed, and then the next step is performed, etc.

The disadvantage of the Monte Carlo method is the large amount of computations involved, which requires high computer performance. If the system consists of several (more than two) types of localized levels, the number of random times that are needed to be generated at each step, in order to select one random event, increases significantly. In particular, systems of this type include models in which the cluster contains competing deep traps, in addition to the main electron traps. The analysis of such models by the Monte Carlo method requires the development of new approaches, in order to optimize the calculations of the TL curves.

Thus, the aim of this work is to improve the method for simulating the TL process based on the Monte Carlo method, and to test it by using the example of a cluster model containing competing deep electron traps.

2. The trap cluster model: excitation stage

The energy band diagram of the cluster model containing deep electron traps is shown in Fig. 1, for the irradiation stage. A complete list of the various parameters in the model is given in Table 1, together with their units and a brief description.

The model includes an emission center (H) and a large amount of independent cluster defects. Each cluster consists of the main active electron traps (N), which can be either in the ground state (n), or in the excited state (n_e), and of the competing deep electron traps (M). It should be noted that this type of model which includes clusters with competing deep traps, has not been considered earlier in the literature.

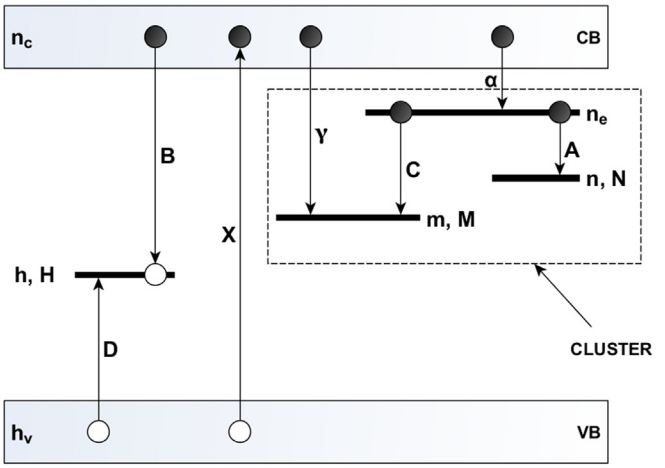

Fig. 1. The energy band diagram of the cluster model of TL with deep electron traps at the irradiation stage.

In Fig. 1, X is the transition corresponding to the formation of an electron-hole pair, and D represents capture of holes from the valence band by the emission center. α is the capture of an electron from the conduction band into the cluster (to the excited state level n_e), and B denotes the radiative recombination of an electron of the conduction band and a hole of the emission center. A represents the electron transition from the excited state of the trap N into the ground state, and C is the capture of an electron from the conduction band by the deep trap into the cluster. Finally, γ is the delocalized capture of an electron from the conduction band, by a deep trap within the cluster.

As previously in Ref. (Mandowski and Swiatek, 1992, 1996), we will consider the behavior of the model in a certain selected unit volume, which contains a number of certain defects. In place of concentrations we have to deal with the absolute number of traps, recombination centers and carriers in delocalized bands. Wherein, the coefficients, characterizing the transition probabilities, have the dimension [s^{-1}].

We introduce the following notations, with the corresponding units shown in Table 1: *X* is a coefficient characterizing the efficiency of formation of electron-hole pairs per time unit; *Z* is the total number of clusters; *N* represents the number of main traps within one cluster; *M* is the number of deep traps within one cluster; *H* is the total number of the emission centers; *A, B, C, D,* γ, *α* are coefficients characterizing probabilities of the corresponding transitions in Table 1.

When implementing the Monte Carlo method, transition times are generated according to the Poisson probability distribution (Mandowski and Swiatek, 1992). This distribution is used in the analysis of the so-called memoryless systems, whose behavior at the current iteration depends only on their corresponding state and does not depend on the states in which the system was at the previous iterations.

The Poisson probability distribution is described by the formula:

$$P(t) = 1 - \exp\left\{-\int_0^t \lambda(\tau)d\tau\right\}, \tag{1}$$

where $\lambda(t)$ is in general a function of time *t*. In the simplest case when λ = constant, expression (1) can be integrated and simplifies to:

$$P(t) = 1 - \exp\{-\lambda t\}, \tag{2}$$

From which we easily evaluate the time *t*:

$$t = -\frac{\ln(1-P)}{\lambda},\ P\varepsilon[0,\ 1). \tag{3}$$

Thus, to generate all the possible transition times in the model when

Table 1
The model parameters used in the TL simulations of this paper.

Notation	Description	Units
Z	Total number of clusters	non-dimensional
N	The number of the main (TL-active) traps per cluster	non-dimensional
M	The number of deep traps per cluster	non-dimensional
H	The number of emission centers	non-dimensional
n	The number of occupied ground state of the main trap per cluster	non-dimensional
m	The number of occupied deep trap per cluster	non-dimensional
n_e	The number of occupied excited state of the main trap per cluster	non-dimensional
h	The number of holes captured in the emission centers	non-dimensional
h_v	The number of holes in valence band	non-dimensional
n_c	The number of electrons in conduction band	non-dimensional
A	Probability coefficient of local trapping to the main trap	s^{-1}
C	Probability coefficient of local trapping to deep trap	s^{-1}
s	The frequency factor for the electron in the ground state of the main trap	s^{-1}
s_{ne}	The frequency factor for the electron in the excited state of the main trap	s^{-1}
E	The energetic distance from the ground state of the main trap to the excited state of the main trap (activation energy)	eV
E_{ne}	The energetic distance from the excited state of the main trap to the conduction band (activation energy)	eV
D	Probability coefficient of hole capture to emission center	s^{-1}
B	Probability coefficient of radiative recombination	s^{-1}
α	The electron capture coefficient to the excited state to the main trap from conduction band	s^{-1}
γ	The electron capture coefficient to the deep trap from conduction band	s^{-1}
X	The efficiency of electron-hole pair's creation	s^{-1}

λ = constant, one can use equation (3) with λ representing the corresponding probability coefficient. For transitions, which occur without involvement of clusters, we will use the equations for λ, which are similar to those in Ref. (Mandowski and Swiatek, 1992). For example, the λ values for transitions D and B in Fig. 1 are:

$$\lambda_D = D(H - h)h_v. \tag{4}$$

$$\lambda_B = Bhn_c. \tag{5}$$

Using equations analogous to (4) and (5) for transitions involving clusters is hindered by the fact that it implies random number generation for each cluster separately. This significantly increases the amount of calculations, and the time of program execution. We developed a new approach, which decreases the number of random number generations for transitions involving clusters.

To describe cluster transitions, it is advisable to introduce numbers of clusters that are in the same state, which we will further call the *cluster group* (Mandowski, 2005). Let us assume that $z(n,m,n_e)$ is the number of clusters with n filled main traps, m filled deep traps, and n_e electrons in the excited state. In the framework of the model under consideration, the following conditions are always met:

$$Z = \sum_{n,m,n_e} z(n, m, n_e) \tag{6}$$

$$n_c + \sum_{n,m,n_e} z(n, m, n_e)\cdot(n + m + n_e) = h_v + h, \tag{7}$$

where Z is a total number of clusters. Equations (6) and (7) correspond to the condition of electric charge neutrality, which are part of any TL model.

By analogy with the previous arguments in Refs. (Mandowski and Swiatek, 1992; Mandowski. and Swiatek, 1998), for each of the $z(n, m, n_e)$ clusters, the probability coefficients λ are expressed as follows:

$$\lambda(\alpha) = \alpha\cdot(N - n - n_e)\cdot n_c \tag{8}$$

$$\lambda(\gamma) = \gamma\cdot(M - m)\cdot n_c \tag{9}$$

$$\lambda(A) = A\cdot(N - n)\cdot n_e \tag{10}$$

$$\lambda(C) = C\cdot(M - m)\cdot n_e \tag{11}$$

We now introduce the more general probability coefficients *for each cluster group* as follows:

$$\lambda(\alpha,z) = z(n, m, n_e)\cdot\alpha\cdot(N - n - n_e)\cdot n_c \tag{12}$$

$$\lambda(\gamma, z) = z(n, m, n_e)\cdot\gamma\cdot(M - m)\cdot n_c \tag{13}$$

$$\lambda(A, z) = z(n, m, n_e)\cdot A\cdot(N - n)\cdot n_e \tag{14}$$

$$\lambda(C, z) = z(n, m, n_e)\cdot C\cdot(M - m)\cdot n_e \tag{15}$$

Since all the clusters are equivalent, once the transition with the shortest time is determined, it is enough to change the state of any cluster according to the transition. At the same time, it is necessary to reduce the number of clusters in the original group (by unity), and to increase the number of clusters in the group that corresponds to the new state (by unity).

The number of possible cluster states is determined by the number of possible values of the population of cluster levels n, m, n_e, and is estimated as $N{\cdot}M{\cdot}N$. If the number of possible cluster states is very large, then at each step a corresponding number of time generations will be required. We will now show how transition times can be generated *for the whole bulk of clusters*, not just for clusters that are in the same state.

Let there be n independent random variables x_i, which are characterized by different values of λ_i, these are described by the following cumulative Poisson distribution of probability:

$$P(x_i < t) = 1 - \exp\{-\lambda_i t\}. \tag{16}$$

Since $\langle x_i < t\rangle$ and $\langle x_i \geq t\rangle$ are opposite events, the sum of their probabilities is equal to one, hence:

$$P(x_i \geq t) = \exp\{-\lambda_i t\}. \tag{17}$$

It is obvious that the probability distribution that the minimum of all n random variables is greater than the time t is expressed as follows:

$$P(\min\{x_1, x_2, ..., x_n\} \geq t) = \prod_{i=1}^{n} \exp\{-\lambda_i t\} = \exp\left\{-\sum_{i=1}^{n} \lambda_i t\right\}. \tag{18}$$

Indeed, for the minimum of all n independent random variables to be greater than some t, it is necessary for each of them to be greater than t. The probability of this event is equal to the product of the probabilities for each quantity x_i.

Therefore, the probability distribution that the minimum of all n random variables will be less than t, is expressed as follows:

$$P(\min\{x_1, x_2, ..., x_n\} < t) = 1 - P(\min\{x_1, x_2, ..., x_n\} \geq t) = 1 - \exp\left\{-\sum_{i=1}^{n} \lambda_i t\right\}. \tag{19}$$

Comparison of equations (2) and (19) shows that a random time

corresponding to several events with different probability coefficients, can be generated by putting a sum of probability coefficients λ into equation (3):

$$\lambda_{\Sigma} = \sum_{i=1}^{n} \lambda_i \tag{20}$$

By using equation (20), one can obtain the corresponding sum-total probability coefficients of each transition, for all the clusters at once:

$$\lambda_{\Sigma}(\alpha) = \sum_{n,m,n_e} z(n, m, n_e)\cdot\alpha\cdot(N - n - n_e)\cdot n_c \tag{21}$$

$$\lambda_{\Sigma}(\gamma) = \sum_{n,m,n_e} z(n, m, n_e)\cdot\gamma\cdot(M - m)\cdot n_c \tag{22}$$

$$\lambda_{\Sigma}(A) = \sum_{n,m,n_e} z(n, m, n_e)\cdot A\cdot(N - n)\cdot n_e \tag{23}$$

$$\lambda_{\Sigma}(C) = \sum_{n,m,n_e} z(n, m, n_e)\cdot C\cdot(M - m)\cdot n_e \tag{24}$$

The times of the corresponding transitions are calculated by using formula (3), in which values λ_{Σ} replaces parameter λ. Using equations (21–24) allows generation of transition times for the whole bulk of clusters, instead of generating the transition times for the same clusters with all possible states.

After obtaining the transition time, it is necessary to find which exact cluster "participated" in this transition. For example, the transition of an electron from the excited state of trap N into the ground one (transition A in Fig. 1), can happen with the involvement of both the cluster with $m = 0$, $n = 0$, $n_e = 1$ and the cluster with m = 0, n = 1, $n_e = 2$. In such a case, it suffices to select a group of identical clusters (with the same m, n and n_e) randomly.

To achieve this aim, we divide the section from 0 to 1 into segments. Every segment corresponds to a group of identical clusters, thus to the corresponding factor $\lambda(z)$ from equations (12–15). With this choice, the length of each segment is proportional to a certain coefficient $\lambda(z)$ associated with this segment. The higher the value of the probability factor, the longer the segment is, and the higher the chance of a random number being generated into its range. Then, we generate a number from 0 to 1, and determine the segment in which it belongs. In this case, the transition is considered to be performed for the specific cluster group, which corresponds to the coefficient $\lambda(z)$ of the selected segment. In such a way we can randomly select a group of clusters, in which this or that transition occurred.

Thus, instead of a very large number of random number generations for all groups of clusters, one can use only two number random generations for each transition, and then search for a group of clusters with the shortest transition time. The first random number generation corresponds to the selection of the *transition*, and the second random number generation corresponds to the selection of the *cluster group* for which this transition occurred.

According to the method described above, at each step it is necessary to calculate all probability coefficients anew, taking into account the fact that in the general case (and primarily for cluster transitions), the calculation of each coefficient consists of a sequence of a large number of arithmetic operations. In addition to reducing the number of these operations, it is desirable to use as simple computational procedures as possible; for example, it is very useful to get rid of the operations of exponentiation, multiplication and division, whenever possible. In this way, instead of recalculating all probability coefficients at each step, it is sufficient to calculate the changes in these quantities *after* each step, depending on the transition.

We illustrate this approach by using the example of the delocalized transition coefficient λ_B. We assume that transition X occurred (the formation of an electron-hole pair) at the previous step. Then the expression for the coefficient λ_B at the next step takes the following form:

$$\lambda_{B\,i+1} = Bh(n_c + 1) = Bhn_c + Bh = \lambda_{B\,i} + Bh. \tag{25}$$

Thus, we have replaced one multiplication operation with an addition operation. Let us show a similar simplification of the calculation of the probability coefficients for transitions associated with clusters, by considering the example of transition γ:

$$\lambda_{\Sigma}(\gamma)_{i+1} = \sum_{n,m,n_e} z(n, m, n_e)\cdot\gamma\cdot(M - m)\cdot(n_c + 1) = \sum_{n,m,n_e} z(n, m, n_e)\cdot\gamma \cdot(M - m)\cdot n_c + \sum_{n,m,n_e} z(n, m, n_e)\cdot\gamma\cdot(M - m) = \lambda_{\Sigma}(\gamma)_i + \frac{\lambda_{\Sigma}(\gamma)_i}{n_c} \tag{26}$$

Similarly, one can simplify the calculation of the remaining probability coefficients. Such considerations allow significant simplification of the calculations, and decrease the execution time of the program by more than one order of magnitude. For example, with the model parameters given later in this paper, the calculation time of a TL curve by using the program developed in C++ without the optimization reported above was approximately 50 s, whereas the calculation time with optimization was only 2.5 s.

3. The trap cluster model: heating stage

The scheme of transitions within the considered model for the heating stage of TL, is shown in Fig. 2. At this stage, additional transitions corresponding to the thermal stimulation of electrons (P_{ne} and p) from active electron traps N are taken into account. The probability of these transitions is described by a Boltzmann factor (Chen and Pagonis, 2011):

$$V = s\exp\left(-\frac{E}{kT}\right), \tag{27}$$

where s (s^{-1}) is the frequency factor, E (eV) is the activation energy, k is the Boltzmann constant, T (K) is the temperature.

We assume that the temperature varies linearly with time. In order to generate the corresponding random times for these additional thermally activated processes, it is necessary to take into account the dependence of the probability coefficients on temperature T, and, therefore, on time t. Thus, to generate random times, it is necessary to use expression (1), in which the Boltzmann factor from equation (27) plays the role of the parameter λ.

Considering that $T = T_0 + \beta t$, where β (K/s) is the heating rate, the time t of the thermally stimulated transition is determined from the following expression:

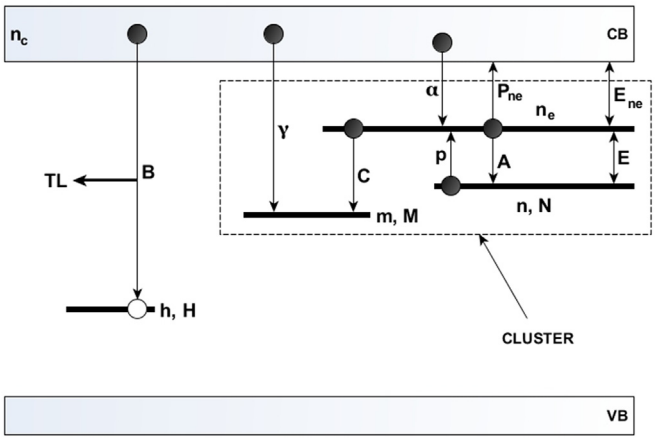

Fig. 2. The energy band diagram of the cluster model of TL with deep electron traps at the heating stage.

$$\int_0^t V dt' = \int_0^t s \cdot \exp\left\{\frac{-E}{k(T_0 + \beta t')}\right\} dt' = -\ln(1 - P). \tag{28}$$

If we replace time with temperature in expression (28), we obtain:

$$\int_{T0}^{T0+\Delta T} s \cdot \exp\left\{\frac{-E}{kT}\right\} dT = -\ln(1 - P) \cdot \beta. \tag{29}$$

The integral of this type is not expressed in terms of elementary functions, and therefore it is impossible to express the time, which determines the change in temperature, from this relation analytically. We suppose that the transitions in the system occur with a very large frequency. Thereby, the temperature change ΔT in the interval between the moments of various transitions is insignificant.

We transform expression (29) as follows:

$$\int_{T0}^{T0+\Delta T} s \cdot \exp\left\{\frac{-E}{kT}\right\} dT = \int_{T0}^{T0+\Delta T} s \cdot \exp\left\{\frac{-E}{kT}\right\} d\left(\frac{T \cdot T}{T}\right) \tag{30}$$

Considering that $T = T_0 + \Delta T$ and the smallness of ΔT, we replace T by T_0 in the numerator under the sign of the differential:

$$\begin{aligned} \int_{T0}^{T0+\Delta T} s \cdot \exp\left\{\frac{-E}{kT}\right\} d\left(\frac{T \cdot T}{T}\right) &\simeq \int_{T0}^{T0+\Delta T} s \cdot \exp\left\{\frac{-E}{kT}\right\} d\left(-\frac{T0^2}{T}\right) \\ &= \frac{k \cdot s \cdot T0^2}{E} \int_{T0}^{T0+\Delta T} \exp\left\{\frac{-E}{kT}\right\} d\left(\frac{-E}{kT}\right) \\ &= \frac{k \cdot s \cdot T0^2}{E} \exp\left\{\frac{-E}{kT}\right\}\Big|_{T0}^{T0 + \Delta T} \end{aligned} \tag{31}$$

From expressions (29) and (31) it follows that:

$$\ln(1 - P) \cdot \beta = -\frac{k \cdot s \cdot T0^2}{E} \exp\left\{\frac{-E}{kT}\right\}\Big|_{T0}^{T0 + \Delta T} \tag{32}$$

From the expression (32) it is possible to express the change in temperature ΔT, which, given the linear heating law, allows us to find the times of thermally stimulated transitions (P_{ne} and p) in the model (Fig. 2).

The calculation of the probability coefficients λ and of the times t for the remaining transitions at the heating stage, is completely analogous to the calculations described in Section 2 for the irradiation stage.

4. The Monte Carlo algorithm for simulation of the TL curve

Fig. 3 shows a flow chart of the Monte Carlo algorithm, which simultaneously describes the process of TL modelling for the stages of excitation, relaxation and heating. The algorithm is a cycle which consists of several operations, corresponding to the process described in Section 2 and 3 of this paper. At the beginning of the cycle, a random time for each transition is generated according to equation (3). Next, the transition with the least time is chosen. If the transition occurs within a cluster, then a group of clusters is also chosen for which this transition took place, by using the method mentioned above. Then, new values of the populations of different localized levels, as well as new values of probability coefficients are calculated, depending on the transition realized. Next, the cycle is repeated and the excitation stage continues, until the exposure time reaches the specified value. The number of required similar cycles at the heating stage is determined by the set maximal temperature value T_k.

5. Results and discussion

Approbation of the developed Monte Carlo methodology for simulating the TL signal from cluster systems, was carried out by calculating the TL curves using different parameters in the model. Two of the parameters varied are the heating rate and the coefficient C of localized capture into a deep trap within the cluster (see Figs. 1 and 2). The

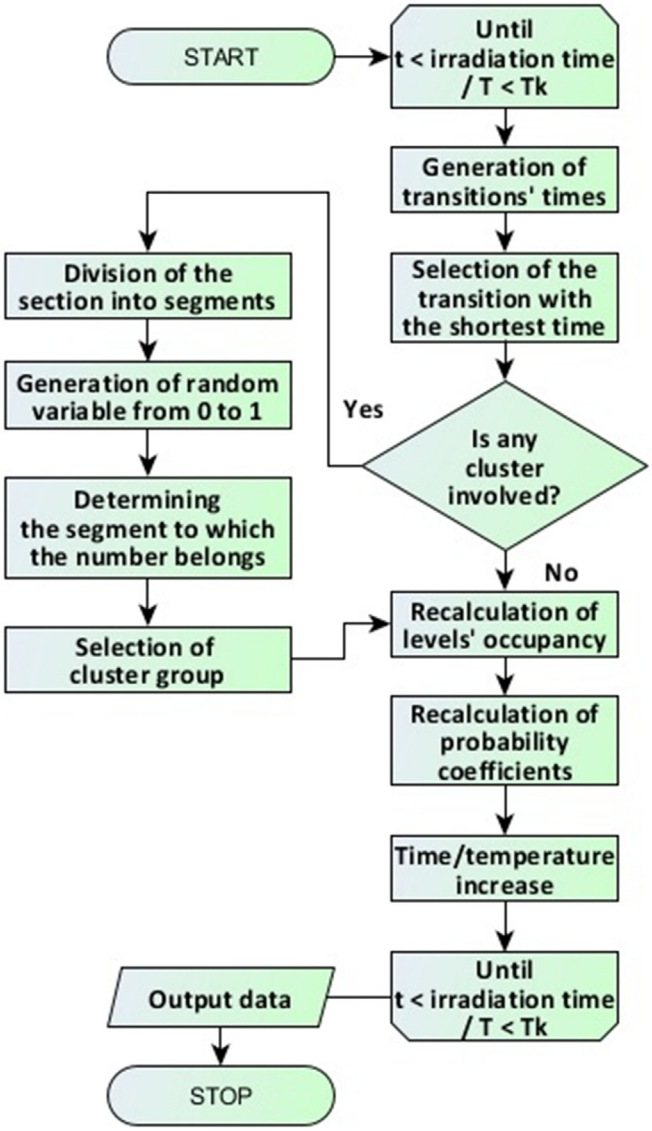

Fig. 3. The algorithm of the program performance for calculation of TL curves.

stages of excitation, relaxation and heating were sequentially analyzed. The following parameters were used in the calculations: $X = 2 \cdot 10^2$ s^{-1}; irradiation time $\tau = 600$ s, total number of clusters $Z = 10^4$; $N = 10$, $M = 20$, $H = 10^9$, $A = 1$ s^{-1}, $D = 10^{-3}$ s^{-1}, $B = 10^{-8}$ s^{-1}, $\gamma = 10^{-3}$ s^{-1}, $\alpha = 2 \cdot 10^{-3}$ s^{-1}, frequency factor of transition p is taken as $s = 10^{10}$ s^{-1}, frequency factor of transition P_{ne} is taken as $s_{ne} = 10^{10}$ s^{-1}, activation energy of transition p is $E = 0.7$ eV, activation energy of transition P_{ne} is $E_{ne} = 0.7$ eV. It should be noted that the radiative recombination coefficient at the luminescence centers B was chosen sufficiently small (much less than the capture coefficient for the deep trap γ), so that in the model the influence of competing processes in the trapping of charge carriers between TL-active and deep traps is mainly taken into account.

At the initial moment of time ($t = 0$), the filling of all the clusters with charge carriers was zero ($Z = z(0, 0, 0)$).

Fig. 4 shows a diagram of the distribution of clusters over the various cluster states, after the end of the irradiation and relaxation stages. The coefficient C in this simulation of the excitation-relaxation stages was C = 0.5 s^{-1}. At the end of the relaxation stage, the value n_e for all clusters was zero. One can see that the distribution has the shape of a peak, whose projections on the (n, z) and (m, z) planes are close to Gaussian curves. In this figure, the distribution maximum (z = 0.0485)

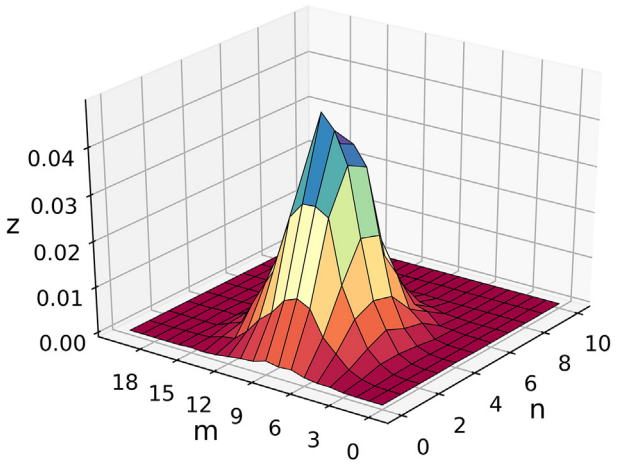

Fig. 4. The distribution of clusters over the states calculated for the instant of the end of the relaxation stage with C = 0.5 s^{-1}. Here n is the number of filled TL-active traps in the cluster, m is the number of filled deep traps, z is the proportion of clusters in the corresponding state: $z = z(n,m,n_e)/Z$.

corresponds to the cluster state with n = 3 and m = 9. This means that 4.85% of all the clusters is in this state. With increasing irradiation time, the position of the peak shifts towards the states corresponding to a larger number of filled TL traps, and to a larger number of filled deep traps in the cluster.

The distribution of clusters over the states presented in Fig. 4 is used as the initial information for calculating the TL at the heating stage. TL curves calculated at different heating rates are shown in Fig. 5. The figure shows that as the heating rate increases, the TL maximum shifts to the high-temperature region, which is consistent with the simplest kinetic concepts (Chen and Pagonis, 2011; McKeever and Chen, 1997). In addition, it can be seen that the TL curves are non-elementary and consist of at least two peaks: a low-temperature peak in the region 340–360 K and a high-temperature peak around 365–380 K. The reasons for the appearance of additional peaks on the TL curves in cluster systems have been discussed previously in Refs. (Mandowski. and Swiatek, 1998; Mandowski, 2006). In particular, it was found that the TL curve acquires a more complex multi-peak shape, when the re-capture probability coefficient on TL active traps increases.

The data in Fig. 5 also show that with an increase in the heating rate, the value of the maximum of the peak increases. A similar feature was observed previously in the analysis of semi-localized TL models, in particular, in YPO_4: Ce^{3+}, Sm^{3+} (Mandowski and Bos, 2011). It was found, that the growth of the TL intensity with increasing heating rate is due to an increase in the ratio of the probability of radiative

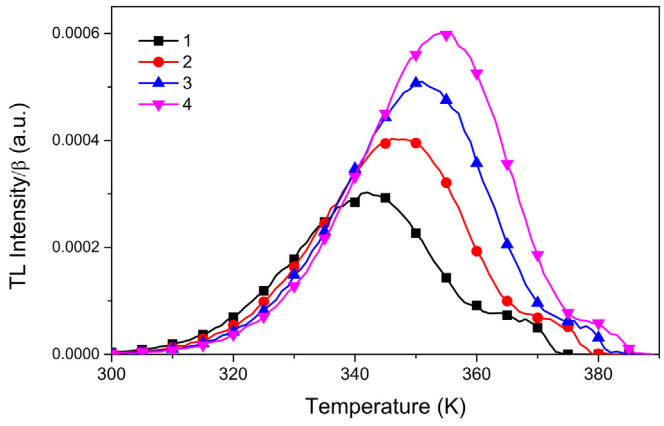

Fig. 5. TL curves calculated at different heating rates: 1 - 1 K/s, 2–1.5 K/s, 3 - 2 K/s, 4–2.5 K/s. $C = 0.5\ s^{-1}$.

delocalized, and non-radiative localized recombinations of an electron during the heating stage.

In the framework of the cluster model of TL with deep electron traps considered in the present work (Figs. 1 and 2), the effect of heating rate on the intensity of the maximum of TL is due to the presence of the transition C in this model (electron capture within the cluster by the deep trap). With increasing temperature, the probability of an electron leaving the cluster increases according to the exponential law in Equations (27), and at a certain temperature this becomes comparable to the probability of transition C. Moreover, the probability of radiative recombination at the luminescence center H also increases. When the heating rate decreases, the temperature at which the probability of an electron leaves the cluster becomes comparable to the probability of capture C, and this temperature is reached significantly later. By this point in time, most of the electrons have time to relax within the cluster, via capturing by deep traps M (transition C). In this case, the number of radiative recombinations decreases (transition B), and the intensity of the TL maximum also decreases.

We made an attempt to ascertain whether it is possible to extract the activation energies of the model by applying the usual method of TL analysis. We used the peak shape and initial rise methods (Chen and Pagonis, 2011) for TL glow curves presented in Fig. 5. Also we calculated the geometrical factor (μ_g) of these curves. The obtained results are shown in Table 2. The calculated μ_g values (0.48–0.52) correspond to kinetics order 1.5–1.9 (Chen and Pagonis, 2011). Taking into account the large value of the retrapping coefficient for traps N ($\alpha = 2{\cdot}10^{-3}$ s^{-1}) compared to the coefficient of radiative recombination ($B = 10^{-8}$ s^{-1}), it follows that the TL should be characterized by a kinetics order close to 2.0, which generally does not contradict the calculated values of μ_g. For more reliable determination of the order of kinetics, it is necessary to investigate the dependence of the maximum temperature of TL curves on the dose of radiation (Sunta et al., 2006). Differences in activation energies in the model (0.7 eV, Fig. 2) and in Table 2 may be due to the fact that the model involves complex kinetics owing to presence of two activation energies E and E_{ne}. A similar situation for the semi-localized transition model was discussed earlier in the Ref. (Pagonis, 2005). Physical interpretation of anomalous values of activation energies determined on the basis of TL curves requires more detailed studies.

We also studied the effect of the localized capture coefficient C in the deep trap, on the intensity and temperature position of the TL peak (at a constant heating rate). TL curves calculated for different values of the parameter C are shown in Fig. 6. It is seen that with increasing coefficient C, the intensity of the TL, as well as the temperature of its maximum, decreases. The drop in the TL output with an increase in the parameter C is due to an increase in the probability of competing capture of electrons by deep traps and, as a consequence, a drop in the number of radiative recombinations. The shift of the TL peak towards lower temperatures may be associated with a decrease in the electron lifetime at the heating stage with increasing C, since this increases the probability of their relaxation within the cluster due to capture into deep traps, which then reduces the number of re-capture events into traps N.

6. Conclusions

This work presents an improved method for calculating the kinetics of TL in complex cluster systems which contain a large number of localized defect states. The method is based on Monte-Carlo calculations, which consist in generating random times for each possible transfer of charge carriers, and selection of the smallest time value. The main feature of the proposed new method, which sets it apart from earlier methods in the literature (Mandowski and Swiatek, 1992; Mandowski. and Swiatek, 1998), is the replacement of a large number of random number generations for all groups of clusters, with only two random number generations. The first random number generation corresponds

Table 2
The parameters of TL glow curves presented in Fig.5.

Heating rate, K/s	TL maximum temperature (Tm), K	Low temperature half-width (ω), K	High temperature half-width (δ), K	Geometrical factor (μ_g)	Activation energy from peak shape method (E_1), eV	Activation energy from initial rise method (E_2), eV
1	342	14	13	0.48	1.11	1.26
1.5	346	13	14	0.52	1.28	1.28
2	351	14	13	0.48	1.17	1.32
2.5	354	14	13	0.48	1.08	1.31

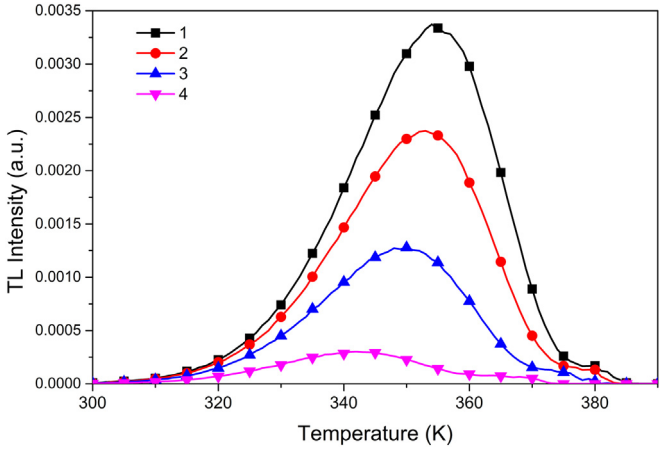

Fig. 6. TL curves calculated with a different coefficient of localized capture *C*: 1–0.1 s^{-1}, 2–0.13 s^{-1}, 3–0.2 s^{-1}, 4–0.5 s^{-1}). Heating rate is 1 K/s.

to the selection of the *transition*, and the second random number generation corresponds to the selection of the *cluster group* for which this transition occurred.

The proposed calculation method was tested using a new cluster model of TL, in which clusters contain deep electron traps along with the active traps, instead of containing recombination centers. In this model, the luminescence centers are considered as uniformly distributed defects.

For the first time, the applicability of the Monte-Carlo method for simulation of TL processes is demonstrated not only for the heating stage, but also for the excitation and relaxation stages. In the framework of the proposed model, the distribution of clusters over the various states is obtained after completion of the irradiation and relaxation stages. It was found that the model explains the effect of increasing TL yield with an increase in the heating rate. The effect of the localized capture coefficient in a deep trap within the cluster, on the intensity and temperature position of the TL peak are also substantiated. The proposed calculation method can be used to simulate TL in other cluster systems, which contain a large number of energy levels and localized and delocalized transitions of charge carriers.

Acknowledgments

This work was financially supported by the Russian Science Foundation, project No. 18-72-10082.

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