RECENT ADVANCEMENTS IN THE THEORETICAL DESCRIPTION OF THERMALLY STIMULATED RELAXATION PHENOMENA

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INTRODUCTION

Physical parameters of trap states are investigated by a variety of methods. Many of them are based on the observation of thermally stimulated relaxation spectra. Among them, thermoluminescence (TL) and Thermally Stimulated Conductivity (TSC) phenomena are some of the basic tools. During these experiments a sample is excited at an appropriately „low" temperature T_0 and then it is heated usually with a constant rate β. While heating, a fraction of charge carriers thermally released from traps recombines with the opposite carriers trapped at „recombination centres" (RC). The probability of thermal excitation of a carrier is assumed to be given by a Boltzmann factor. A series of peaks appearing on TL or TSC spectrum may be attributed to trap levels having different activation energies E_i. Theoretical description of these non-equilibrium phenomena usually assumes uniform distribution of traps and recombination centres [1,2].

Another extreme case was the model of localised transitions by Halperin and Braner [3] regarding hole-electron pairs trapped close to each other. Only for the two cases it was possible to formulate differential equations describing charge carriers' kinetics. Using recently developed Monte Carlo technique, the kinetics of trapping and recombination may be studied in systems with different kind of spatial correlation between traps and recombination centres [4]. This allows to study a variety of cases much closer to the reality. In some situations, the spatial correlation comes as a consequence of the structure of a solid – *e.g.* in polycrystalline samples. However, one can expect similar distribution in every case, where a sample (semiconductor or insulator) is exposed to a high-energy radiation, which produces large defects - traps and recombination centres, most probably assembled into groups [5]. The latter case is especially important due to dosimetric applications of TL [6]. In this paper we present a review of classical models for TL. The applicability of these models is discussed with respect to the recent results obtained by exact numerical calculations. Unquestionably, the basic analytical models for the non-equilibrium trapping and recombination kinetics, though mathematically quite complex, do not cover the variety of all physically admissible cases. For some typical trap parameters, in the presence of spatial correlation, TL and TSC curves reveal unusual properties that cannot be described in terms of standard models.

BASIC THEORETICAL MODELS

The Simple Model

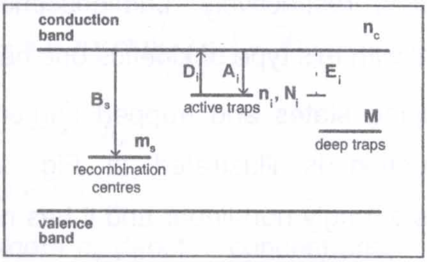

Figure 1. The classical band model commonly used for the explanation of thermally stimulated relaxation phenomena. Allowed transitions are described by the respective probability densities: trapping (A_i), recombination (B_S) and detrapping (D_i).

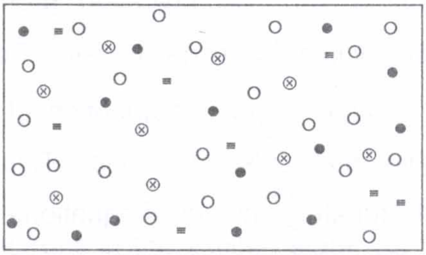

Figure 2. Homogenous spatial distribution of traps and recombination centres used in the simple model. ● - filled traps, ⊗ - empty traps, ≡ - thermally disconnected (deep) traps, ○ - recombination centres.

The model most frequently used for the theoretical description of TL and phosphorescence decay assumes the energy diagram [1,2] schematically presented in Figs. 1,2. The model consists of a set of discrete 'active' trap levels characterised by activation energies E_i and frequency factors ν_i. For the sake of simplicity, it is assumed that only one type of charge carriers, *i.e.* electrons, may be released from traps. Analysing kinetics of charge carriers' trapping and recombination one can write the following set of differential equations [1]:

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

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

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

where N_i, n_i, and m_s denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in RC. 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. Luminescence intensity is proportional to $(-\dot{m})$. To deal with this type of kinetics one has to assume uniform distribution of trapping states and trapped carriers within the bulk of solids. This situation is illustrated in Fig. 2. Unfortunately, the set of equations (1) is strongly non-linear and it has no analytical solutions. Hence, only numerical solutions are possible.

Localised Transitions

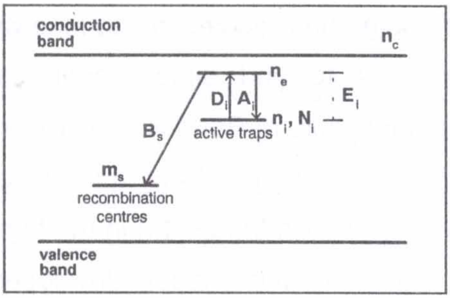

Figure 3. The model of localised transitions of Halperin and Braner.

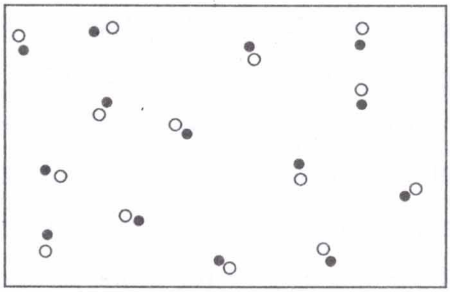

Figure 4. Spatial distribution of trapped electrons and trapped holes in the model of localised transitions.

Another extreme situation was considered by Halperin and Braner [3] and later modified by Land [7] and Chen [8]. They assumed that traps and recombination centres 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 recombination centre (Figs. 3,4). Following Land [7] we can write the kinetic equations:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT}\right) - \overline{A}n_e, \tag{2a}$$

$$-\dot{m} = \overline{B}n_e, \tag{2b}$$

$$m = n + n_e, \tag{2c}$$

where n_e denotes concentration of electrons in the excited state. As the displacement of charge carriers does not take place through conduction band, the TL peak should not be accompanied by thermally stimulated conductivity. $\overline{A}$ and $\overline{B}$ have similar meaning as A_i and B_s in eq. (1).

General order kinetics

Since the basic model (1) describing trapping and recombination kinetics is non-linear, there were many attempts to find simple analytical approximations of the model. Fundamental results of Randall and Wilkins [9], and Garlick and Gibson [10], derived for weak and strong retrapping, respectively, were later generalised by May and Partridge [11] in the form of so-called 'general order kinetics' model. In this model, developed further by Chen [12], it is assumed that intensity J of the process is described by the following relation:

$$J = -\dot{n} = \nu' n^b \exp\left(\frac{-E'}{kT}\right) \tag{3}$$

where E' is the activation energy, ν' is the pre-exponential factor and b is the kinetic order. In the case of b=1 this equation is consistent with the solution of Randall and Wilkins [9] ('first-order' or 'monomolecular' kinetics) and in the case of b=2 one comes to the equation derived by Garlick and Gibson [10] ('second-order' or 'bimolecular' kinetics). Solving this equation for $b \neq 1$ one gets:

$$J = \nu'(n_0)^b \exp\left(\frac{-E'}{kT}\right)\left[1 + \frac{(b-1)\nu' n_0^{(b-1)}}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E'}{kT'}\right) dT'\right]^{\frac{-b}{(b-1)}}, \tag{4}$$

and for b=1:

$$J = \nu' n_0 \exp\left(\frac{-E'}{kT}\right) \exp\left[-\frac{\nu' n_0}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E'}{kT'}\right) dT'\right]. \tag{5}$$

Considering solutions for b<1 it should be noted that the equation (4) is valid within the range $\langle T_0, T_{\text{end}} \rangle$ where T_{end} is defined by the following integral equation:

$$\int_{T_0}^{T_{\text{end}}} \exp\left(\frac{-E'}{kT'}\right) dT' = \frac{\beta n_0^{(1-b)}}{(1-b)\nu'}. \tag{6}$$

For an arbitrary $b<1$ this equation has finite solution for T_{end}. For kinetic orders' $b \geq 1$ the formulae (4,5) are valid within the range $\langle T_0, \infty \rangle$. Using the 'general order kinetics' model, it is possible to estimate three unknown parameters: E', ν' and b. The most important is E'. Usually it is believed that E' differs from the 'true' activation energy not more than a few per cent.

Analysis of TL data

As the analysis of experimental TL data on the basis of eqs. (1-2) is very difficult, usually the GOK model is applied for these purposes. According to suggestions of Chen [2] and Chen and Kirsh [2], this approximation is very accurate and suitable for both the simple model and the localised transitions (Fig. 5).

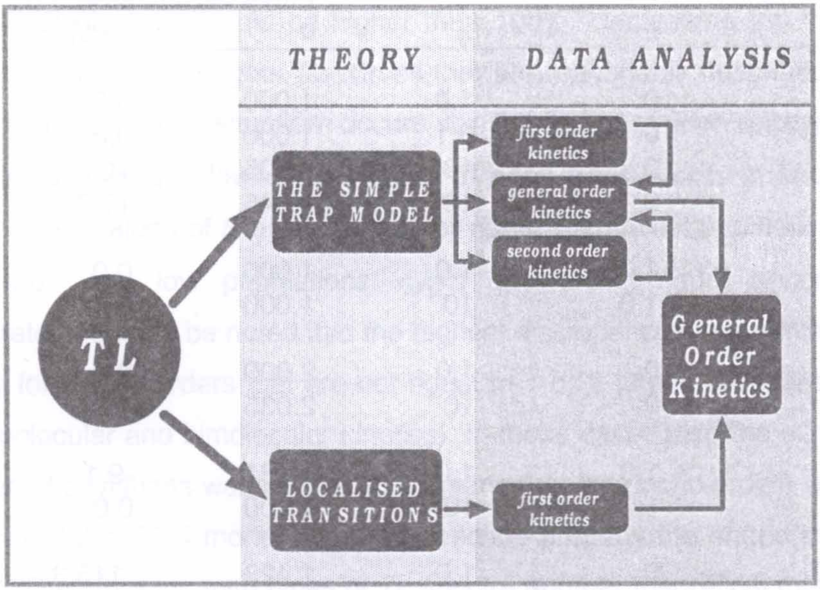

Figure 5. Illustration of standard theoretical description and analysis of TL data.

Numerical verification of GOK

Although the general order kinetics model is very popular in practical applications, it should be emphasised that it has been also criticised by many authors. For example, Moharil [13] and Opanowicz [14,15] found that the kinetic order is usually non constant during a thermally stimulated process and should not be used for characterisation of TL. Lewandowski and McKeever [16] and Lewandowski *et al.* [17] suggest to use a kinetic order function instead of the kinetic order constant.

Table 1. Results of fitting thermoluminescence data calculated from eq. (1) to GOK model for various retrapping coefficients r, relative concentration of deep traps ω and relative initial filling ratio η_0. Other parameters used for the calculations: E=0.9 eV, $\nu=10^{10}$ s^{-1}, $N=10^{15}$ cm^{-3} and $B=10^{-11}$ cm^3/s. Fitted parameters are: the kinetic order b and the relative deviation of E_{fit} from E.

Input parameters			Fitted parameters	
r	ω	η	*b*	ε [%]
0	0	1.0	1.000	0.0
0	0	0.1	1.000	0.0
0	0	10^{-2}	1.005	+0.3
0	0	10^{-4}	1.345	+7.7
0	1.0	1.0	1.000	0.0
0	1.0	10^{-4}	1.000	0.0
1	0	1.0	2.000	0.0
1	0	10^{-4}	2.035	+0.4
1	1.0	1.0	1.161	-9.1
1	1.0	10^{-4}	1.000	0.0
10^4	0	1.0	1.423	-115.3
10^4	0	0.1	2.028	-1.4
10^4	1.0	1.0	0.858	-128.8
10^4	1.0	0.1	1.034	-3.8

To check numerically the validity of GOK model, we constructed four parameter curve-fitting algorithm (the program GENOR) based on the Powell method. The program was applied to the analysis of TL data generated numerically by solving the basic set of differential equations (1). Some typical results are shown in Table 1. The data were calculated for a variety of trap parameters including retrapping coefficients $r=A/B$, relative concentration of deep traps $\omega=M/N$ and the relative initial filling ratio η_0. Fitted parameters reported in the table are: the kinetic order b and the relative deviation of the fitted activation energy defined as follows: $\varepsilon=(E_{fit}-E)/E_{fit}$. Looking at the results one can see that the dependence of ε on trap parameters is rather complex. For most typical parameters the GOK model yields correct values of the activation energy. However, for some of them, it is not applicable. This is true especially in the region of high retrapping coefficients and full initial filling of traps. In this region the error of calculating E could be higher than 100%. Decreasing the initial population of traps one gets TL curves that are reasonably described by GOK. Quite different situation occurs for the case of low retrapping coefficients $r<<1$ and low concentration of deep traps $\omega<<1$. In such a case, correct values of E are obtained for rather high initial population of traps. For very low populations $\eta_0<<1$ the GOK model becomes inaccurate. It should be noted that the highest discrepancies are achieved usually for kinetic orders that are not equal to 1 or 2 (these are classical monomolecular and bimolecular kinetics). In these cases also the sum of squares of deviations was very high. It means that for kinetic orders other than 1 or 2 the GOK model does not describe properly the shape of TL curves. Therefore for such types of TL spectra another theoretical models should be used.

QUASI-EQUILIBRIUM APPROXIMATION

It was found [18] that an approximation of the simple model (1) may be written in the form:

$$\frac{-E}{kT(t)} = \ln\left[\mathrm{L}(t)\right] + \ln\left\{\frac{1}{M+\mathrm{U}_\infty - \mathrm{U}(t)}\left[\frac{1}{\mathrm{U}_\infty - \mathrm{U}(t)} + L_1\right]\right\} + \ln(L_2). \quad (7)$$

where L(t) and U(t) are proportional to the measured TL intensity and the area under TL curve, respectively. The definitions are:

$$\mathrm{L}(t) \equiv -\dot{m}(t), \quad (8)$$

$$\mathrm{U}(t) \equiv \int_0^t \mathrm{L}(t')dt' = m_0 - m(t), \quad (9)$$

U_∞ is proportional to the total area under TL curve. L_1 and L_2 are constants:

$$L_1 = \frac{B-A}{AN+BM}, \quad (10)$$

$$L_1 = \frac{AN+BM}{\nu B}. \quad (11)$$

It was found that this approximation is very accurate with an error less then 0.1% for the whole visible TL peak and for majority of trap parameters. Equation (7), in the special case M=0, is consistent with the solution obtained by Maxia et al. [19] and Aramu and Maxia [20]. The application of this equation to the analysis of a single glow peak requires numerical calculation of constants M and L_1 in the sense that the plot of the right-hand side of eq. (7) would give a straight line. In the case when the parameter M is known from other measurement (*e.g.* from simultaneous TL/TSC measurements [21] using eq. (5)) the fit is simple.

In some cases the generalised initial rise equation can be simplified. The first case is $M \gg \mathrm{U}_\infty = n_0$. It can be proved that in this case $|L_1| \ll \left[\mathrm{U}_\infty - \mathrm{U}(t)\right]^{-1}$ also holds. This way eq. (7) simplifies to:

$$\Theta(t) \approx \frac{(1-\alpha)\tau_t \nu_0}{\alpha}\left(1.8\nu_0 t\right)^{-(1-\alpha)}. \tag{12}$$

where

$$L' = \frac{AN + BM}{\nu BM}. \tag{13}$$

The result means that the plot $\ln\left\{L(t)/\left[U_\infty - U(t)\right]\right\}$ *vs.* (1/*T*) should give a straight line with the slope of (-*E*/*k*). The second case is $M \ll n_0$ and $A \cong B$. Eq. (7) now reduces to

$$\frac{-E}{kT(t)} = \ln\left[L(t)\right] - 2\ln\left[U_\infty - U(t)\right] + \ln(L_2). \tag{14}$$

In this case, linearizing a TL spectrum requires plotting the dependence $\ln\left\{L(t)/\left[U_\infty - U(t)\right]^2\right\}$ vs. 1/*T*.

KINETICS OF TL IN SPATIALLY CORRELATED SYSTEMS

Unquestionably, the basic models for the non-equilibrium luminescence kinetics – *i.e.* the simple model and the model of localised transitions – though mathematically quite complex, do not cover the variety of all physically admissible cases. Looking at Figs. 2 and 4 one can see that spatial distribution of traps is considered only in two limiting cases. To study the influence of spatial correlation on trapping and recombination kinetics one could not formulate the problem in terms of differential equations. It can be solved by application of Monte Carlo simulation. Details of the algorithm were presented in some previous papers [4,5,22]. Below, we present only the most important points. Energy band diagram used in the simulation is presented in Fig. 1. The model consists of a set of discrete 'active' trap levels characterised by activation energies E_i and frequency factors ν_i. For the sake of simplicity it is assumed that only one type of charge carriers – *i.e.* electrons may be released from traps.

Furthermore, we assume that traps and recombination centres are correlated in space – *i.e.* they are assembled into groups. The energy diagram (Fig. 1) relates to each group of traps and RC separately. The probabilities of each allowed transition, *i.e.* detrapping of a carrier to the conduction band D_i, trapping T_i from the conduction band to a given trap, and recombination R_s of a carrier from the conduction band directly to recombination centre are given by the following equations:

$$D_i = \nu_i \exp\left(\frac{-E_i}{kT}\right) \tag{15}$$

$$T_i = A_i(N_i - n_i), \tag{16}$$

$$R_s = B_s m_s. \tag{17}$$

Moreover, the charge conservation law (1c) holds. In each step of Monte Carlo calculations the times of all allowed transitions t_i were calculated. Each time only one transition was executed, characterised by the lowest value of t_i. To decrease statistical fluctuations, the calculations were repeated many times with the same initial conditions. To calculate TL spectra with trap levels that are initially not fulfilled with carriers, first one has to calculate distribution of charge carriers in the system. The process of filling the traps can be easily simulated using Monte Carlo technique. The results of the preliminary Monte Carlo simulations are the input data for the main simulation program. In the all presented cases TSC was calculated assuming that the probability of transition of a carrier between groups is considerably smaller than recombination and trapping probabilities. Typical results of calculation are presented in Fig. 6. Curves *a* and *f* correspond to classical cases: localised transitions and the simple model, respectively. Several curves (b, c, d, e) have unusual shape that cannot be described in terms of standard models.

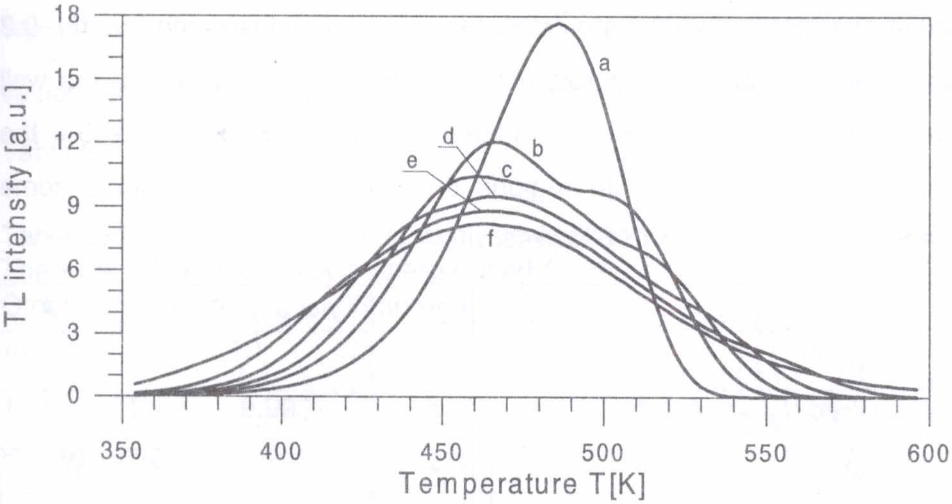

Figure 6. The dependence of the shape of TL spectra on the number of carriers in a single cluster of traps. The curves were calculated for r=100, ω=0 and different population of traps in a single separate group: a) n_0=1, b) n_0=2, c) n_0=3, d) n_0=5, e) n_0=10, f) n_0=100.

To describe the discrepancy of TL quantitatively, we calculated the deviation of TL kinetics from standard theoretical models. The deviation is defined as follows:

$$\varepsilon_i = \left[\int_{T_0}^{\infty} J(T)dT\right]^{-1} \int_{T_0}^{\infty} \left|\bar{J}_i(T) - J(T)\right| dT \tag{18}$$

where $\bar{J}_i(T)$ is the TL intensity as predicted by a standard model and *J*(*T*) is the TL intensity calculated for a given spatial configuration of traps. In Fig. 7 the effective deviation ε is plotted in the form of a contour map. These figures show the dependence of ε on the recombination coefficient *r* and the initial number of 'active' charge carriers in a single separate group of traps. The effective deviation is defined as $\varepsilon=\min(\varepsilon_1,\varepsilon_2)$, where $\varepsilon_1,\varepsilon_2$ denote relative deviations, defined by eq. (18) for the localised transitions model and the simple model respectively. Two first diagrams were plotted for ω=0 and ω=1 respectively. It is shown that the regions of huge divergence (>20%) are greater for low ω. The areas start from $r\approx0.2$ and $r\approx8$ for $\omega=0$ and $\omega=1$ respectively. The regions with $\varepsilon<1\%$ are well described by standard kinetic models. In regions where $1\%<\varepsilon<5\%$ the models are acceptable. In regions of $\varepsilon>20\%$ one can observe some peculiarities of TL and TSC curves.

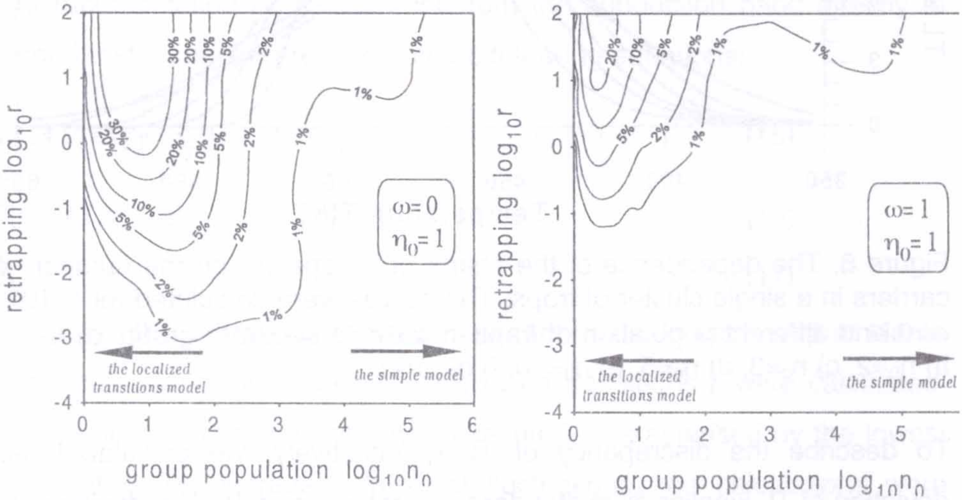

Figure 7. The dependence of the deviation of TL kinetics from standard theoretical models on the number of carriers n_0 in a single separate group of traps and the retrapping coefficient r. The deviation was calculated as $\varepsilon=\min(\varepsilon_1,\varepsilon_2)$, where $\varepsilon_1,\varepsilon_2$ denote relative deviations, defined by eq. (18), from the localized transitions model and the simple model respectively. The calculations were performed for $\omega=0$, $\eta_0=1$ (diagram 1); $\omega=1$, $\eta_0=1$ (diagram 2).

It appears that the curves, calculated for monoenergetic trap level, have a complex structure. Moreover, applying typical curve fitting techniques, one can easily deconvolute the whole curve for individual first order peaks (5). The number of peaks equals to the number of carriers in a single separate group of traps. Typical examples for $n_0=3$ are shown in Fig. 8. Further calculations show that for low initial filling doses the discrepancy between the two standard kinetic models increases. Nevertheless, it is interesting to note that many of these peaks are of first order. Applying eq. (5) for determination of the activation energy we get reasonable values for TSC in the range $0 \leq n_0 \leq 10^2$. This range is lower for TL (see Table 2).

Table 2. Results of peak fitting analysis applied to TL and TSC curves. The true value of activation energy used for the simulation is E=0.9 eV. Other parameters: r=1, ω=0 and η_0=0.01.

n_0 =	1	10	100	1000
E (eV) - TL	0.903	0.879	0.721	0.587
E (eV) - TSC	0.903	0.897	0.843	0.616

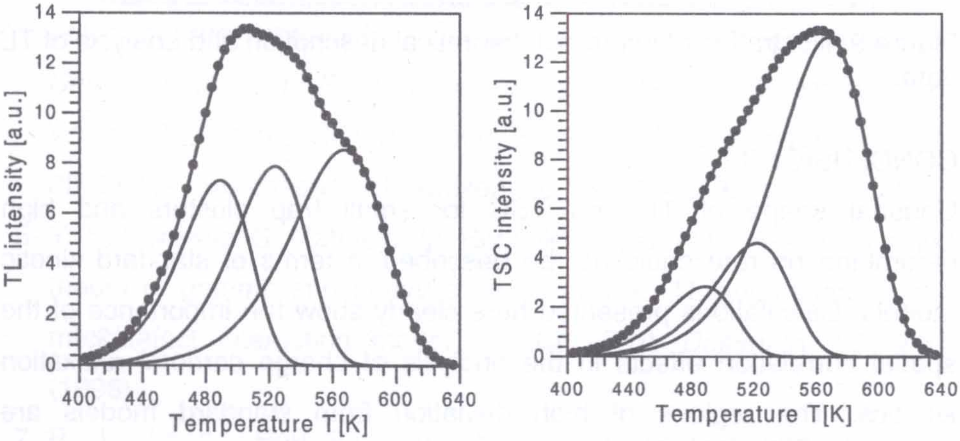

Figure 8. Results of glow curve deconvolution performed for a single 'spatially correlated' TL and TSC peak calculated for E=0.9 eV, ω=0, n_0=3 and r=1000. The spectrum can be perfectly deconvoluted for three first-order peaks with fitted activation energies E_1=0.89 eV, E_2=0.91 eV and E_3=0.93 eV in the TL case and E_1=0.90 eV, E_2=0.92 eV and E_3=0.90 eV for TSC.

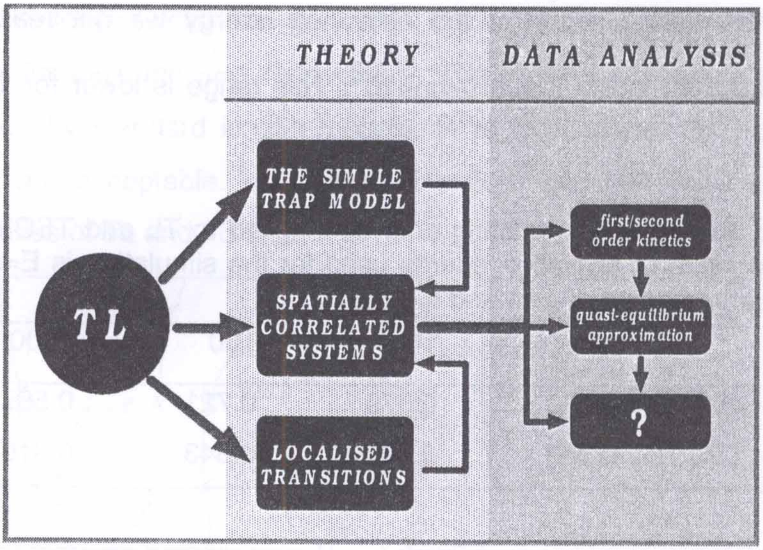

Figure 9. Illustration of improved theoretical description and analysis of TL data.

CONCLUSIONS

Unusual shape of TL and TSC for small trap clusters and high recombination rate could not be described in terms of standard kinetic models. Calculations presented here clearly show the importance of the spatial correlation effects in the analysis of charge carriers' relaxation kinetics. The regions of high deviation from standard models are characterised especially by high values of the retrapping coefficient r and low concentrations of deep traps ω. As the spatially correlated kinetics model includes also localised transitions and the simple model as its special cases, it should be considered as the basic model for theoretical description of TL and TSC phenomena. Unfortunately, until now there is no analytical theory describing this type of kinetics. In some special cases when the kinetics may be described by one of the standard models, it should not be analysed in the framework of GOK. Instead of GOK we may use the first or second order kinetics (if applicable) or the more general QE approximation. This is schematically presented in Fig. 9.

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