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ON THE INFLUENCE OF SPATIAL CORRELATION ON THE KINETIC ORDER OF TL

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Abstract — The dependence of the kinetic order of TL (thermoluminescence) on spatial correlation of traps and recombination centres was studied. TL spectra simulated for different trap parameters and different correlations between traps and recombination centres were analysed in terms of 'general order' formalism. It was found that many spectra calculated for strongly correlated systems have an unusual shape that cannot be described by the general order model. It was found that for some trap parameters TL glow curves appear to consist of two first order peaks.

INTRODUCTION

The theoretical description of thermally stimulated relaxation phenomena such as thermoluminescence (TL) and thermally stimulated conductivity (TSC) is based on the concept of traps[1,2]. The typical energy configuration usually assumed in theoretical descriptions of thermally stimulated processes is presented in Figure 1. Elementary transitions between the allowed energy states can be described by the respective probability densities:

$$D_i = \nu_i \exp\left(\frac{-E_i}{kT}\right) \tag{1}$$

$$T_i = A_i(N_i - n_i) \tag{2}$$

$$R_s = B_s m_s \tag{3}$$

Here D_i denotes detrapping of a carrier to the conduction band, T_i denotes trapping of an electron from the conduction band to a given trap having the energy depth E_i and characterised by the frequency factor ν_i and R_s denotes recombination of a carrier from the conduction band directly to a recombination centre. The remaining symbols have the following meaning: n_i stands for the concentration of electrons in the i^{th} trap level, n_c for the concentration of electrons in the conduction band, N_i for the total number of trapping states in this level, m_s for the number of holes in recombination centres, and A_i and B_s for the trapping and recombination coefficients, respectively. Assuming, in addition, appropriate homogeneous distribution of traps and recombination centres in space one can write the following set of equations describing charge carrier kinetics:

$$-\dot{n}_i = n_i D_i - n_c A_i (N_i - n_i) \qquad i = 1..p \tag{4a}$$

$$-\dot{m}_s = B_s m_s n_c \qquad s = 1..k \tag{4b}$$

$$\sum_{s=1}^{k} m_s = \sum_{i=1}^{p} n_i + n_c + M \tag{4c}$$

here M stands for the number of electrons in the thermally disconnected traps. The equations define the 'simple model'. To check its applicability to a description of experimentally observed phenomena Fields and Moran[3] and later Fillard and Gasiot[4] used the correlated TSC/TL measurement technique. Their results indicated that the mathematical model (Equations 4) is not valid. There were various ideas to explain the discrepancy. Fields and Moran[3] suggested spatial correlation between traps and recombination centres as the reason for the phenomenon. Later, Fain and Monnin[5] proved that the model with spatial correlation is also able to explain supralinear dependence of TL on dose. The first numerical calculations of TL and TSC in spatially correlated systems were published by Mandowski and Świątek[6]. It is quite natural that the cases of traps and recombination centres closely situated in space can be found, e.g. in polycrystalline[7] and low-dimensional structures[6]. However, one can expect a similar effect 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. Since there is no analytical theory to describe this type of kinetics, it is important to study properties of thermally stimulated relaxation spectra by means of numerical simulation.

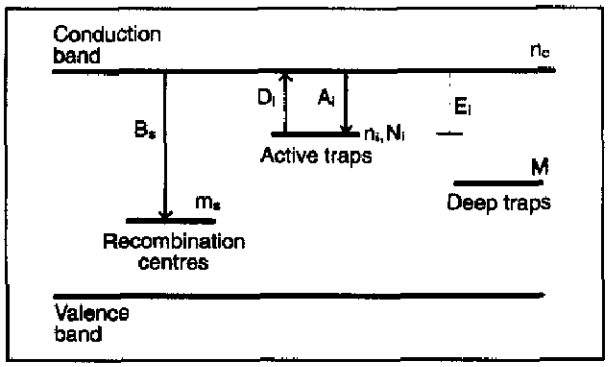

Figure 1. The classical band model commonly used for the explanation of thermally stimulated relaxation phenomena. Allowed transitions are described by the respective probability densities: trapping (A_i), recombination (B_s) and detrapping (D_i).

The spectra obtained in numerical calculations were compared with classical ('no correlation') solutions of the set of Equations 4 and with the general order kinetics model.

THEORETICAL BACKGROUND

Fundamentals of the Monte Carlo simulation

The energy diagram used for the calculation is presented in Figure 1. Allowed transitions are defined by Equations 1–3. In TL simulation it was assumed that the temperature T varies linearly with time, i.e. $T(t) = T_0 + \beta t$, where β stands for the heating rate. TL intensity was defined as follows:

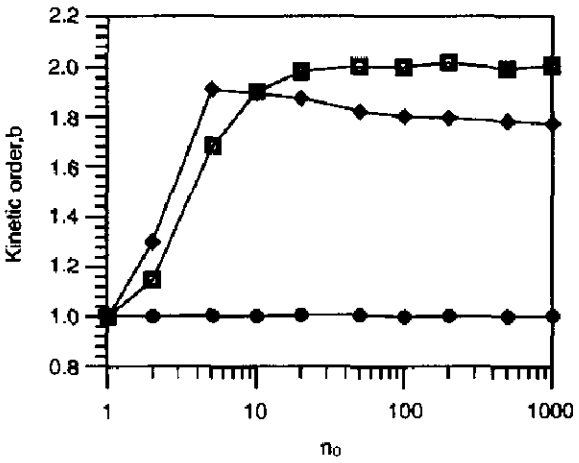

Figure 2. The dependence of the kinetic order of TL on the population of carriers in a single separate group n_0, during heating of the solid with a constant rate $\beta = 1$ K.s^{-1}. The figures were calculated for initial filling ratio $\eta_0 = 1$, E = 0.9 eV, $\nu = 10^{10}$ s^{-1}, M = 0, B = 10^{-11} cm^3.s^{-1} and different coefficients: r = 0 (●), r = 1 (□) and r = 10 (◆).

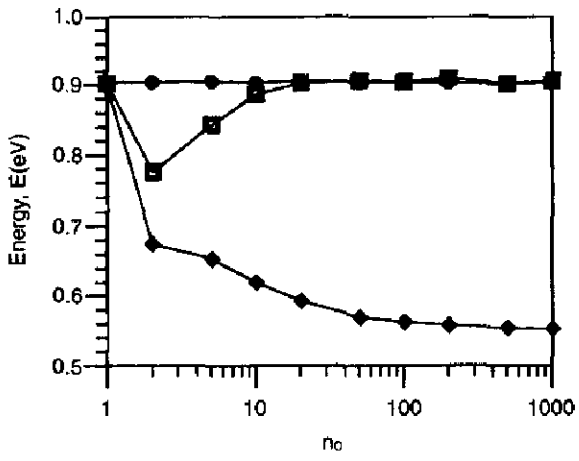

Figure 3. The dependence of the energy fitted from the general order kinetics model on the population of carriers in a single separate group n_0. All the spectra were simulated using E = 0.9 eV. Other parameters are the same as in Figure 2.

$$J_{TL}^{(s)} = -\alpha dm_s/dt \quad (5)$$

where α is a proportionality coefficient. It was assumed that the solid consists of a number of separate groups having the same configuration of energy levels (Figure 1). Each group can be considered, approximately, as a separate system. The method of calculation has been described in detail in a previous paper[6]. Below, only the basic rules are presented.

To perform Monte Carlo simulation one has to deal with a finite number of carriers (e.g. $N = 10^6$ in these calculations) trapped in a solid. Therefore, in place of

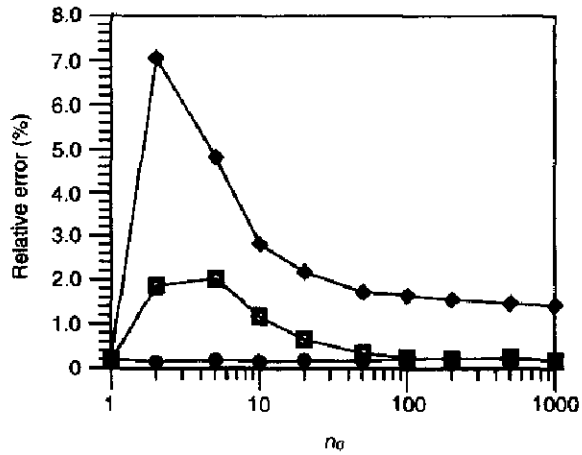

Figure 4. The dependence of the fit error due to the application of the general order kinetics model on the population of carriers in a single separate group n_0. Other parameters are the same as in Figure 2.

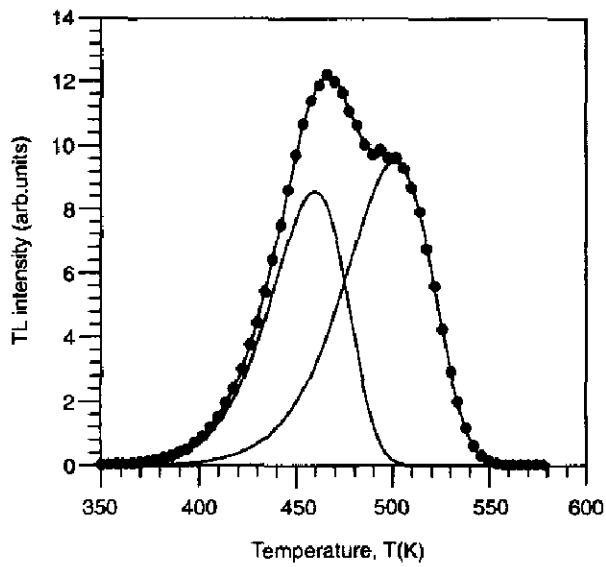

Figure 5. The dots (●) denote the TL spectrum simulated for $n_0 = 2$ and r = 100. The other parameters are the same as in Figure 2. The spectrum was numerically 'resolved' for two peaks (solid line). The fitted values of energy were: $E_1 = 0.893$ eV and $E_2 = 0.918$ eV. The sum (solid line) of those two artificial peaks covers the simulated TL spectrum exactly.

concentrations (n_i, n_c, m, N_i, M) and capture coefficients (A_i, B_s) we have to deal with the absolute number of traps, trapped carriers and recombination centres in each group denoted as $\overline{N}_i$, $\overline{n}_i$ and $\overline{m}_s$ respectively. To compare the quantities with macroscopic parameters appearing in Equation 3 the following relation must hold

$$\begin{cases} \overline{n}_i,\overline{n}_c,\overline{m},\overline{N}_i,\overline{M} \rightarrow \chi n_i,\chi n_c,\chi m,\chi N_i,\chi M \\ \overline{A}_i,\overline{B}_s \rightarrow A_i/\chi,B_s/\chi \end{cases} \quad (6)$$

In the above equation the over-bars indicate quantities used in the Monte Carlo simulation and χ stands for a constant having the dimensions of a volume. In each Monte Carlo simulation with full initial filling of traps the calculations were repeated for each group separately with the same initial conditions[6]. Nevertheless, to calculate TL spectra for a system containing traps that are initially not fully filled with carriers, one has first to calculate the distribution of charge carriers in the system, i.e. the population of all groups. The process of filling the traps can be easily simulated using the Monte Carlo technique[8]. Consequently the full simulation consists of two steps. First one simulates the process of filling traps (i.e. excitation) and then, during linearly rising temperature, the processes of trapping and recombination.

General order kinetics model

There is no theory for the description of charge carrier kinetics in spatially correlated systems. For this reason attempts were made to compare the results obtained with some classical models. Solutions of the set of 'stiff' differential equations (Equations 4) may be obtained numerically. Nevertheless, because of the very great difficulty in obtaining analytical solutions or approximations of these equations many different methods were developed. One of the most popular in the description of TL is the general order kinetics model. In this model it is assumed that intensity J of a thermally stimulated process is described by the following relation:

$$J = -\dot{n} = \nu' n^b \exp\left(\frac{-E'}{kT}\right) \quad (7)$$

where E' is the activation energy and b is the kinetic order. Solving this equation one gets for $b \neq 1$:

$$J = \nu'(n_0)^b \exp\left(\frac{-E'}{kT}\right) \left[1 + \frac{(b-1)\nu' n_0^{(b-1)}}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E'}{kT'}\right) dT'\right]^{-b/(b-1)} \quad (8)$$

and for $b = 1$:

$$J = \nu' n_0 \exp\left(\frac{-E'}{kT}\right) \exp\left[-\frac{\nu' n_0}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E'}{kT'}\right) dT'\right] \quad (9)$$

Using the model it is possible to estimate the four unknown parameters, i.e. E', b, n_0 and ν', by fitting the theoretical curve to experimental results.

RESULTS AND DISCUSSION

The Monte Carlo calculations were performed for one kind of trap and recombination centre. The spectra were calculated for a solid having one active trap level characterised by the energy depth $E = 0.9$ eV and the frequency factor $\nu = 10^{10}\ s^{-1}$. It was assumed that there are no 'thermally disconnected traps', i.e. $M = 0$, the recombination coefficient equals $B = 10^{-11}\ cm^3.s^{-1}$ and the relative initial filling ratio $\eta_0 = 1$. The spectra were calculated for different values of retrapping coefficient $r \equiv A/B$ ranging from 0 to 100. The TL spectra obtained were analysed in terms of the general order kinetics model by fitting unknown parameters in Equation 8 to numerical results. Results of fit are presented in Figures 2, 3 and 4. The fit error was defined as:

$$\Delta = \left[\sum_{i=1}^{N} \left(\frac{J_{th} - J_i}{J_{max}}\right)^2 \Big/ N\right]^{1/2} \quad (10)$$

where J_i denotes intensities calculated in the simulation, J_{th} denotes theoretical (general order) values and J_{max} is the observed maximal intensity of the peak. The fitted activation energy, the kinetic order and the fit error depend on spatial correlation that is represented by the number of carriers in a single separate group of traps and recombination centres n_0. It is noteworthy that for $n_0 = 1$ (one carrier and one recombination centre in a group) the spectra are of first order, and the activation energy calculated from the general order model is close to the expected value $E = 0.9$ eV (i.e. used in the simulation). The result does not depend on particular trap parameters. This conclusion may be considered as an additional argument for the explanation of the data that most experimentally observed TL and TSC curves reveal first order kinetics[9]. A huge discrepancy between the simulated spectra and the model can be observed for high values of the retrapping coefficient and medium correlations $1 < n_0 < 50$. The case $n_0 = \infty$ corresponds to the classical 'no correlation' case. A typical TL spectrum calculated for $r = 100$ and $n_0 = 2$ is presented in Figure 5 (dots). It appears that the spectrum consists of two closely situated peaks. Moreover, applying the curve fitting technique to this curve, one can easily 'resolve' the spectrum into two first order peaks having energies $E_1 = 0.893$ eV and $E_2 = 0.918$ eV. Although the fit is excellent it has no physical sense. This example convinces one that spatial correlation may play a very important role in TL kinetics. Neglecting these effects may lead to erroneous interpretations and conclusions.

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